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Final Report

STUDIES OF COLOR CENTERS IN ALKALI HALIDES

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PART I

SUMMARY

This final report is divided into three parts. Part II is in the form of a Master's thesis submitted to the University of Maryland by Kenneth Lee Eckerle in January, 1968, and entitled "High Pressure Effects on Color Centers in Alkali Halides." This thesis is currently being rewritten for publication in Physical Reviews. Part III is a paper, "Pressure Effect on Color Centers in RbF, RbCl, RbBr, and CsI", by Hans Knof and William G. Maisch. This paper has been accepted for publication in the Journal of the Chemistry and Physics of Solids.

Although other groups at the Institute for Molecular Physics were engaged in high pressure research, this project was the first of its kind and required that a special laboratory be set up for its performance. A spectrometer was acquired by the University and modified to accommodate the high pressure apparatus between the exit slit and the detector. It was modified further for use in the required spectral region and then calibrated. A press and two high pressure optical cells, of the type designed by Drickamer for the study of solids at pressures up to 50,000 atm, were built. The windows of the second cell were enlarged for better optical performance, thus limiting its usefulness to 25,000 atm. Two other pieces of apparatus were assembled: a pressure bench for the generation and measurement of high pressures; a vacuum system for use in the preparation of samples. A small tubular furnace, also for use in the coloration of the crystals, and a voltage regulator for the stabilization of the spectrometer

were purchased. Dr. Venugopal Kesavulu, a post-doctoral research associate from India, worked on the project at this stage.

The rubidium halides were chosen for investigation for several reasons. Previous studies of the F and M bands in the potassium halides by Eppler, Minomura, Maisch and Drickamer revealed both the existence of a new band above the phase transition and a regularity in the discontinuity of the absorption frequencies of the F and M bands at the phase transition. Furthermore, the recent interest of other investigators in crystals having the CsCl structure made the study of such crystals even more essential. The following table shows the crystals studied, the pressure ranges covered, and the bands observed:

Crystal	Bands	Pressure Range (atm)
RbF	F	1-33,000
RbCl	F	1-50,000
RbBr	F, No.3	1-50,000
RbI	F, No.3	5,000-50,000
CsI	F,M	1-50,000

Both phases of RbCl and RbBr were studied, the high pressure phase above 5,000 atm in the apparatus described above and the low pressure phase in a hydrostatic high pressure optical cell of the Drickamer type. Samples of colored RbI large enough for this cell could not be obtained. RbF undergoes phase transition at 33,000 atm, resulting in a large shift of the F band to a region inaccessible to our equipment. This phase transition has been reported only recently by Piermarini and Weir. Their reported transition pressure of 9-15 kbars is inconsistent with our results, a matter further discussed in Part III of this report. CsI exists only in the CsCl structure.

The dependence on pressure of the frequency maxima of the observed bands was determined and compared with the Ivey plot. A large deviation is observed. The No.3 band, the new band observed above the phase transition in KI, was found in RbBr and RbI. No evidence of this band has been observed in any other crystals having the CsCl structure. The frequency of this band has a pressure dependence similar to that of the M band. The possible origins of this band are discussed in Part II of this report. The discontinuous shift toward higher frequencies of the absorption maxima of the F bands in RbCl and RbBr at the phase transition decreases from RbCl to RbBr. This is in agreement with the above-mentioned regularities observed previously in the potassium halides. A discussion of this phenomena appears in Part II.

The measurements on the rubidium halides above the phase transition were made by a graduate student, Kenneth Lee Eckerle. Mr. Eckerle also repeated some of the measurements made in Drickamer's laboratory as a check on the consistency of our work with Drickamer's and helped to put the new equipment in working order after the laboratory was set up. The other measurements were made by Hans Knof, a post-doctoral research associate from Germany.

PART II

HIGH PRESSURE EFFECTS ON COLOR
CENTERS IN ALKALI HALIDES

by

Kenneth Lee Eckerle

Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the degree of
Master of Science
1963

ACKNOWLEDGEMENTS

This is to gratefully acknowledge the many suggestions and conscientious guidance given by Dr. W. G. Maisch for the completion of this work. The excellent work done by Mr. Kopp, the machinist; Mr. Trembly, the glassblower; and Mrs. Morris, the typist should be mentioned. Also, the complete faculty at the Institute for Molecular Physics should be complimented for the maintenance of a stimulating atmosphere. Dr. H. Schamp and Dr. H. Knof, who were particularly interested in this work, were very helpful. Most of this work was sponsored by the Office of Scientific Research of the United States Air Force for which I am deeply indebted.

TABLE OF CONTENTS

Chapter Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1. The Color Center - A Lattice Imperfection. Some of the most important properties of solids are due to imperfections in their structure. Since the alkali halides are among the simplest of all ionic crystals, a knowledge of their imperfections is basic. One kind of imperfection is the color center, which is investigated in this thesis.

Color centers have been the subject of much research, and the number that has been discovered to date is very large. In general, color centers are of three types, electron-excess or F-type centers, hole-excess or V-type centers, and centers due to impurity ions.

The F center itself (from the German word for color, Farbe) is the most well-known. Three models have been proposed for the F center -the interstitial model, the de Boer vacancy model, and the "charge-transfer" complex. The interstitial model, a Frenkel defect, proposes that the F center absorption is due to a negative ion at an interstitial site in the lattice. The de Boer model is a Schottky defect with an electron trapped at a negative ion vacancy.[1] Recently, however, Papazian[2] proposed that the optical absorption could be due to a "charge transfer" complex, while the spin resonance would be due to the de Boer center. The charge-transfer complex would consist of a dative bond between a neighboring anion and cation.

The de Boer model has been generally accepted. The density of a colored crystal is less than that of an uncolored crystal, an occurrence typical of a Schottky defect. Also, the static paramagnetism of the F center is close to that of one electron. The conventional de Boer model is used in this paper.

The frequency maximum of the F center absorption band varies from the infrared region of the spectrum for the crystals of the high molecular weight salts to the ultraviolet region for the crystals of the low molecular weight salts. However, the F band lies in the visible region for most alkali halide crystals, where these crystals are normally transparent. At room temperature the F band is asymmetrical. On the high energy side of the F absorption curve, there exists a hump and a tail for which various explanations have been proposed. The hump arises from an unresolved K band, which will be discussed below. It has been suggested[3] that the tail might be due to transitions from the ground state into the conduction band. Besides the F center itself, more complicated structures exist. Traps may be formed from various combinations of positive and negative ion vacancies. These traps may then capture one or more electrons or holes. An example is the M center which is currently regarded as the F_2 center, i.e., two negative ion vacancies with two trapped electrons.[4]

The V-type centers may be considered to be antimorphs of the F-type centers. For example, the V_1 center consists of a metal ion vacancy and a hole, the antimorph of the F center.

Absorption bands can also arise from certain impurity ions present in the lattice.

Electron-excess or hole-excess centers can be introduced into the crystal by additive coloration, electrolysis, or irradiation. F-type or V-type centers can be produced in the alkali halide crystals by the introduction of a stoichiometric excess of alkali metal or halogen atoms, respectively. Electrolytic coloration is accomplished by the application of an electric field across the crystal. A pointed cathode produces F-type centers and a pointed anode produces V-type centers. Irradiation of the crystals with x rays, electrons, or other high energy particles forms both F-type and V-type centers.

2. Recent Research. The original investigations of the properties of color centers were done by Pohl and his associates.[5] The work on color centers to 1954 is summarized by Seitz in two review papers.[6,7] Some pertinent experiments are listed below. Electron spin resonance experiments show that the F center exhibits magnetic properties typical of an unpaired electron.[8] An electron raised to the first excited state of the F center may either re-emit the radiation and drop down to the ground state or be excited further to the conduction band by thermal interaction with the lattice. Luminescence has been observed after such excitation, indicating that the first process takes place. There are also manifestations of the second process. Irradiation of a colored crystal with light of the absorption frequency of the color center forms new bands in some cases, e.g. irradiation with light of the F band absorption frequency results in the diminution of the F band and an increase in M center absorption. Also, photoconductivity can be observed if an electric field is simultaneously placed across the crystal.

Various theoretical calculations for color centers are discussed by Gourary and Adrian in Solid State Physics.[9] The model for their calculations for the F center is that of one electron trapped at a negative ion vacancy (the de Boer model) in a lattice made up of point charges of appropriate sign.

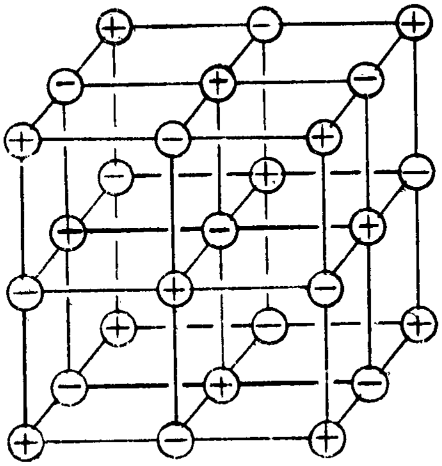
Recently, Lüty[10] discovered three new bands (the L bands) on the high energy side of the F band. He suggested that these bands might be due to electronic transitions from the ground state of the F center into either bound or free states. It is difficult to reconcile the former interpretation with the accepted view that the first excited state of the F center lies very near the conduction band. The latter interpretation presents difficulties in the explanation of the band structure. Gold[11] postulated that the L bands, as well as the K band, might be due to transitions originating in the F_2^+ center (anion vacancy pair plus an electron). There is evidence that the K band, too, results from a higher transition of the F center, i.e. it has been observed that the K and F band absorption intensities are proportional during initial growth.[12] One observes that even the most well known color centers are not completely understood.

One atmosphere and room temperature studies of color centers indicate a unique dependence of the transition energies on the interionic distance. At low temperatures, the absorption bands are narrower than at room temperature, and the peak frequencies are usually higher. As the temperature is increased, the bands broaden and the peak frequencies shift toward the red (lower frequencies). At very high temperatures, the color centers are destroyed, and the crystals become transparent. The changes in lattice spacings produced by temperature changes are relatively small. Measurements as a function of pressure, however, may be made over a much larger range of this parameter. High pressure experiments on the alkali halides are made even more interesting by the fact that some of the crystals undergo a phase transition at high pressures. New bands are sometimes observed when the crystals are compressed or when they undergo a phase transition. RbCl, RbBr, and RbI change from the NaCl structure to the CsCl structure at 4950, 4550, and 4010 atm, respectively.[13] The corresponding potassium halide crystals undergo this same transition in the neighborhood of 20,000 atm. The NaCl structure has a face-centered cubic space lattice, fcc. The positive and negative ion lattices are separated by one-half the body diagonal of a unit cell. The CsCl structure has a simple cubic space lattice, sc. Every ion of a given sign is in the center of a cube formed by eight ions of opposite charge. These two structures are shown in Figs. 1(a) and 1(b). The observed transition is not sharply defined, and the crystals become opaque over a pressure range of about 5,000 atm.

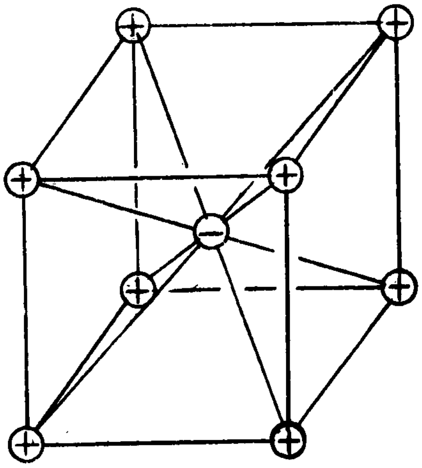
Several previous high pressure experiments have been performed on color centers. Burnstein et.al.[14] studied the behavior of the F band in three alkali halide crystals at pressures up to 2,000 atm. Jacobs[15] studied the F band absorption in seven alkali halide crystals at pressures up to 5,000 atm. He also calculated the change of the lattice constant in the neighborhood of the F center with respect to that of the bulk crystal. After comparing this with his experimental results, he concluded that the F center is more compressible than the bulk crystal.

In 1957, Maisch and Drickamer[16] published results of optical absorption experiments at pressures up to 50,000 atm on the F center in six alkali halide crystals and the M center in one other. They observed that the peak frequencies always increase with pressure except at the phase transition, where the behavior varies from crystal to crystal. The optical bleaching of various centers in crystals under pressure and the appearance of three new bands, the No. 1, No. 3, and the K' bands were reported.

In 1960, Eppler and Drickamer[17] made similar measurements at



(A) NACL STRUCTURE



(B) CSCL STRUCTURE

FIGURE 1

pressures up to 166,000 atm. Calculations similar to those of Jacobs were done with the aid of Bridgman's compressibility data[18] and the Ivey equation,[19] an empirical formula which is discussed later. Eppler and Drickamer also conclude that the F center is more compressible than the bulk crystal.

Minomura and Drickamer[20] studied the optical absorption of the M center in KCl, KBr, NaCl, and KI at pressures up to 50,000 atm. They recorded frequency shifts and absorption intensities for the M bands as well as the frequency shifts for the F, N, and R_2 bands in KCl. Their calculations show that the compressibility of the M center is less than that of the F center but still greater than that of the bulk crystal.

The optical absorption of the F center in CsCl and CsBr was studied as a function of pressure by Maisch and Drickamer.[21] Rabin and Schulman[22] have studied the F center in the cesium halides at room temperature, liquid nitrogen temperature, and liquid helium temperature. They found component structure in the F band at liquid helium temperature, a feature unique in these crystals. This structure is in addition to the K band, which appears at the high frequency side of the F band and is of much lower intensity than the newly observed components. Lüty[23] has studied the optical absorption of the rubidium halides at low temperature and at room temperature. Jacobs[24] studied the optical absorption of the F center in RbCl at pressures up to 5,000 atm.

In summary, most studies of the F center have been made with the sodium and potassium halides. Only recently has renewed interest been shown in the cesium halides. Since the potassium and rubidium halides have the CsCl structure above their transition pressures, they provide another way of studying color centers in the sc structure.

3. Present Research. No previous studies have been made of the pressure dependence of the optical absorption of the F center in RbBr and RbI in either phase or in RbCl above the transition point. The purpose of this research is to study the F center above the transition point in the rubidium halides, thus partially filling this gap. (Similar studies are currently being made at this laboratory on CsI and on the rubidium halides under the transition point.)

The variation with pressure of the peak frequencies of various bands is reported and discussed in terms of the dependence of the transition energies on the interionic distance. An attempt is made to identify the various bands and their origins and to correlate the spectrum of the CsCl-type structure and that of the NaCl-type structure. Changes in the intensities and half-widths of various bands are recorded and compared with previous measurements. Finally, the discontinuous jump at the phase transition of the peak energies of the F and M bands in the rubidium and potassium halides is reported.

CHAPTER II

EXPERIMENTAL

1. Coloration of Crystals. The rubidium salts were obtained from Semi-Elements Inc., and the potassium salts and sodium chloride from the Harshaw Chemical Company. The crystals were colored either additively or electrolytically.

The apparatus for additive coloration is drawn in Fig. 2(a). The three sections, A, B, and C are made of Pyrex tubing. Approximately 0.25 cm^3 of sodium or potassium was placed in section A. After section A was fused to section B, an uncolored alkali halide crystal about 1x1x2 cm was placed in section B. Section C was fused to section B. The resulting tube was evacuated with a two stage mechanical pump. The alkali metal was distilled at 110°C into section B, leaving behind most of the oxides in the first chamber. The distillation was accomplished by sliding a tubular furnace onto section A. After all of the metal had passed through the first constriction, the crystal chamber was sealed off. This evacuated cell was then placed in the tubular furnace and heated at a temperature of 550°C for one to two days. The crystal chamber was then cooled, and the colored crystal was removed and stored in the dark to prevent bleaching.

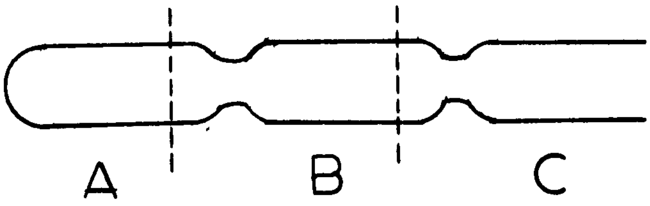
The concentration of F centers has been found to be proportional to the concentration of metal atoms in the vapor and to decrease with increasing temperature of the crystal.[25] The rate of coloration, however, increases with increasing temperature. These factors, along with the softening temperature of the Pyrex tube, determined the conditions used in coloring the crystals.

This method produces uniform coloration throughout the crystal. The samples used for the experiments were always taken from the interior of the bulk crystal by cleaving, thus providing good optical surfaces as well as an uncontaminated specimen. RbCl, RbBr, KCl, KBr, and KI crystals were colored by the addition of potassium atoms, while sodium was used to color NaCl. A sufficiently high concentration of color centers for optical measurements on RbI could not be obtained by this method. Consequently, it was necessary to color RbI electrolytically.

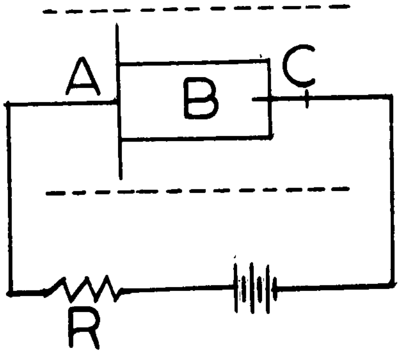
In figure 2(b) the apparatus used for the electrolytic coloration of the crystals is shown. The resistor, R, is a 3000 ohm current limiting resistance. The anode, A, is a flat strip of nickel which covers one end of the crystal. A crystal having a cross sectional area of 0.5 to 2 cm^2 and 1 to 2 cm long was fused to the anode. The cathode, C, is a pointed platinum wire imbedded about 1.0mm into the crystal. It was necessary to preheat the crystals to prevent cracking when fusing them to the electrode. The system was then placed in the oven and heated to a temperature 100°C below the melting point of the crystal. The oven is represented by the dashed lines in figure 2(b).

A potential of several hundred volts produced currents up to several milliamperes in the crystal. The time necessary for completion of electrolysis, a function of voltage, varied from ten seconds to a few minutes. One can actually see the coloration due to the F center progress from the cathode toward the anode.

The coloration produced additively was uniform. The uniformity of the F center density in electrolytically colored crystals increases



(A) ADDITIVE COLORATION



(B) ELECTROLYTIC COLORATION

FIGURE 2

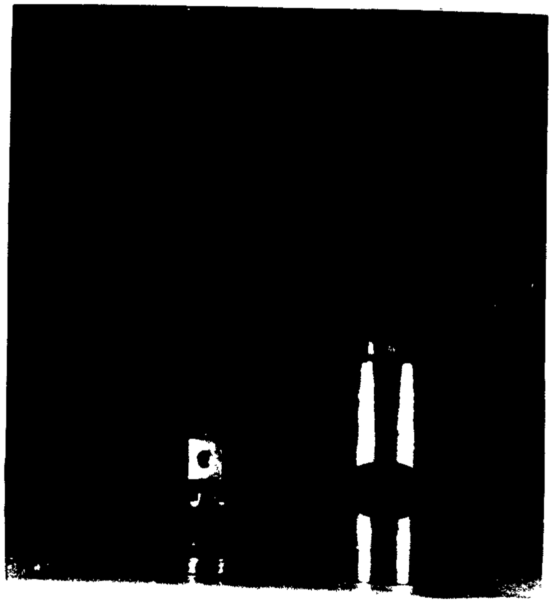
with decreasing voltage. Although much greater concentrations of F centers could be obtained by use of electrolytic coloration, there was a concentration gradient. It should be mentioned that improved uniformity in coloration was achieved electrolytically in later experiments by the use of a larger diameter platinum wire for the cathode. This is presumably due to the fact that better electrical contact was made between the crystal and the cathode.

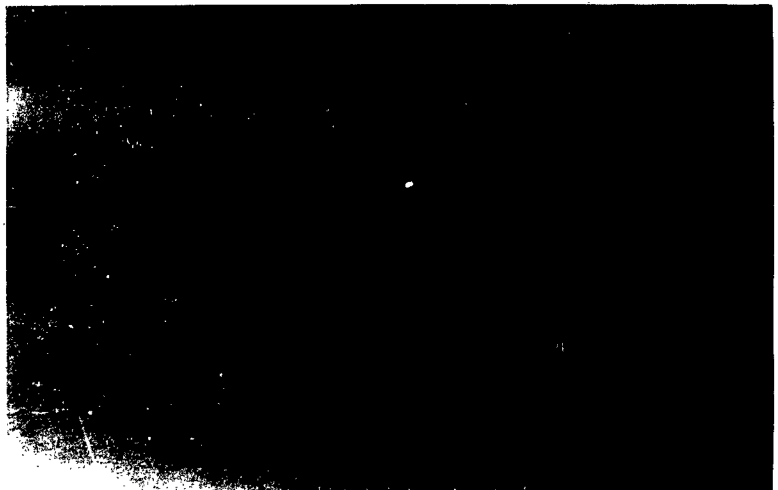
2. High Pressure Apparatus. The high pressures were achieved by a two stage system which has been described in great detail previously by Drickamer et.al.[26] There are two parts to the low pressure system, a hydraulic press (Fig. 3) and a hand operated pump. The press has a 4.5 in. piston and is designed to fit in a spectrometer. Two openings on opposite sides of the cylinder walls permit light to pass through the press and the high pressure cell. Oil is used as the pressure transmitting fluid. A Heise Bourdon gauge, which has a range of 0 to 1,000 psi, is connected to the low pressure system. This gauge was calibrated with a precision pressure balance.

The high pressure bomb is an ingenious device for producing nearly hydrostatic pressures on solids while spectroscopic measurements are simultaneously performed on the compressed samples. The bomb is shown in Fig. 4. The outer steel jacket, B, is 3 5/16 inches in diameter and has a hardness of 46-48 Rockwell C. The inner cell, A, is one inch in diameter and has a hardness of 58-60 Rockwell C. The cylindrical sample chamber has a 0.125 in. diameter and a 0.1875 in. length. The pistons, C_1 and C_2, are made of carboloy and are supported by steel jackets. C_2, the lower, fixed, piston is tapered to 0.125 in. The piston, C_1, has the same diameter as the sample chamber, 0.125 in.,

Fig. 3 Hydraulic press for producing high pressures in the high pressure optical cell. The optical cell is resting on the base of the press at the left.

Fig. 4 Disassembled high pressure optical cell. The various parts are, from the left, (1) window piston guide, (2) window piston, (3) flat (F), (4) inner cell (A), (5) outer jacket (B), (6) fixed piston (C_2), (7) retaining ring for fixed piston, (8) movable piston (C_1), and (9) guide for the movable piston. The letters are used in the text in the description of the cell.





and slides into that chamber as pressure is applied from above by the 4.5 in. piston. The 0.125 in. flat, F, is made of hardened steel. It is placed in the sample compartment next to C_2 to prevent the sample from extruding under high pressure.

The window holes consist of four concentric cylindrical openings having progressively smaller diameters from the outer jacket to the sample chamber. The largest hole has a 0.250 in. diameter. The three smaller holes in the inner cell have diameters of 0.067, 0.047, and 0.028 in. with respective lengths of 0.188, 0.125, and 0.125 in. The windows are formed from single crystals of NaCl forced into the holes at a pressure of 20,000 atm. The frictional forces between the salt and the walls of the bomb are sufficient to retain the pressure exerted from within by the compressed sample.

The piston in the press has a cross sectional area which is 1296 times as large as that of the 0.125 in. carboloy piston. Consequently, the pressure in the inner chamber would be 1296 times the gauge pressure if there were no friction. The calibration of this pressure apparatus was originally done by Drickamer et.al.[27] using the phase transition of bismuth at 24,700 atm and the transition of tellurium at 43,500 atm as primary standards. The apparatus was checked in this laboratory by comparing the shift of the F center absorption maximum in NaCl with previously published measurements.[28] Data were taken only to 50,000 atm since the moving carboloy piston breaks somewhere between 50,000 and 60,000 atm.

3. Optical Apparatus. The absorption measurements were made with a modified Beckman 1R-3 Spectrophotometer. The dispersing elements of this instrument are two LiF prisms, arranged in series. Since the light

passes through each prism twice, high dispersion is obtained. All lenses were made from either KBr or quartz. The mirrors were coated with aluminum. An auxillary optical system was constructed to accommodate the large hydraulic press. This was placed above the monochromator (Figs. 5 and 6) between the exit slit and the detector.

The wavelength region accessible with this instrument extends from 2250 Å to 6 u. A modification of the wavelength drive mechanism was necessary to attain the short wavelength limit.

The instrument was calibrated in the ultraviolet and visible regions with cadmium, neon, and mercury emission lines.[29,30] The vibration-rotation spectra of several gases were used for the calibration in the infrared region.[31]

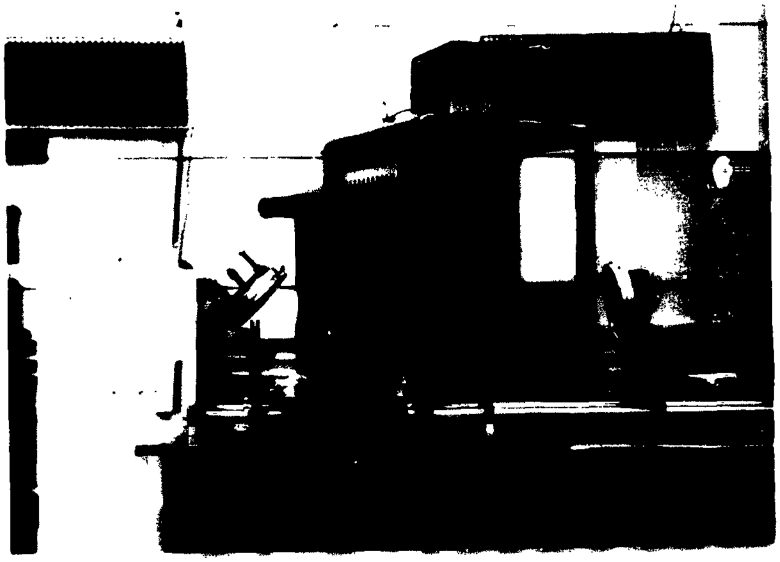
The light source for the absorption measurements was a tungsten lamp, General Electric type 1958. It is a high intensity lamp with a 0.5 inch filament enclosed in a quartz envelope. Its maximum operating conditions are 150 watts at 28 volts. It has an extremely long lifetime and constant emission due to the presence of iodine vapor in the envelope.

The detector was an RCA 1P21 photomultiplier tube. Its useful range for this experiment was from 3200Å to the near infrared.

The background absorption of the atmosphere and the optical elements, the emission curves of the source, and the wavelength dependence of the detector sensitivity must be accounted for in these measurements. The IR-3 is a single beam instrument, but it is designed so that it can compensate for these factors. A preliminary scanning of the spectrum must be made without the sample in the light path. During the scanning an electronically controlled system compares the signal output from the detector with a standard voltage and automatically corrects any

Fig. 5 Auxiliary optical system mounted on top of spectrometer. The monochromator is at the right, with the exit slit (hidden) below and to the right of the plane mirror in the center of the picture. The detector is at the left, below the lens. In the center, between the detector and the plane mirror, is the high pressure optical cell resting on the base of the hydraulic press.

Fig. 6 Auxiliary optical system, with hydraulic press in position. The light-tight cover for the optical system and the oil lines to the press have been removed.



imbalance by adjusting the width of the slits. The movements of the slit and wavelength drives are recorded on magnetic tape. When the taped program is played back into the spectrometer, the original movements of these drives are reproduced. If a sample has been placed in the light path, its spectrum will be recorded directly as percent absorption.

In the present research, an uncolored crystal was placed in the light path during the preliminary scanning. The instrumental slit width, which can vary between 0.01 and 2.55 mm, was nearly at its minimum over the region where the absorption maxima of the F centers of the various crystals occurred.

The absorption spectra were recorded by a Brown potentiometer as percent absorption versus a scale linear in the wavelength drive position. Reference marks, which could be converted into wavelength readings by means of the above-mentioned calibration, were made by a marking pen which was actuated by the wavelength drive.

4. Spectral Measurements - One Atmosphere Spectra. A background run was made at one atmosphere with an uncolored crystal of appropriate thickness in the light path of the spectrometer. A sample holder was constructed which masked the unused portion of the slit image and permitted only radiation which had passed through the sample to reach the detector. A colored crystal of the same alkali halide was then placed in the sample holder, and its spectrum was recorded.

The tungsten lamp was operated at 23 volts in this region, but it was still necessary to place a limiting aperture after the exit slit of the monochromator to prevent saturation of the photomultiplier tube. The range of observation could be extended to about 2250Å by removing the limiting aperture, using an RCA 1P28 photomultiplier tube, and increasing the voltage across the tungsten lamp to 27.1 volts.

The peak energies for the F band at one atmosphere are listed in Table 1 for NaCl, KCl, KBr, KI, RbCl, RbBr, and RbI. The sample thicknesses for those crystals whose spectra appear in the figures at the end of this paper are also listed.

5. Spectral Measurements - High Pressure Spectra. Separate background recordings were made for the high pressure runs to eliminate the effects of the NaCl windows, the absorption of the uncolored crystal, refraction, and the geometry of the high pressure bomb.

The thickness of the colored samples was chosen so that total absorption did not occur at any pressure. This thickness, of course, varied with the concentration of color centers in each crystal. An uncolored crystal with thickness equal to that of the colored sample was used for the background recordings. The maximum sample thickness was always less than the 0.125" limit of the sample chamber since thin slabs of NaCl were placed between the colored crystals and the windows to prevent contamination of the latter. Before each run, the NaCl windows were re-pressed to give reproducible light paths.

Background recordings were made at several different pressures for crystals of a few of the alkali halides. It was determined that the pressure at which these background recordings were made did not influence the shape of the absorption spectra of the corresponding colored crystals. In a simpler procedure, followed for all the crystals studied, the background recording was made at one pressure and then used to obtain the spectrum of the same uncolored crystal at several pressures. Other than a slight, frequency-independent increase in absorption, no significant effects of pressure were observed over the spectral region where the absorption bands of the colored crystals occur. The general decrease in transmission could, of course, be compensated for by an increase in signal amplification. As a result, only one background recording was used for each crystal. Those for the rubidium halides were made at 15,000 atm (above the transition point), and those for KBr and NaCl, at 5,000 atm.

The measurements were made at intervals of 5000 atm up to a maximum pressure of 50,000 atm with a colored crystal of identical size as the blank in the high pressure bomb. The calibration and all runs were made by scanning from long wavelengths toward short wavelengths to eliminate any backlash effects of the wavelength scanning mechanism.

The uncertainty of pressure measurements below 5,000 atm in the high pressure bomb prevented observation of the shift of the F center absorption peak in the rubidium halides below their phase transition. Hence, all measurements for RbCl, RbBr, and RbI, except those at one atmosphere, are for the CsCl type structure. Since the transition in KBr occurs at much higher pressures, both phases could be studied.

Some of the crystals were irradiated with light having a frequency band centered on the frequency maximum of the absorption band being studied. The spectra of these crystals were observed before and after such irradiation, and the change in intensity of various bands were noted. These results were then compared with similar ones obtained from crystals whose bands were known. Such information was useful in the identification of the unknown bands.

CHAPTER III

RESULTS

1. Presentation of Data. The results are presented in three ways. First, the absorption maxima, E_m, in units of electron volts, are shown as a function of pressure in atmospheres in Figs. 7 to 11. Secondly, the absorption curves are replotted in the form of the optical density, $\log_{10}(I_o/I)$, versus the frequency, γ, at selected pressures in Figs. 12 to 16. I_o is the intensity of the incident light, and I is the intensity of the light transmitted by the sample. γ is expressed in electron volts. Thirdly, plots of $\log_{10} E_m$ against $\log_{10} a$ are presented in Figs. 17 to 20. The dotted extensions of the graphs are extrapolations to the transition pressure. a, the interionic distance in Angstrom units, was calculated from Bridgman's compressibility data[32]. For the NaCl structure, $a = \left(\frac{M}{2\rho}\right)^{1/3}$, where M is the molecular weight in grams and ρ is the density in gm/cm^3. For the CsCl structure, $a = \sqrt{3}/2 \left(\frac{M}{\rho}\right)^{1/3}$. These structures are illustrated in Figs. 1(a) and 1(b).

In Table 1, the peak energies of the F center for seven alkali-halides at one atmosphere are listed. These energies agree well with those tabulated in the literature. The method of coloration is not significant since the same peak F center energy is obtained by additive coloration with Na or K, or by electrolysis.

The half-widths at one atmosphere, which include the contribution of the unresolved K band (or perhaps K bands), agree with those found by Luty[33] at 20°C (Table 3).

The one atmosphere data for the various crystals are plotted as

$\log_{10} E_m$ versus $\log_{10}$ a in Fig. 20. This illustrates the Ivey relationship for the F center which will be discussed in the next section. The high pressure data are presented in detail separately for each crystal. The behavior of each crystal is different, and new bands appear above the transition point in some crystals.

The half-widths obtained from the replotted high pressure data are listed in Table 4.

With a notation similar to that of Jacobs[34], the negative values of the slopes of the $\log_{10} E_m$ versus $\log_{10}$ a plots will be defined as:

$$n_1(P) \equiv - \frac{\partial \log_{10} E_m}{\partial \log_{10} a} \tag{1}$$

This quantity is understood to be evaluated at constant temperature. The subscript "1" denotes the type of color center involved. The measured values of n_1, which are always positive quantities, are listed in Table 2.

2. NaCl. In Fig. 7, the shift of E_m with pressure for the F center in NaCl is compared to that found by previous investigators.[35] The agreement is excellent. It is seen that E_m increases monotonically with P, and that the rate of increase decreases at higher pressures.

The F center spectra in NaCl are replotted at various pressures in Fig. 12. The one atmosphere spectrum is not shown. There is a large number of colloidal particles present in the crystal at this pressure at the expense of F centers. As a result, the F band is diminished in intensity and is overlapped on the low frequency side by the colloid absorption band. The colloid centers could have been removed by quenching the colored crystal. However, since the application of pressure removes the colloid centers and simultaneously introduces new F centers, quenching was unnecessary in this experiment. The half-width of the F center at 5,000 atm is larger than the true value since the F center has not yet shifted away from the M and R centers. Also, some colloid centers, whose behavior under pressure are not fully known, might still persist. At 15,000 atm, the F center peak has shifted away from these bands. No broadening of the F band could be observed by increasing the pressure to 50,000 atm.

As seen in Fig. 17, where the data of Eppler and Drickamer for NaCl and NaBr is shown for comparison, n_F is not constant. For NaCl at pressures less than 25,000 atm, n_F is 1.9 times that in the region 50,000 to 100,000 atm. This ratio for NaBr is about 1.6[36].

3. <u>KBr</u>. In Fig. 8, the shift of E_m with P is shown. The data for an additively colored KBr crystal from the experiments by Maisch and Drickamer[37] are shown for comparison. They saw two components, the K' and F bands. The high frequency component, the K' band, was very weak at low pressures, increased in intensity with increasing pressure, and finally overwhelmed the low frequency component, the F band. Only one band was observed in the present experiment. The frequencies observed just below the transition pressure agree with those of the K' band, while the frequencies observed at lower pressures agree with those of the F band. Since these absorption bands are relatively broad, it is possible they were not resolved in the present research. Another possibility is that the splitting of the band into two components is due to an instrumental effect, since the minimum between them appears at the same frequency in all of the crystals where it has been observed. However, the F band has been shown to have component structure in some alkali halide crystals at low temperatures.[38]

The half-width of the F band remains constant with increasing pressure except at the phase transition where it increases by a factor of 1.3. Simultaneously, the maximum optical density, $\log_{10}\left(\frac{I_o}{I}\right)_{max}$, decreases. These two effects oppose each other, and the integrated area tends to remain constant. It was also observed that the M center, which was very weak below the transition point, became clearly visible in the sc structure.

n_F for KBr is constant in this pressure region. With the data of Maisch and Drickamer[39] for KCl and KI, n_F was obtained from plots of $\log_{10} E_m$ versus $\log_{10} a$. These plots are shown in Fig. 18 for comparison.

Only one band is seen above and below the transition in KCl. The situation is complicated in KI by the appearance of new bands under compression, the K', No. 1, No. 2, and No. 3 bands.[40] The K' band was seen below the transition, the No. 2 and No. 3 bands were seen above the transition, and the No. 1 band was found only after the transition point was crossed from above.

$n_{No.2}$ corresponds numerically to n_F, providing partial evidence that the No. 2 and F centers are identical. Also, $n_{No.1}$ and $n_{No.3}$ approximate the negative slope for the M center, n_M.

4. RbCl As mentioned previously, the high pressure measurements for the rubidium halides were all made above the transition points. Unlike in the Na and K halides, the shift of E_m with P for the F center in the rubidium halides is nearly linear with pressure in this region, i.e., from 5,000 to 50,000 atm.

Only one absorption band was observed in RbCl. The slope of the curve in Fig. 9 is $\frac{\Delta E_m}{\Delta P} = 1.0 \times 10^{-5}$ ev/atm. The replotted spectra at selected pressures are shown in Fig. 14. The half-width of the F band above the transition point is 1.2 times the one atmosphere half-width. Above the transition point, further increases in pressure do not change the half-width. The peak optical density decreases by a factor of 2 when the transition point is crossed (Fig. 14).

The extent of bleaching which occurred when the compressed crystal was irradiated with light of F band frequency increased with time of irradiation. The F band could be largely restored by changing the pressure. This behavior is consistent with the bleaching properties of the F band in the sodium and potassium halides at high pressures.[41]

5. RbBr. Two bands were observed above the transition point in RbBr. The shift of the peak frequencies with pressure can be seen in Fig. 10. The curve for the band at lower frequencies has a slope, $\left(\frac{\Delta E_m}{\Delta P}\right) = 1.08 \times 10^{-5}$ev/atm, which is almost identical to that for the F band above the transition point in RbCl. The curve for the band at higher frequencies has a slope, $\left(\frac{\Delta E_m}{\Delta P}\right) = 4.75 \times 10^{-6}$ ev/atm. Also, from the plots of $\log_{10} E_m$ versus $\log_{10} a$ in Fig. 18, it can be seen that the curve for the absorption band at lower energies has a slope typical of the F band for crystals having the fcc structure. The curve for the band at higher energies has a slope, $n_1 = n_{No. 3}$. In other words, the two bands correspond to the F band and the No. 3 band, which has been observed in KI.

As can be seen in the replotted spectra in Fig. 15, the two bands are not completely resolved. They are almost indistinguishable at 50,000 atm since the F band shifts to higher energies at a greater rate than the No. 3 band.

Optical bleaching occurred when the compressed crystals were irradiated in either of these bands. A change in pressure, either an increase or decrease, restored the bands.

6. RbI The one atmosphere spectrum shows a considerable amount of structure. The structure on the low energy side is probably due to the M and R centers, and the hump on the high energy side is presumably due to the K band.

Two bands were seen in RbI above the transition point corresponding to the two bands seen in RbBr and KI. From Fig. 11, $\frac{\Delta E_m}{\Delta P} = 9.08 \times 10^{-6}$ ev/atm is obtained for the F band, and $\frac{\Delta E_m}{\Delta P} = -5.00 \times 10^{-6}$ ev/atm is obtained for the No. 3 band. The values of n correspond to n_F and $n_{No.3}$, respectively.

In Fig. 16, it can be seen that the F band and the No. 3 band were nearly equal in intensity, but that they were not completely resolved. The half-width of the F band is about 1.5 times that of the No. 3 band. Optical bleaching of the compressed crystals occurred, just as in the case of RbBr. Similarly, the intensity of absorption could be restored by changing the pressure on the crystals.

CHAPTER IV

DISCUSSION

1. Dependence of Peak Energy on Interionic Distance. Mollwo[42] found experimentally that, at one atmosphere and 25°C, the absorption maximum of the F center in several alkali halide crystals could be represented approximately by:

$$E_m a^2 = \text{Constant.} \tag{2}$$

A correlation of the data by Ivey[43] showed that

$$E_m a^{1.84} = 17.6 \tag{3}$$

if E_m is in electron volts and a is expressed in Angstrom units. The latter equation applies only to crystals having the fcc structure and states that the absorption peak depends only on the interionic distance and is independent of the host crystal. Similar relationships for other color centers in fcc crystals were found by Ivey. Recently, Avakian and Smakula[44] found for the absorption maximum of the F band in CsCl, CsBr, and CsI;

$$E_m a^{2.5} = \text{Constant.} \tag{4}$$

In the particle-in-a-box model, the peak energy is inversely proportional to the square of the box diameter, i.e., to the lattice parameter.[45] This is essentially the Mollwo relationship. For a higher approximation, more extensive calculations are necessary, and a more complicated dependence of the energy on the lattice parameter is found. In the following section, the discussion of this dependence is limited to a comparison of the high pressure data for each alkali halide crystal with the one atmosphere data for all the crystals (the Ivey relationship).

2. Effect of Pressure on the Absorption Maxima. In Fig. 20, the curves of $\log_{10} E_m$ as a function of $\log_{10} a$ are shown both at one atmosphere and at high pressures. The lower dotted line is obtained from the Ivey equation for the F center in the fcc structure, Eq. 3 above. The upper dotted line represents the data of Avakian and Smakula[46] for CsCl, CsBr, and CsI at one atmosphere and 25°C.

For the sodium and potassium halides in the fcc structure, n_F is greater than 1.84, the magnitude of the Ivey slope. Since the one atmosphere points lie approximately on the Ivey curve (which, in fact, they help determine), the curves are not collinear.

Above the transition point, in the sc structure, n_F for the potassium and rubidium halides is greater than the Ivey slope for the cesium halides, -2.5. A change in anion for either potassium or rubidium does not produce the same displacement of these curves as in the fcc structure; and in fact, the curves for a given cation are nearly collinear. Note also that the curves for the potassium compounds in the sc structure lie well below the curves for the rubidium halides as well as the one atmosphere cesium halide line. The rubidium halide curves all rise upwards toward the left from the vicinity of the upper dotted line. This is typical of all of the curves in the fcc structure. However, the curves for the potassium halides do not even cross the one atmosphere line. If an equation of the Ivey form could be written for a given structure, all of the curves should originate from a point near the upper dotted line. This illustrates the limitation of an Ivey type equation.

$n_{No.3}$ for RbBr, RbI, and KI approximate n_M in KBr to within 10°/o.

Since n_F and $n_{No.3}$ are constant (at least in the region from 0 to 50,000 atm), one can describe the high pressure data for each crystal in a given structure by the equation of a straight line,

$$\log_{10} E_{mi} = - n_i \log_{10} a + \log_{10} C_j \tag{5}$$

where the C_j's are constants. This can be written as

$$E_{mi} \, a^{n_i} = C_j . \tag{6}$$

Each equation applies to one color center in a particular crystal (denoted by the subscript j) and structure. Eq. 6 has the same form as the Ivey equation. However, the Ivey equation applies to all crystals of a given structure only one C_j is necessary for a given structure.

For a zero-order calculation, Gourary and Adrian conclude that at one atmosphere lattice distortion effects in the neighborhood of the F center are small and may be neglected. Our experiment indicates that this is probably not the case at high pressures.

Jacobs derived the expression,

$$- \left(\frac{\partial \ln E}{\partial \ln a} \right)_T = \frac{3 \gamma_G T}{E} \left(\frac{b}{\Theta} \right) - f_T \left(\frac{\partial \ln E_o}{\partial \ln R} \right)_T \tag{7}$$

where γ_G = Gruneisen Constant

Θ = Characteristic Temperature (Debye)

b = Coupling constant

$E_o = E_o \left[R\ (a) \right]$ = Transition Energy at Absolute Zero

$f_T = (\partial \ln R / \partial \ln a)_T$

The subscript T denotes constant temperature. The first term on the right represents the interaction of the electron with the optical lattice vibrations, and the second term represents the shift due to changes in the lattice spacings. Jacobs concluded that the former contribute less than 5 °/o of the pressure shift while the remainder is due to the latter.

f_T describes the change of the lattice spacing in the neighborhood of the F center with respect to the lattice spacing in the bulk crystal. Jacobs calculated f_T from a continuum model and also from experimental data. He found that $f_T > 2$ for NaCl, NaBr, KCl, KBr, KI, and RbCl. The value of f_T for CsCl was 1.5 for the continuum model and 1.0 from the experimental calculation. This means thatthe compressibility of the F center is greater than that of the bulk crystal except possibly in CsCl. Eppler and Drickamer[47], assuming the Ivey relationship, extended these calculations to 20,000 atm for several alkali halides. Their experimental values of f_T varied from 1.7 to 2.3 for five alkali halides.

If the Ivey type relationship for the F center under compression is valid, then

$$E_m R^{1.84} = \text{Constant} \tag{8}$$

is obtained.

For fcc crystals, the result obtained from Eq. 7 is

$$f_T \approx n_f / 1.84 \tag{9}$$

since the optical interactions (the first term in Eq. 7) with the lattice are small.

A corresponding relation for the simple cubic structure can not be written with confidence since the curves for potassium in Fig. 20 do not originate from the upper dotted line. If it is assumed that

$$E_m R^{2.5} = \text{Constant} \tag{10}$$

for the sc structure and if the optical interactions are small, a result similar to that for the fcc structure,

$$f_T \approx n_f / 2.5 \tag{11}$$

is obtained.

n_f found in this experiment for the fcc crystals was greater than 1.84 and for the sc structure greater than 2.5. It does not seem likely that experimental error could account for the deviation of f_T from unity. Any error in the pressure measurement would be in the wrong direction. If the pistons encountered unusual frictional forces in a particular experiment, then the pressure indicated on the guage would be greater than the pressure in the cell. The interionic distances calculated from these readings and the compressibility data would then be too large. A correction for this would increase f_T still further. An error of this sort could explain the fact that the potassium halide plots in the sc structure are displaced from the rubidium and cesium halide curves in that structure. However, the F center absorption in these crystals has been measured in several different laboratories with similar results.

On the basis of the model of an electron trapped in a well, it can be concluded that the compressibility of the F center is much greater than that of the bulk crystal. Other models might not yield the same conclusion. The deviation of the NaCl and NaBr $\log_{10} E_m$ vs $\log_{10}$ a plots from linearity at pressures greater than 50,000 atm could be explained by the introduction of repulsive forces as the ions are pushed toward each other.

3. Identity of the No.3 Band. As seen above, new bands appear in some crystals under compression. Some have been identified, while others have not. From the trends in the frequency shift of the F band maximum in the fcc structure to the No. 2 band maximum in the sc structure for various crystals, others have concluded that the No. 2 band is the F band.[48] Also, the No. 2 band is the more intense, further indicating

that it is the F band. The fact that the F band is the most intense band in the fcc structure has been used by others in identifying the F band in crystals having the sc structure.[49] The fact that $n_{No.2}$ for RbBr, RbI, and KI is typical of the F center provides additional evidence that the No. 2 band is the F band. The No. 2 band is therefore accepted as the F band in the sc structure.

However, the No. 3 band has not been identified. $E_{No.3}/E_F$, the ratio of the peak energy of the No.3 band to that of the F band, varies from 1.27 to 1.16 in RbI and from 1.22 to 1.09 in RbBr. In KI, this ratio varies from 1.28 at 30,000 atm to 1.24 at 40,000 atm. The corresponding ratio for the No.1 band in KI varies from 1.32 at 5,000 atm to 1.26 at 20,000 atm.

Both the No.1 and No.3 peak energies are approximately a factor of 2 greater than the one atmosphere M center energy in KI, RbBr, and RbI. This ratio does not vary much with pressure in KI where the shift of the M center is known. Since $n_{No.3} \approx n_M$, it is possible that the two bands are due to transitions in the same center. Another band attributed to the M center has previously been observed.[50] By the use of polarized light to stimulate emission at one atmosphere, absorption related to the M center has been observed in the region of the F band. The assignment of the No.3 transition to the M center would require a rather high excited state for this center, higher than permitted by the model of this center in the fcc structure. However, this center is fundamentally different in the two crystal structures, so that such a level might be possible in the sc structure. The enhanced intensity of the M band just above the transition point is an indication that the M center is more stable in the high pressure structure. Such an increased stability could mean a deepening of the trap, which in turn would make possible the presence of another discrete energy level.

The No. 1 and No. 3 energies are greater than the F energy. Thus the possibility of their origin in the F center should be examined. If the F center were hydrogenlike, the ratio between the absorption to a second excited state to the first transition would be 1.18. The ratios in Table V, $E_{No.1}/E_F$ and $E_{No.3}/E_F$, are remarkably close to this. The particle-in-a-box model, however, would require a much higher excited state. Just as in the case of the M center above, the presence of this higher state below the conduction band would have to be justified. Each of these assignments is appealing in that it does not require the postulation of another center. The fact that $n_{No.3}$ is less than n_F might be more difficult to justify if all levels in a given center show the same dependence on the interionic distance.

Another possibility is the identification of the No. 3 band with either the K band or the L_1 band. These bands have been observed on the high energy side of the F band in the spectrum of crystals having the fcc structure. An estimate of the half width of the No. 3 band in RbI yielded 0.3 ev. This is approximately that found for the K band, 0.32 ev, and the L, band, 0.26 ev by Lüty.[51] Unfortunately, the behavior of the K band and the Lüty bands with pressure is unknown. The Lüty bands have not been reported in crystals having the sc structure, so their exact location in the spectrum relative to the F band is not known. From the relative frequencies of these bands in the spectra of the crystals in the fcc structure, it would appear that the No. 3 band lies between the L band and the K band. As stated previously, the comparison might be invalid, due to the fundamental difference in the two structures.

Still another possibility presents itself. The No. 1 band seen in KI by Maisch and Drickamer[52], and which was identified by them as the counterpart of the No. 3 band below the phase transition, appeared only after the transition point was crossed from above. This identification is supported by the fact that $n_{No.1} \approx n_{No.3}$. The No. 1 band was extremely unstable. It disappeared completely when the pressure was lowered to one atmosphere or when the crystal was illuminated with light having the same frequency as the No. 1 band. The centers responsible for these bands, therefore, may be completely new centers which have never been detected in the crystals at one atmosphere. Since the difficulty of explaining the higher energy levels in the F and M centers seems so great, this may be the most probable explanation of these two bands.

4. Half-width and Absorption Measurements. The peak optical density for the F band tends to increase with increasing pressure within a given crystal structure, but decreases sharply when the structure changes from the fcc to the sc lattice. Similarly, the half-width remains constant within a given structure and increases sharply upon crossing the transition point from below. These two opposing effects tend to make the integrated area under the absorption curves constant. The M band, which was very weak in KBr below the transition pressure, became clearly visible in the sc structure. The reverse transition restores all bands to their original shapes.

A small increase of $(\log_{10}\frac{Io}{I})_{max}$ within a given structure is not unexpected since the density of color centers in the light path is increased. $n_v(\rho_1)$ the number of color centers per unit volume at some density ρ_1, is related to the number density at ρ_2 by

$$n_v(\rho_1) = \left(\frac{\rho_1}{\rho_2}\right) n_v(\rho_2) \qquad (11)$$

If the absorption coefficient is ϵ_{max} and the concentration is c, we have for a path length x,

$$\log_{10} I_o / I = \epsilon_{max}\, c\, x \propto n_v(\rho) \tag{12}$$

For a constant path length at the absorption peak,

$$\left(\log_{10} \frac{I_o}{I}\right)_{\rho_1} = \left(\frac{\rho_1}{\rho_2}\right) \left(\log_{10} \frac{I_o}{I}\right)_{\rho_2} \tag{13}$$

The density increases by about $10^{o}/o$ from one atmosphere to the transition point for the potassium halides and another $10^{o}/o$ to 50,000 atm. The density increase above the transition to 50,000 atm for the rubidium halides is $20^{o}/o$. The increase from one atmosphere to 50,000 atm is typically about $40^{o}/o$ for the sodium halide crystals.

The magnitude of the half-widths above the transition points is not characteristic of the simple cubic structure. At one atmosphere and temperatures where data are available, the half-widths of the F center in the fcc and sc structures are about the same.[53] The fact that the absorption bands assume their original strengths and shapes when the pressure is lowered beneath the transition point indicates that it is not compression *per se* or disorder introduced at the transition which produces these effects. From this, one might conclude that the interactions and different energy configurations in the sc structure are responsible for the changes. However, it was pointed out above that this apparently is not true.

Another explanation seems possible. New bands , which were unresolved, may be formed in the sc structure. Several facts support this postulate. M centers may be formed from F centers when the transition point is crossed. The M band in KBr increased in intensity above the transition point. The No. 3 band, the new band which appears in the spectrum of KI, RbBr, and RbI above the transition point, may arise from a center formed from F centers. It was shown in this paper that the No. 3 center possesses a compressibility similar to that of the M center and could be M center absorption. It was stated above that absorption related to the M center was observed by van Doorn and Haven in the region of the F band. As was also mentioned above, the F band has been shown to have structure in the cesium halides at low temperatures. According to this interpretation, the reduced peak optical density of the F band means either that some F centers have been used in the formation of new centers or, perhaps, that these centers already existed in the fcc structure and the absorption bands are further apart in the spectrum of crystals having the sc lattice.

5. At the Transition Points. The peak frequencies of the F and M bands exhibit a discontinuity at the transition point where the crystals change from the NaCl to the CsCl structure. In some crystals, such as KCl, the peak frequency increases. In others, such as KI, there is a decrease in peak frequency. In general, for a given metal ion, the change in energy becomes less positive in the order Cl^-, Br^-, and I^-. A decrease is qualitatively consistent with the fact that the interionic distance increases at the transition point, by as much as 3°/o in some crystals even though the density increases.[54] This can be seen by remembering that it has been shown that the peak energy is inversely proportional to some power of the interionic distance greater than one.

The reasons for an energy shift at the transition arise from two factors, the change in density and structure at the transition pressure. Unfortunately, these are not independent since the interionic distance at a given density is different for the two structures. A density increase for a given structure will cause a shift to higher energies since the interionic distance will decrease. If the structure changes, the number and distances of the neighboring anions and cations from the lattice vacancy will change. In other words, not only does the interionic distance change when the transition point is crossed, but the values of n_F and C_j in Eq. 6 also change. In Tables VI and VII, calculations of various energy ratios are made to illustrate some of these effects. The values used in determining these ratios were obtained from the extrapolation of the curves in Fig. 20 utilizing the densities ρ_1 above, and ρ_2 below the transition point. The determination of these energies which are defined below, is illustrated in Fig. 21-(A) and 21-(B) for Table VI and Table VII, respectively. Some relationships between these quantities are also derived below.

First, consider Table VI. Let the subscript 1 denote the CsCl structure and the subscript 2 the NaCl structure and the prime denote values above the transition pressure. Then, the peak energies E_1' and E_2 are real while E_1 and E_2' are virtual quantities. From Eq. 6, we obtain

$$E_1' = \left(k_1\ \rho_1^{-1/3}\right)^{-n_1} C_1 \text{ and } E_1 = \left(k_1\ \rho_2^{-1/3}\right)^{-n_1} C_1 \qquad (14\text{-a,b})$$

$$E_2' = \left(k_2\ \rho_1^{-1/3}\right)^{-n_2} C_2 \text{ and } E_2 = \left(k_2\ \rho_2^{-1/3}\right)^{-n_2} C_2 \qquad (14\text{-c,d})$$

with $k_1 = (\sqrt{3}/2)\ M^{1/3}$ and $k_2 = (M/2)^{1/3}$ for ρ_1 above and ρ_2 below the transition point. Then the quantities

$$\frac{E_1'}{E_1} = \left(\frac{\rho_1}{\rho_2}\right)^{1/3\ n_1} \qquad (15\text{-a})$$

and

$$\frac{E_2'}{E_2} = \left(\frac{\rho_1}{\rho_2}\right)^{1/3\ n_2} \qquad (15\text{-b})$$

represent the effect on the peak energy of the change in density at the transition point for a given lattice structure. These ratios are listed in Table VI, columns 4 and 5. Since the density always increases when the transition point is crossed from below, a shift to higher energies is expected for a given structure. Thus, if there were no change in structure, the peak energy for the crystals listed in Table VI would increase from 14^{o}/o to 20^{o}/o (see columns 4 and 5, where these ratios are tabulated). Any decrease of the peak energies arises from a change in structure.

The ratios E_1'/E_2' and E_1/E_2 which represent the effect of crystal structure on the peak energy at ρ_1 and ρ_2, respectively, are given by:

$$\frac{E_1'}{E_2'} = {\frac{k_2}{k_1}}^{(n_2-n_1)} \rho_1^{1/3\,(n_1-n_2)} \frac{C_1}{C_2} \qquad (16\text{-a})$$

and

$$\frac{E_1}{E_2} = {\frac{k_2}{k_1}}^{(n_2-n_1)} \rho_2^{1/3\,(n_1-n_2)} \frac{C_1}{C_2} \qquad (16\text{-b})$$

Eqs. 16-a and 16-b are about the same for a given crystal since n_1 is approximately equal to n_2, i.e. the curves in Fig. 20 are nearly parallel. Unlike Eqs. 15-a and 15-b, they vary from crystal to crystal. The ratio (C_1/C_2) appears here. According to our model, which implies coulomb interactions, this ratio must be related to the effective charge acting on the F electron in the CsCl structure relative to that in the NaCl structure. The values obtained are listed in columns 2 and 3.

In Table VII, the effect of structure and interionic distance is considered at the transition point, where $a_1 = k_1\rho_1^{-1/3}$ and $a_2 = k_2\rho_2^{-1/3}$.

Then,

$$E_1' = a_1^{-n_1} C_1 \tag{17-a}$$

$$E_1 = a_2^{-n_1} C_1 \tag{17-b}$$

$$E_2' = a_1^{-n_2} C_2 \tag{17-c}$$

$$E_2 = a_2^{-n_2} C_2 \tag{17-d}$$

The ratios,

$$\frac{E_1'}{E_1} = \left(\frac{a_1}{a_2}\right)^{-n_1} \tag{18-a}$$

$$\frac{E_2'}{E_2} = \left(\frac{a_1}{a_2}\right)^{-n_2} \tag{18-b}$$

represent the change in energy to be expected if there were no change in structure but a change in interionic distance from a_2, the interionic distance in the NaCl structure, to a_1, the interionic distance in the CsCl structure. These ratios must be less than one since a_1 is greater than a_2,and n_1 and n_2 are greater than one. These ratios which predict an energy decrease, are listed in columns 4 and 5. However, the experimentally observed F band peak energy does not decrease in all of the crystals. This is explained by the fact that a real structural change occurs.

The values,

$$\frac{E_1'}{E_2'} = a_1^{(n_2-n_1)}\left(\frac{C_1}{C_2}\right) \tag{19-a}$$

and

$$\frac{E_1}{E_2} = a_2^{(n_2-n_1)}\left(\frac{C_1}{C_2}\right), \tag{19-b}$$

illustrate the effect of crystal structure on the peak energy of the absorption band at a_1 and a_2, respectively. These ratios, listed in columns 2 and 3, predict a shift to higher energies, which becomes less for the small cations and large anions. The ratios in Table VI are functions of ρ_1 and ρ_2, the densities above and below the transition point, respectively. The ratios in Table VII are functions of a_1 and a_2, the interionic distances above and below the transition point, respectively.

The quantities appearing in Tables VI and VII are expressed in Tables VIII and IX, respectively, as percentages of the energy below the transition point. These percentages are defined as

$$P_1/100 = \left(\frac{E_1'}{E_2'} - 1\right) \frac{E_2'}{E_2} = \frac{E_1' - E_2'}{E_2} \qquad (20\text{-a})$$

$$P_2/100 = \left(\frac{E_2'}{E_2} - 1\right) = \frac{E_2' - E_2}{E_2} \qquad (20\text{-b})$$

$$P_3/100 = \left(\frac{E_1}{E_2} - 1\right) = \frac{E_1 - E_2}{E_2} \qquad (20\text{-c})$$

$$P_4/100 = \left(\frac{E_1'}{E_1} - 1\right) \frac{E_1}{E_2} = \frac{E_1' - E_1}{E_2} \qquad (20\text{-d})$$

The experimental shift is included in the latter two tables both as the ratio E_1'/E_2 and as the percentage increase P_o, where

$$P_o/100 = \frac{E_1' - E_2}{E_2} \qquad (20\text{-e})$$

These quantities are defined so that

$$P_o = P_1 + P_2 = P_3 + P_4 \qquad (21)$$

and so that a positive quantity indicates a shift to higher energies.

P_1 and P_3 are the percentage increases above E_2 due to a structural change. In Table VIII, these would correspond to the effects of a change in structure at ρ_1 and ρ_2 and in Table IX, to the similar effects at a_1 and a_2. P_2 and P_4 are the percentage increases above E_2 due to a change in density from ρ_2 to ρ_1 in Table VIII and a change in interionic distance from a_2 to a_1 in Table IX.

The columns P_1, P_2, P_3, and P_4 in both tables become less positive in progressing from top to bottom. However, the largest changes in the two tables occur in columns P_1 and P_3, the columns to which the structural effect is attributed. These trends all correspond to the trend for the actual shifts in column P_o.

The values in Table VIII can be discussed in terms of a semi-continuum model.[55] P_2 and P_4 represent the contribution of the continuum around the cavity containing the electron, while P_1 and P_3 represent changes in the structure and dimensions of the ion shells surrounding the cavity. In terms of this model, the difference in behavior among the various crystals arises primarily from the latter effect. On the other hand, since the effect of interionic distance is separated from other effects in Table IX, the values in this Table are best discussed in terms of the Ivey-type equation. Again, the major contribution to the difference in behavior among the crystals can be attributed to a structural effect rather than to the effect of interionic distance. Note, for example, that the occurrence of a greater shift to lower energies in KI than in the other crystals can quantitatively be ascribed to a smaller increase in energy due to the structural change rather than to a greater shift to lower energies due to a change in interionic distance.

The simple model adopted above does not take account of gross lattice distortions which occur in the vicinity of the color center. Also, the ratio of the radii of the ions at one atmosphere might not be a valid concept at high pressures where the ions can overlap to a greater extent. This would be especially true for the larger ions. The polarizability of the ions could become a significant factor under compression. Nevertheless, the above discussion does point out the inadequacy expressing the F band energy as a function of interionic distance alone, especially when the bands of different crystals are compared.

V SUMMARY

It has been observed that the peak energy of the F band in the alkali halides which were studied is very sensitive to changes in the lattice spacing, e.g., a pressure change from 25,000 to 50,000 atm and a change in the interionic distance of 0.15 Å in KBr is accompanied by a change in the peak energy of 0.14 eV. The high pressure measurements indicate that the Ivey equation is fortuitous in the sense that the peak energy is not uniquely determined by the interionic distance of the bulk crystal, but also depends upon the host crystals.

It was observed that the half-widths of the F band above the transition point were greater than below the transition point and that the peak optical density decreased. It was postulated that new centers might be formed from F centers and that the F band might contain unresolved components similar to the K^1 band which could not be resolved at room temperature with the present apparatus. The possibility that the No. 3 center might be related to the F center or the M center was discussed.

In order to test these postulates, several experiments could be performed. An examination of these spectra under higher resolution would be desirable. It would also be advantageous to perform low temperature and high pressure experiments simultaneously. Quantitative bleaching experiments with or without the use of polarized light might be fruitful. Fluorescence measurements in the infrared region of the spectrum could be done. In addition, further investigation of the Lüty bands might also help in the interpretation of the present results.

The discussion of the discontinuous jumps of the peak of the F band in the various crystals at the transition point shows that the variation from crystal to crystal can be attributed to certain effects, the most important being the effect due to the change in structure.

Table I

F Band Energies and Sample Thicknesses

Crystal	E_m[a] (ev)	Sample Thickness (cm)[a,b]
NaCl:Na	2.69	0.24
KCl:K	2.24	-
KBr:K	2.00	0.20
KI:K	1.81	-
RbCl:K	1.98	0.068
RbBr:K	1.81	0.061
RbI:Electrolytic	1.66	0.064

a Value at one atmosphere

b Samples used for high pressure measurements

Table II

Negative Slope (n_i) of Log E_m vs Log a Plot for the Color Centers in Eight Alkali Halide Crystals

Crystal	n_F[a]	n_F[b]	$n_{No.3}$	$n_{No.1}$	n_M[a]	n_M[b]
RbCl	3.40[c]	3.19	-	-	-	-
RbBr	3.75[d]	3.48	1.48	-	-	-
RbI		3.13	1.38	-	-	-
KCl	3.85[e]	3.92[e]	-	-	-	-
KBr	4.00	3.87	-	-	2.43	1.50
KI	3.43[e]	3.60[e]	1.52[e]	1.35[e]	-	-
NaCl	4.47[f]	2.33[f]	-	-	-	-
NaBr	5.00[f]	3.07[f]	-	-	-	-

[a] Below the phase transition. n_F in NaCl and NaBr are measured in pressure range P = 0 - 25,000 atm.

[b] Above the phase transition. n_F in NaCl and NaBr are measured in pressure range P = 50,000 - 100,000 atm.

[c] I. S. Jacobs, Phys. Rev. 93, 993 (1954).

[d] H. Knof and W. G. Maisch (Private Communication).

[e] W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids 5, 328 (1958).

[f] R. A. Eppler and H. G. Drickamer, J. Chem. Phys. 32, 418 (1960).

Table III

F Center Half - widths for Various Crystals at One Atmosphere Pressure and Room Temperature.

Crystal	H (ev)
NaCl[a]	0.50
KCl[b]	0.36
KBr	0.37
KI	0.36
RbCl	0.35
RbBr	0.36
RbI[b]	0.335

[a] G. A. Russell and C. C. Klick, Phys. Rev. 101, 1473 (1956).

[b] F. Lüty, Z. Physik. 160, 1 (1960).

Table IV

F Center Half - widths at High Pressures and Room Temperature.

Crystal	Pressure(atm)	Half-width(ev)
KBr	5,000	0.34
	5,000[a]	0.38
	10,000	0.36
	10,000[a]	0.38
	19,200	0.37
	30,000	0.45
	40,000	0.46
	50,000	0.45
NaCl	15,000	0.49
	25,000	0.48
	35,000	0.46
	50,000	0.48
RbCl	15,000	0.40
	25,000	0.40
	35,000	0.41
	45,000	0.40

a - After lowering pressure from 50,000 atmospheres.

Table V

Relationship of the No.1 and No.3 Peak Energies to F and M Peak Energies.

RbBr		RbI	
P (10^3atm)	$E_{No.3}/E_F$	P (10^3atm)	$E_{No.3}/E_F$
11.7	1.22	9.6	1.27
13.3	1.22	-	-
15.0	1.20	15.0	1.26
20.0	1.18	20.0	1.23
25.0	1.17	25.0	1.21
30.0	1.16	30.0	1.21
35.0	1.14	35.0	1.17
40.0	1.13	40.0	1.18
45.0	1.09	45.0	1.16
50.0	1.10	50.0	1.16

KI

P (10^3atm)	$E_{No.1}/E_F$	$E_{No.3}/E_F$	$E_{No.1}/E_M$	$E_{No.3}/E_M$
5	1.32	-	1.99	-
10	1.28	-	1.99	-
15	1.27	-	1.97	-
20	1.26	-	1.96	-
30	-	1.28	-	1.84
35	-	1.25	-	1.84
40	-	1.24	-	1.83

Table VI

Energy Ratios Pertaining to the Discontinuous Shift at the Transition Point.[a]

Crystal	E'_1/E'_2[b]	E_1/E_2	E'_1/E_1	E'_2/E_2
RbCl[c]	0.971	0.980	1.19	1.20
RbBr[d]	0.927	0.919	1.20	1.19
KCl[e]	0.885	0.885	1.18	1.18
KBr	0.826	0.826	1.18	1.18
KI[e]	0.746	0.730	1.14	1.14

[a] Energies are a function of density - ρ_1 above the transition point and ρ_2 below the transition point.

[b] Subscript 1 refers to CsCl structure; subscript 2 refers to NaCl structure. Primed quantities are defined above transition pressure; unprimed quantities are defined below transition pressure.

[c] The data obtained by Jacobs below the transition point was used. I. S. Jacobs, Phys. Rev. 93, 993 (1954).

[d] The data obtained by H. Knof and W. G. Maisch below the transition point was used. (Private Communication).

[e] W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids 5, 328 (1958).

Table VII

Energy Ratios Pertaining to the Discontinuous Shift at the Transition Point.[a]

Crystal	E_1'/E_2'	E_1/E_2	E_1'/E_1	E_2'/E_2
RbCl[c]	1.33	1.31	0.901	0.886
RbBr[d]	1.23	1.26	0.858	0.876
KCl[e]	1.24	1.24	0.856	0.847
KBr	1.17	1.16	0.835	0.839
KI[e]	1.02	1.02	0.836	0.838

a Energies are a function of interionic distance - a_1 above the transition point and a_2 below the transition point.

b Subscript 1 refers to CsCl structure; subscript 2 refers to NaCl structure. Primed quantities are defined above transition pressure; unprimed quantities are defined below transition pressure.

c The data obtained by Jacobs below the transition point was used. I. S. Jacobs, Phys. Rev. 93, 993 (1954).

d The data obtained by H. Knof and W. G. Maisch below the transition point was used. (Private Communication).

e W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids 5, 328 (1958).

Table VIII

Percentage Increase in the Peak Energy of the F Band at the Phase Transition - Values Derived from Table VI.

Crystal	E_1'/E_2	P_o[a]	P_1[b]	P_2[b]	P_3[b]	P_4[b]	(P_1+P_2)	(P_3+P_4)
RbCl	1.18	+18	-4	20	-2	19	16	17
RbBr	1.08	+8	-9	19	-8	18	10	11
KCl	1.06	+6	-14	18	-12	16	4	4
KBr	0.975	-2	-21	18	-17	15	-3	-2
KI	0.856	-14	-29	14	-27	10	-15	-17

[a] P_o is the experimental value.

[b] P_1, P_2, P_3, and P_4 are obtained from columns 1, 4, 2, and 3, respectively, of Table VI by use of the general equation

$$P_i = 100\ (X - 1)\ \frac{E_j}{E_2}$$

where X is the appropriate term in Table VI and E_j is the quantity appearing in the denominator of the appropriate column heading.

Table IX

Percentage Increase in the Peak Energy of the F Band at the Phase Transition - Values Derived from Table VII.

Crystal	E_1'/E_2	P_o[a]	P_1[b]	P_2[b]	P_3[b]	P_4[b]	$(P_1 + P_2)$	$(P_3 + P_4)$
RbCl	1.18	+18	29	-11	31	-13	18	18
RbBr	1.08	+8	20	-12	26	-18	8	8
KCl	1.06	+6	20	-15	24	-18	5	6
KBr	0.975	-2	14	-16	16	-19	-2	-3
KI	0.856	-14	2	-16	2	-17	-14	-15

a P_o is the experimental value.

b P_1, P_2, P_3, and P_4 are obtained from columns 1, 4, 2, and 3, respectively, of Table VII by use of the general equation

$$P_1 = 100\ (X - 1)\ \frac{E_j}{E_2}$$

where X is the appropriate term in Table VII and E_j is the quantity appearing in the denominator of the appropriate column heading.

Fig. 7. Absorption maximum as a function of pressure: The F band in NaCl. All measurements made at room temperature.

○ —NaCl:Na

△ —Eppler and Drickamer

☐ —Maisch and Drickamer

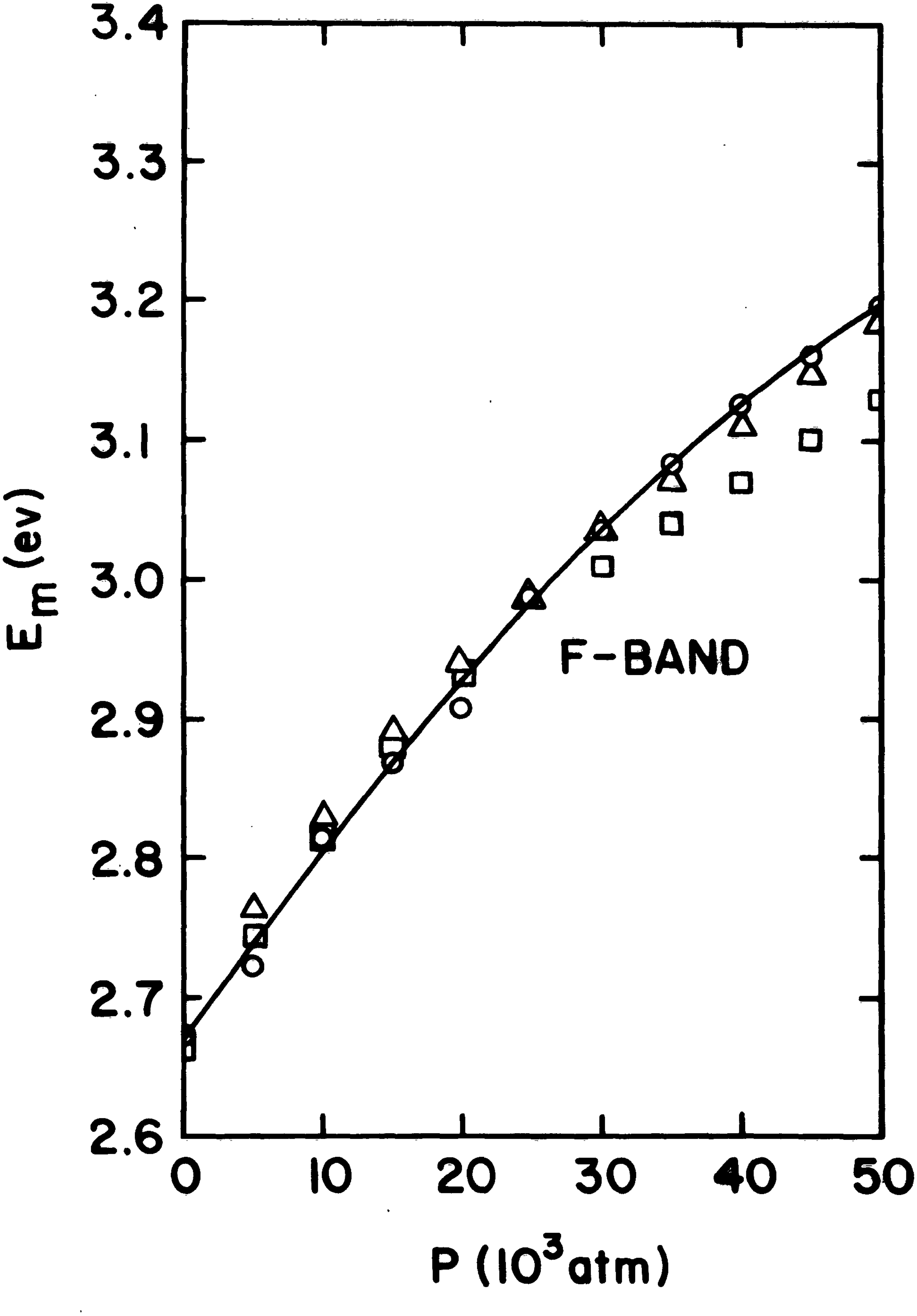

3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
E_m (ev)
F-BAND
0
10
20
30
40
50
P (10^3atm)

Fig. 8. Absorption maximum as a function of pressure: The F band in KBr. All measurements made at room temperature.

○ —KBr:K

Δ —Maisch and Drickamer

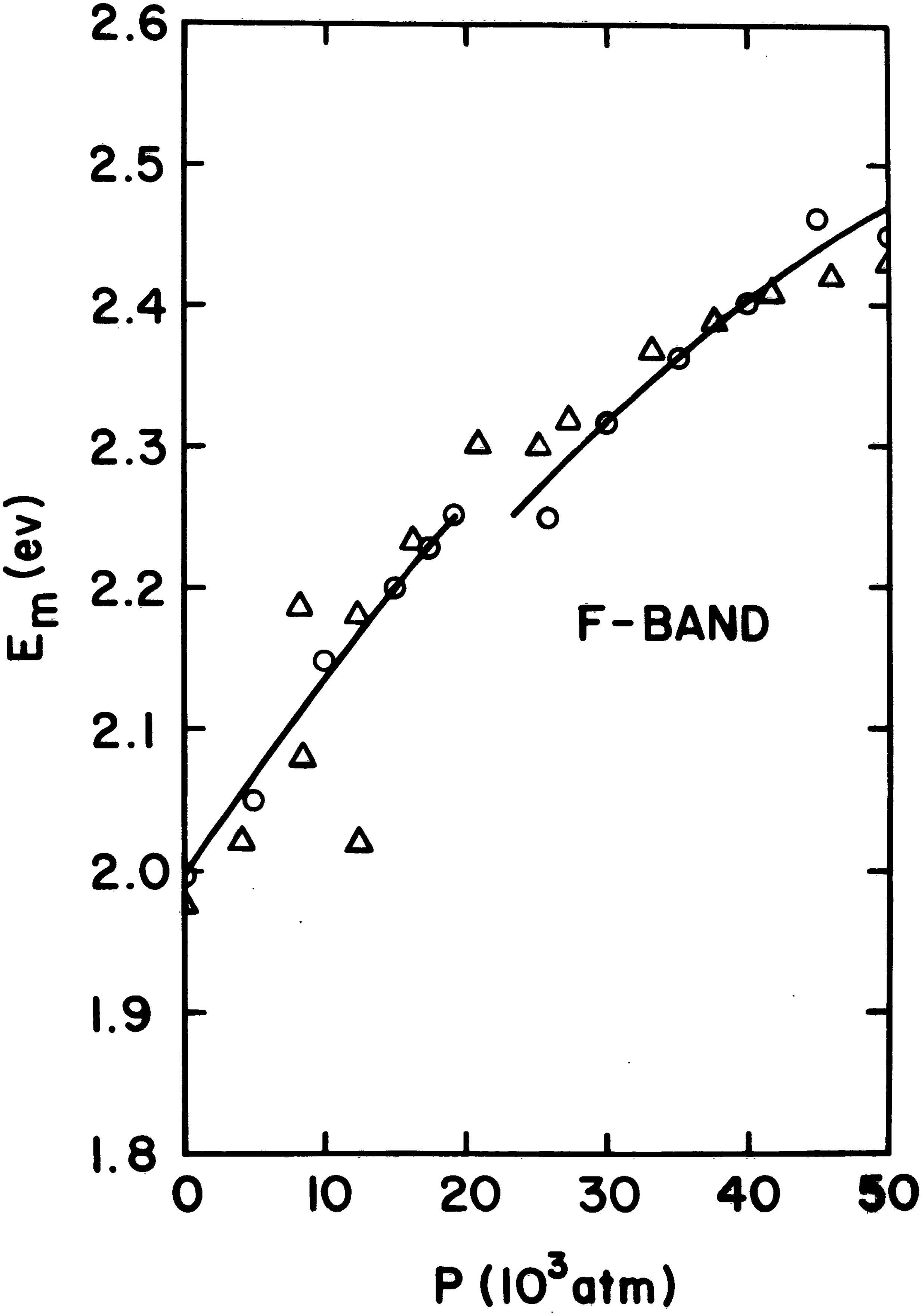

2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
E_m (ev)
F-BAND
0
10
20
30
40
50
P (10^3atm)

Fig. 9. Absorption maximum as a function of pressure:
The F band in RbCl above the transition point.
All measurements made at room temperature.
---- Extrapolation to transition pressure.

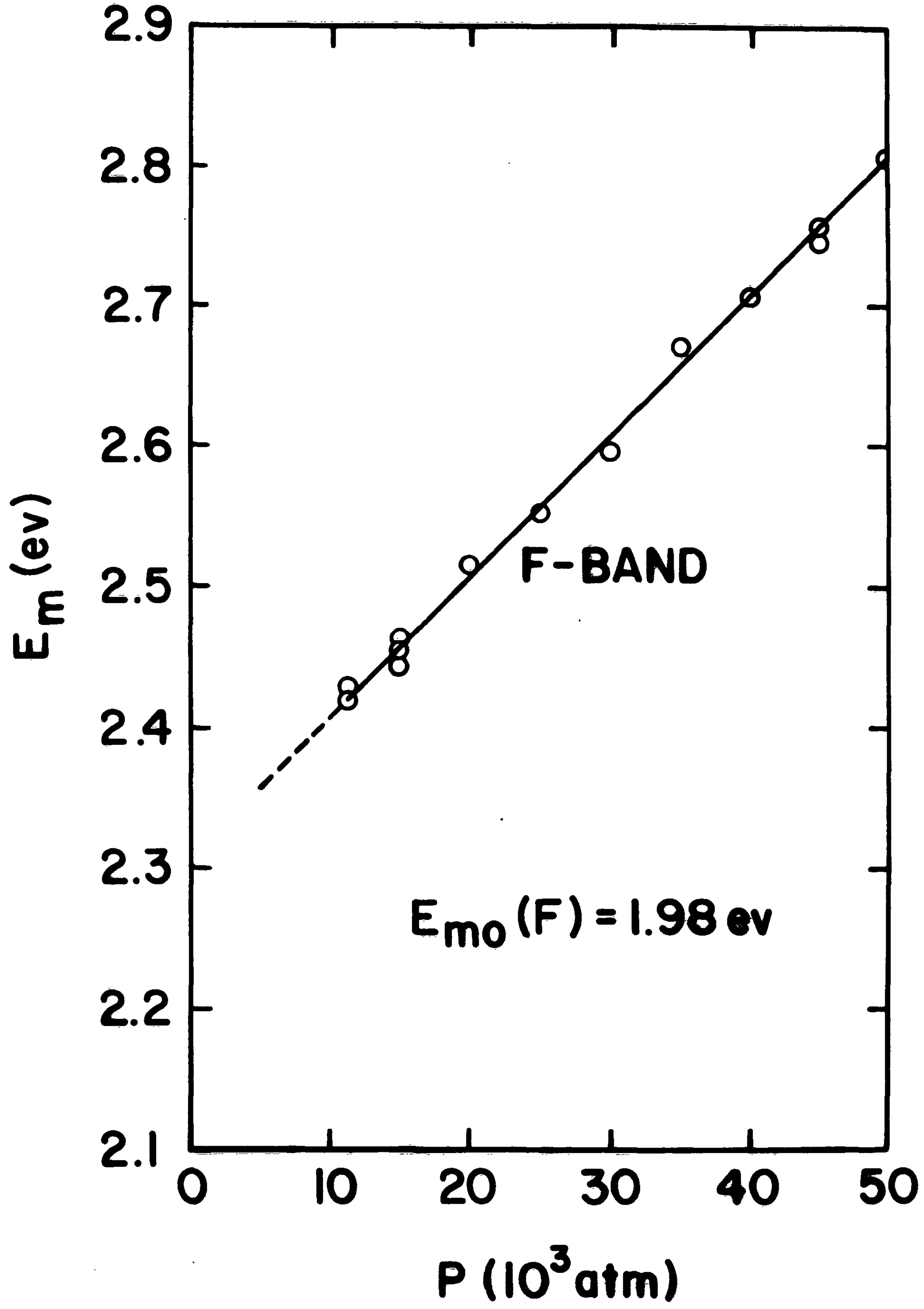

2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
E_m (ev)
0
10
20
30
40
50
P (10^3atm)
F-BAND
E_{mo}(F) = 1.98 ev

Fig. 10. Absorption maxima as a function of pressure: The F band and No. 3 band in RbBr above the transition point. All measurements made at room temperature.

---- Extrapolation to transition pressure

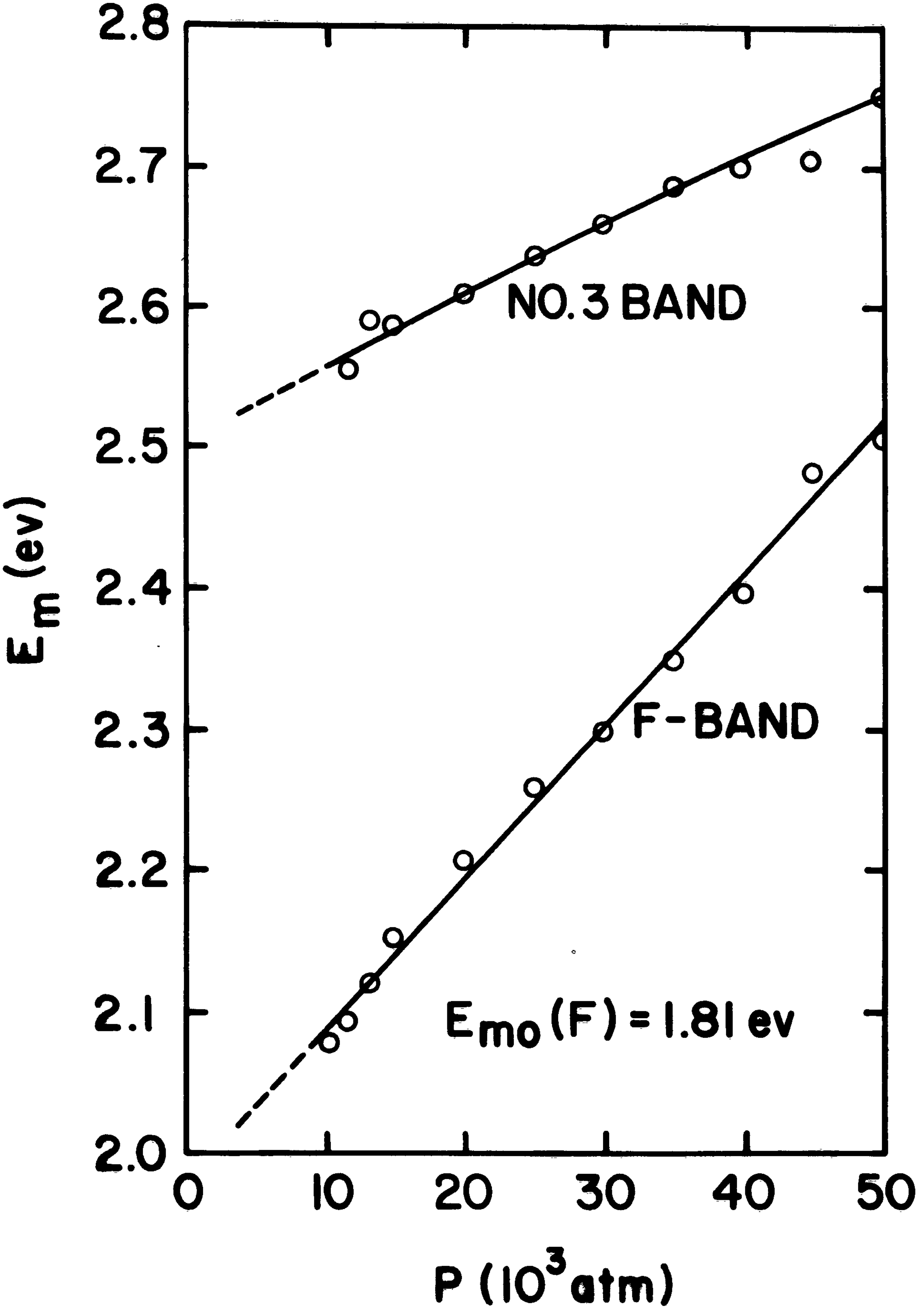

2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
E_m (ev)
NO. 3 BAND
F-BAND
$E_{mo}(F) = 1.81$ ev
0
10
20
30
40
50
P (10^3 atm)

Fig. 11. Absorption maxima as a function of pressure: The F band and No.3 band in RbI above the transition point. All measurements made at room temperature.

---- Extrapolation to transition pressure

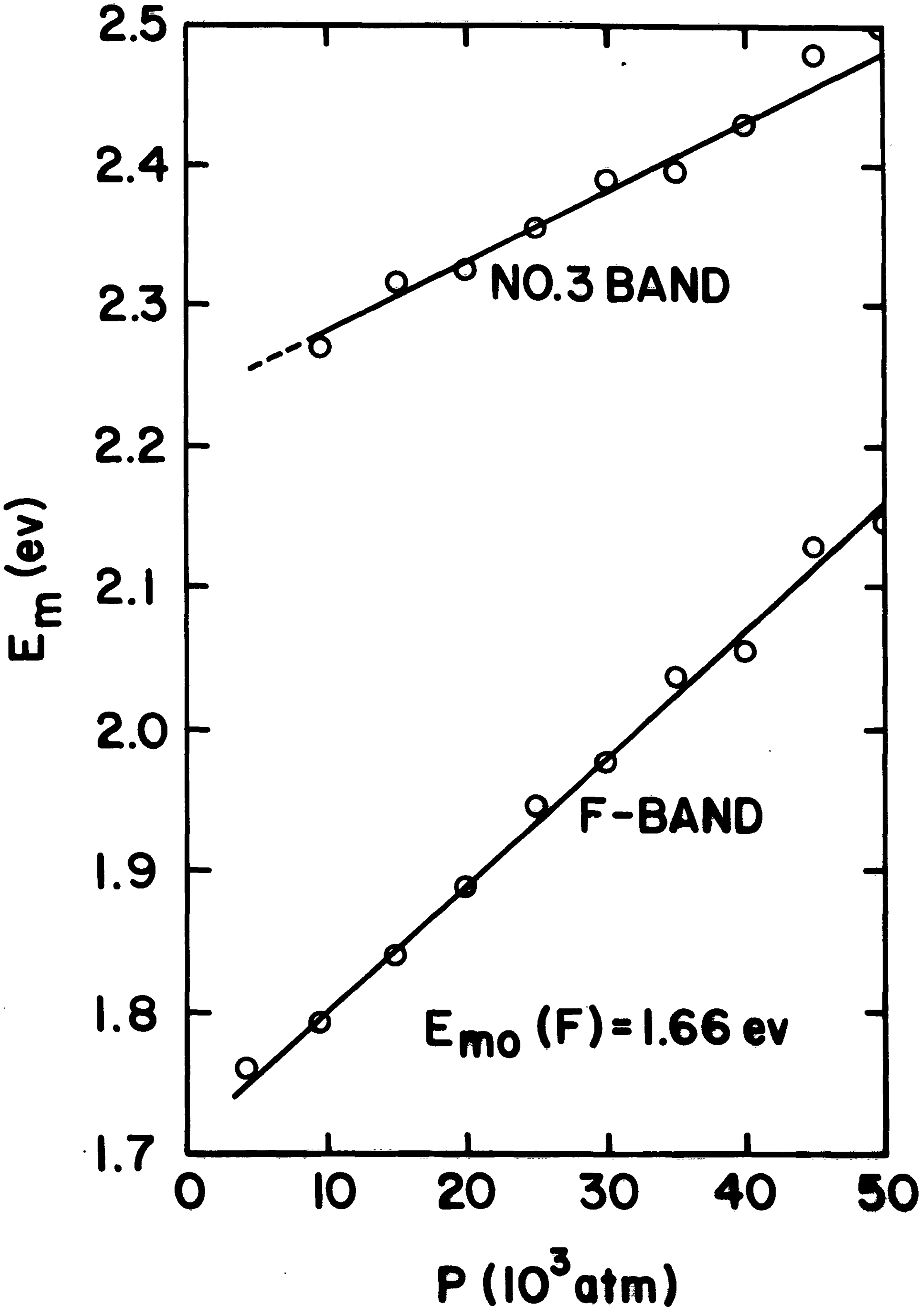
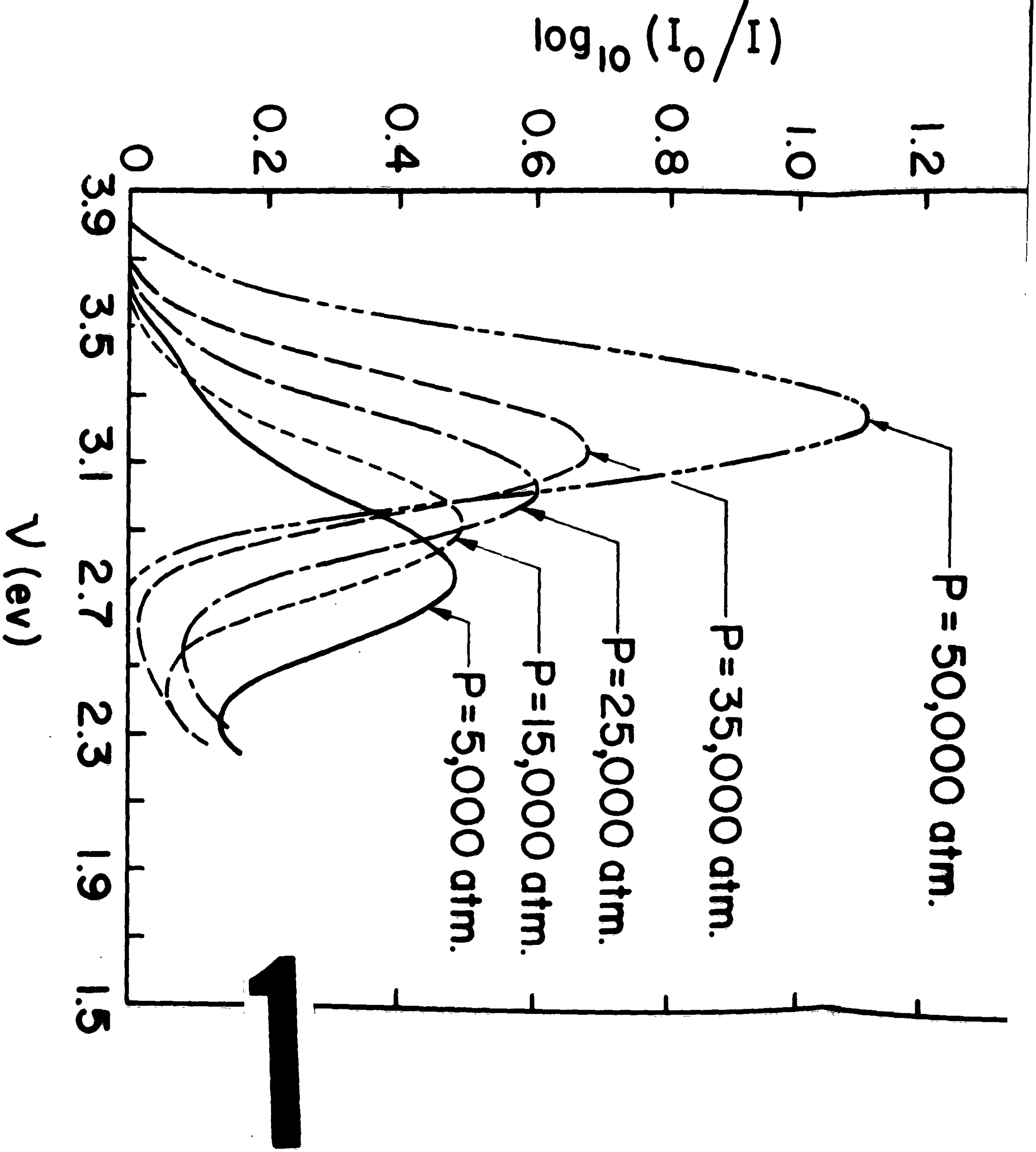
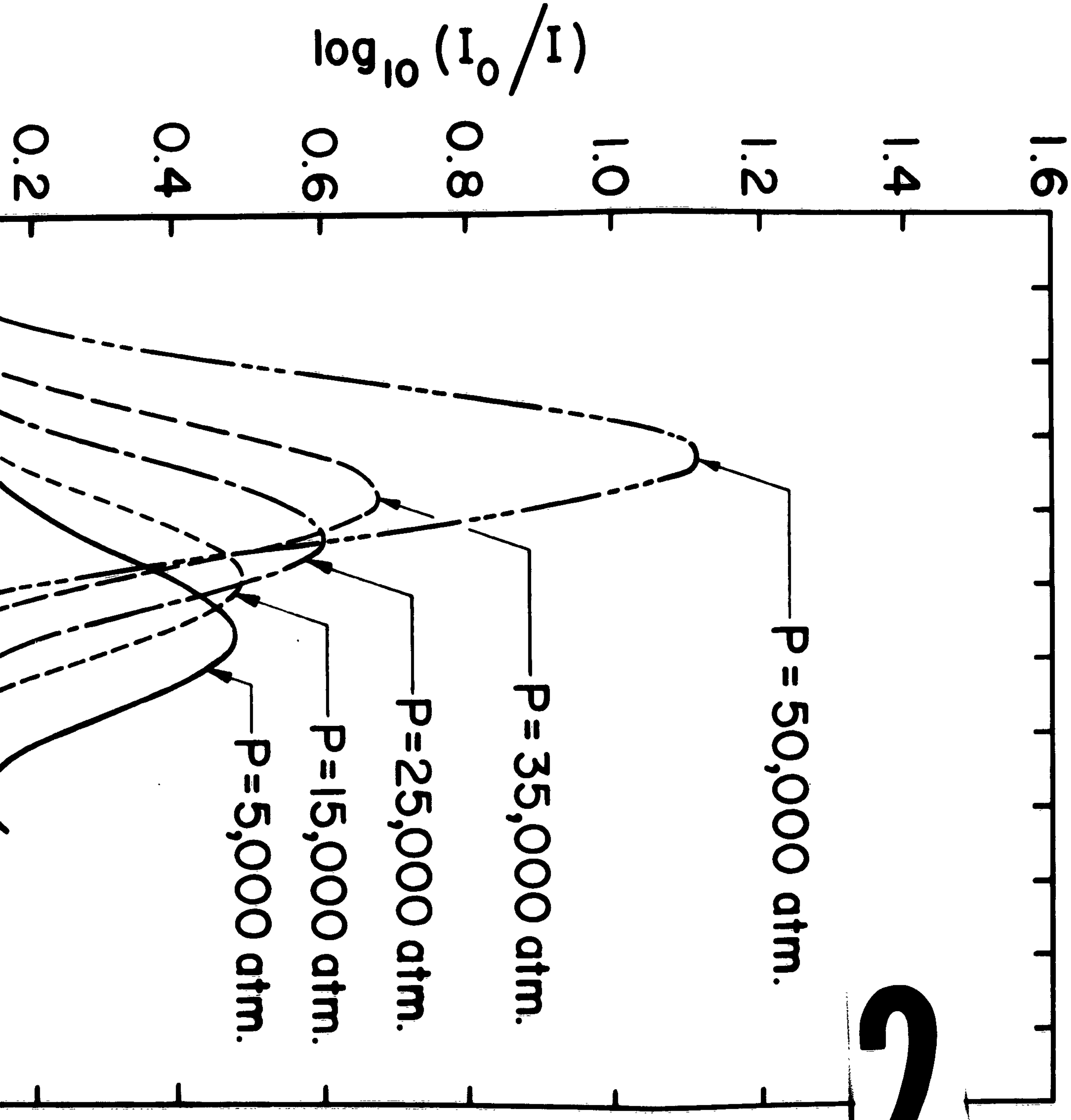

2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
E_m (ev)
0
10
20
30
40
50
P (10^3atm)
NO.3 BAND
F-BAND
E_{mo} (F) = 1.66 ev

Fig. 12. The absorption spectrum of NaCl. The F band is shown at several pressures. All measurements made at room temperature.



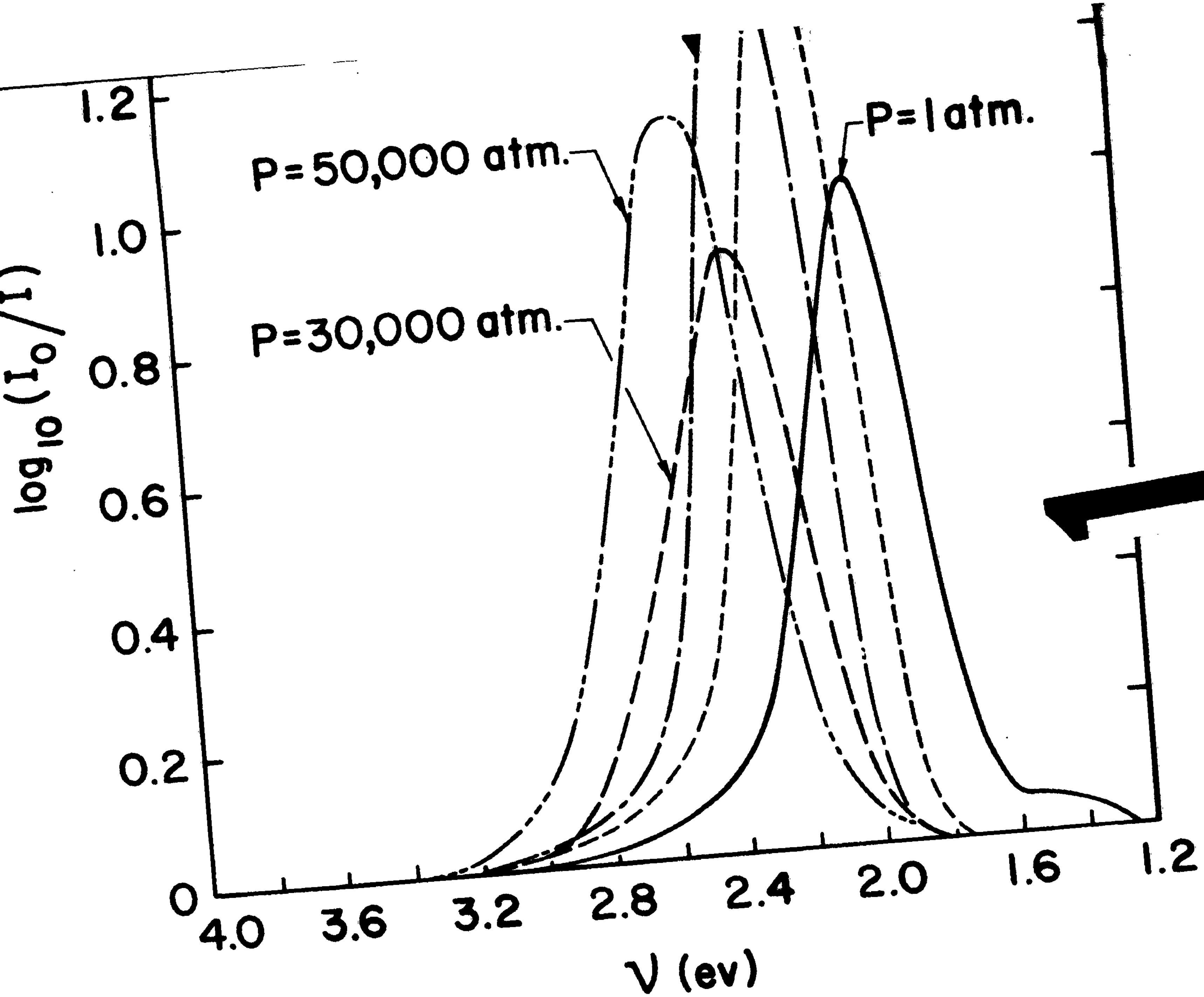
log$_{10}$ (I_0/I)
0
0.2
0.4
0.6
0.8
1.0
1.2
3.9
3.5
3.1
2.7
2.3
1.9
1.5
ν (ev)
P = 50,000 atm.
P = 35,000 atm.
P = 25,000 atm.
P = 15,000 atm.
P = 5,000 atm.

1

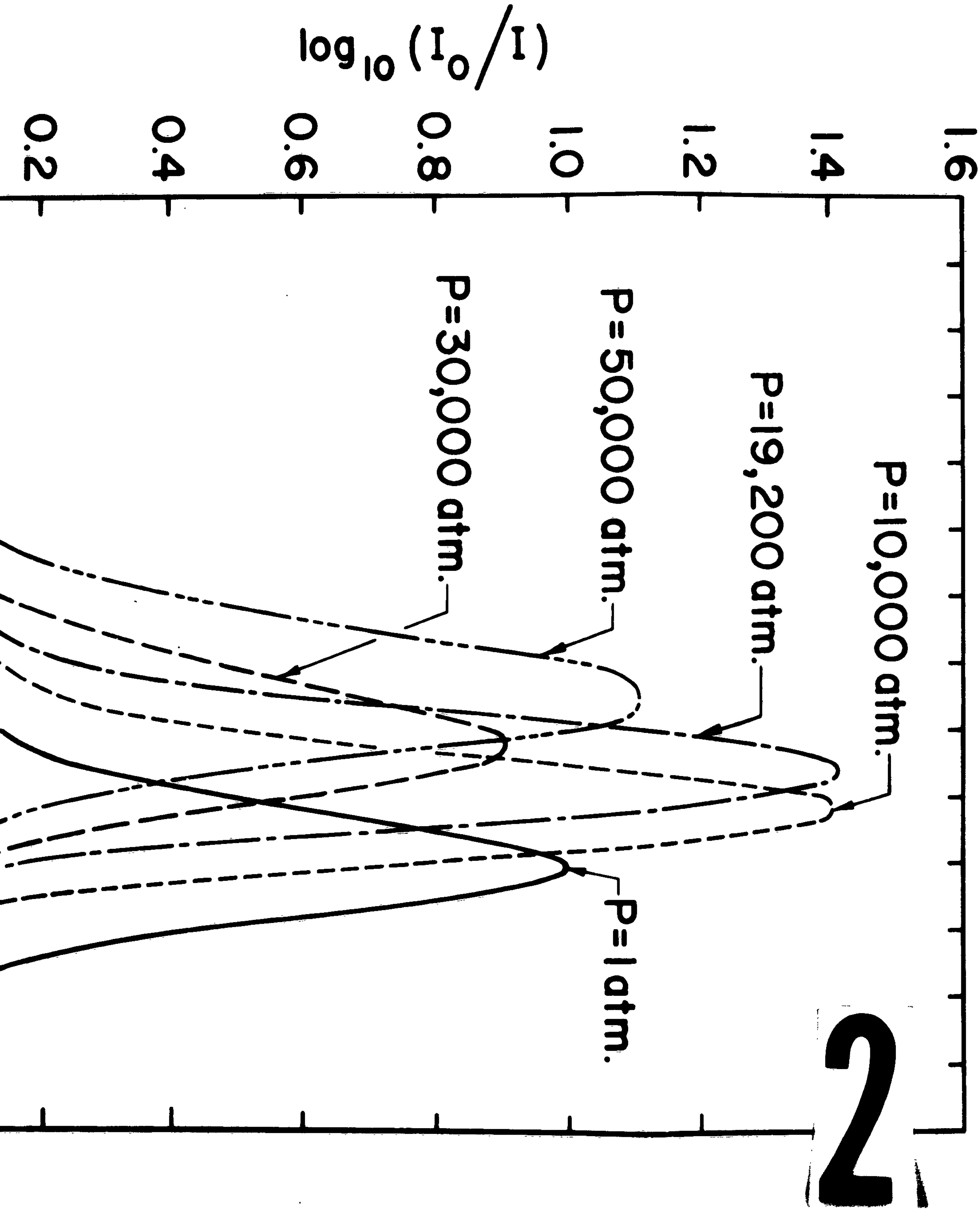

log$_{10}$ (I$_0$/I)
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
P = 50,000 atm.
P = 35,000 atm.
P=25,000 atm.
P=15,000 atm.
P=5,000 atm.

2

Fig. 13. The absorption spectrum of KBr. The F band is shown at several pressures. All measurements made at room temperature.

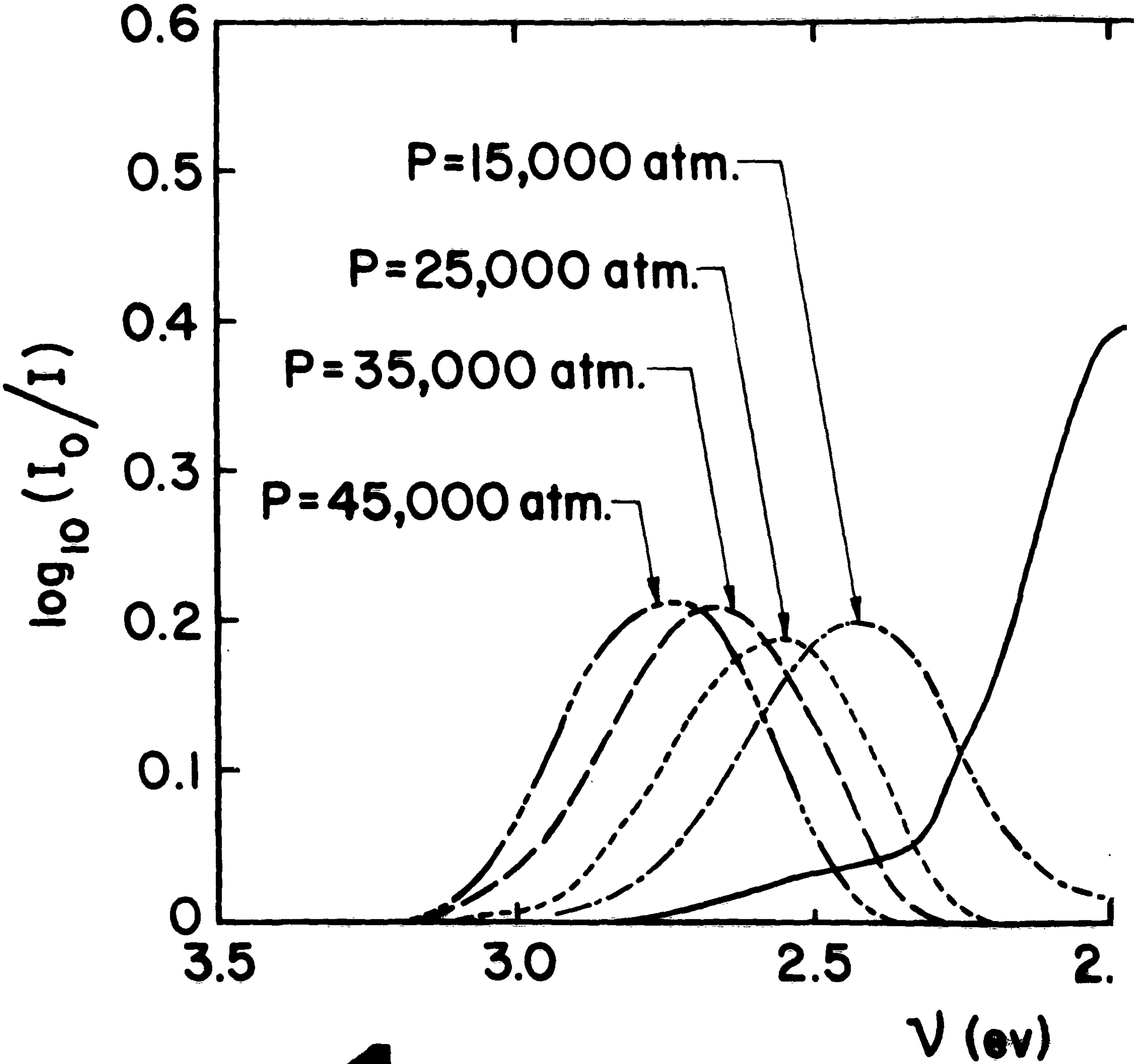

P=50,000 atm.
P=30,000 atm.
P=1 atm.
$\log_{10}(I_0/I)$
0
0.2
0.4
0.6
0.8
1.0
1.2
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
ν (ev)

1

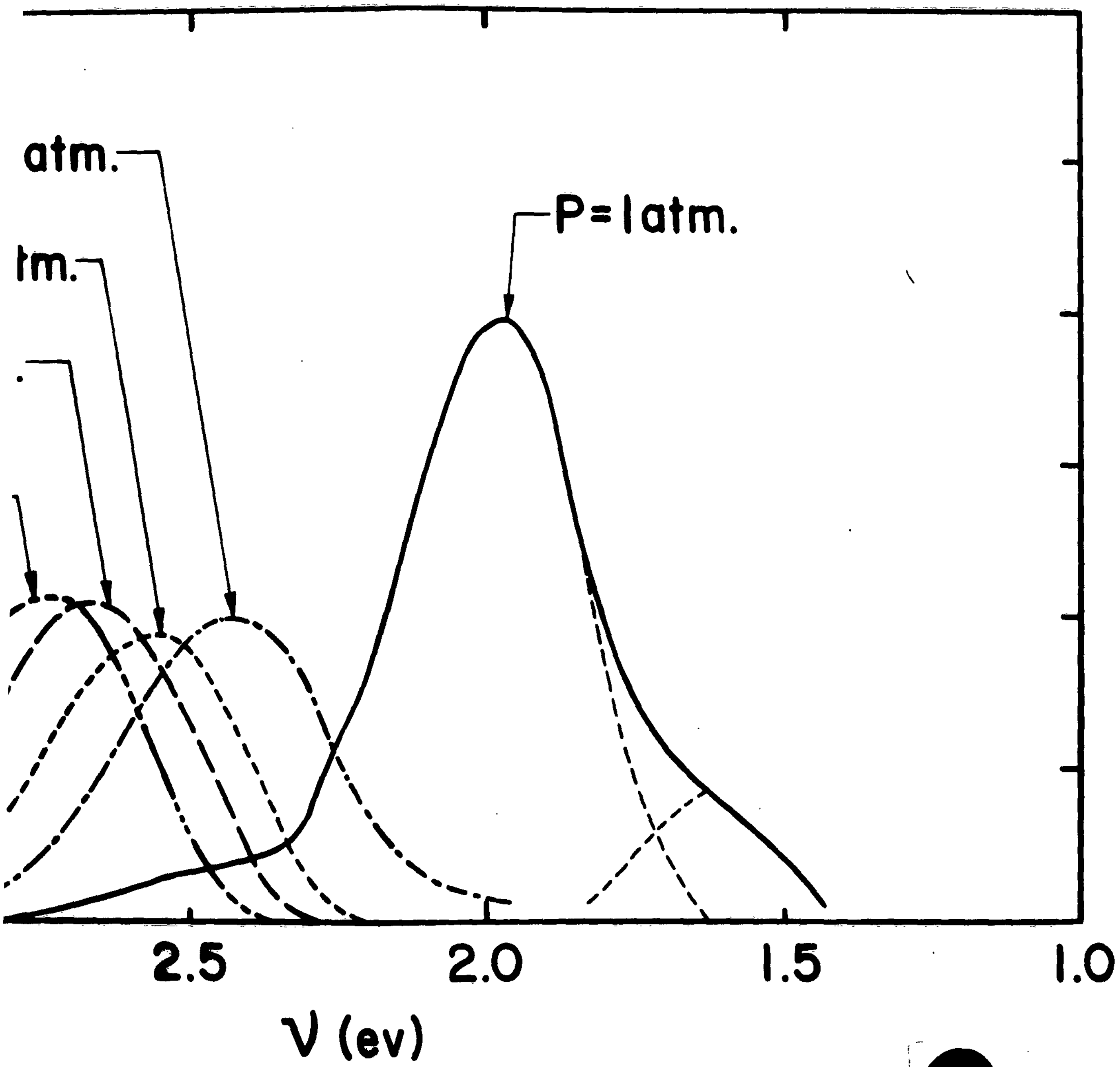

$\log_{10}(I_0/I)$
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
P=10,000 atm.
P=19,200 atm.
P=50,000 atm.
P=30,000 atm.
P=1atm.

2

Fig. 14. The absorption spectrum of RbCl. The F band is shown at several pressures. All measurements made at room temperature.

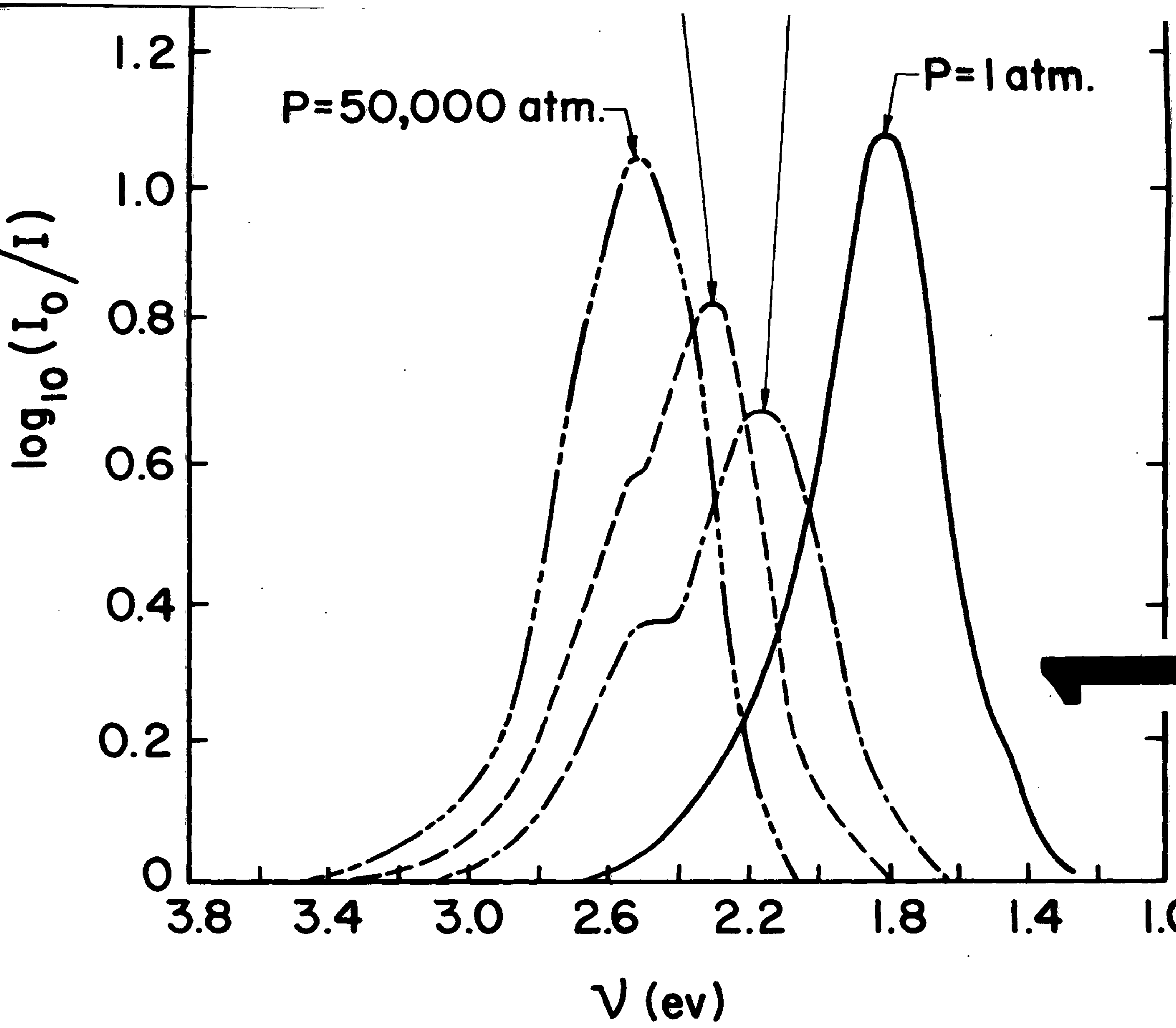

0.6
0.5
0.4
0.3
0.2
0.1
0
$\log_{10}(I_0/I)$
P=15,000 atm.
P=25,000 atm.
P=35,000 atm.
P=45,000 atm.
3.5
3.0
2.5
2.
ν (ev)

1

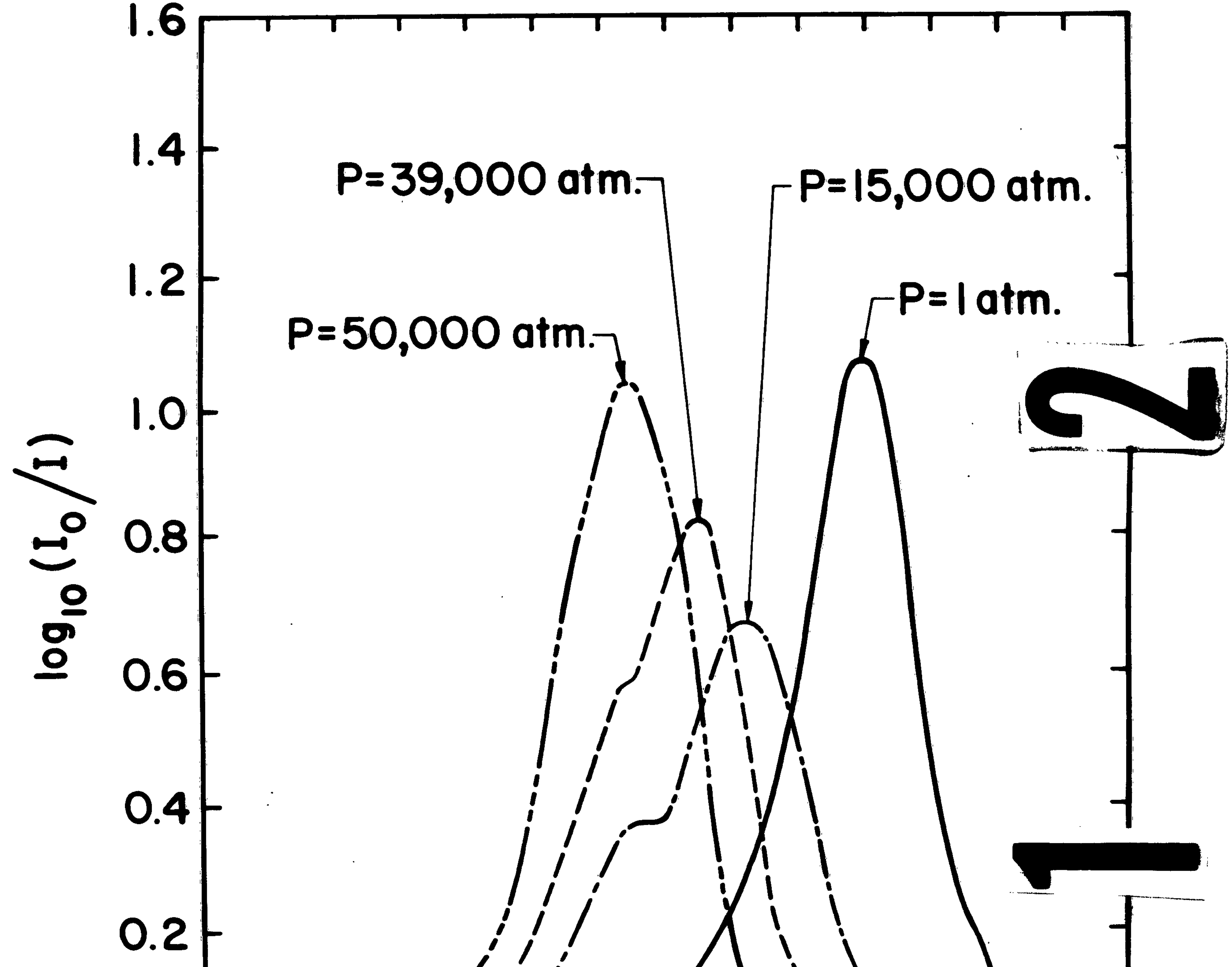


2

Fig. 15. The absorption spectrum of RbBr. The F band (low energy peak) and the No. 3 band (high energy peak) are shown at several pressures. All measurements made at room temperature.

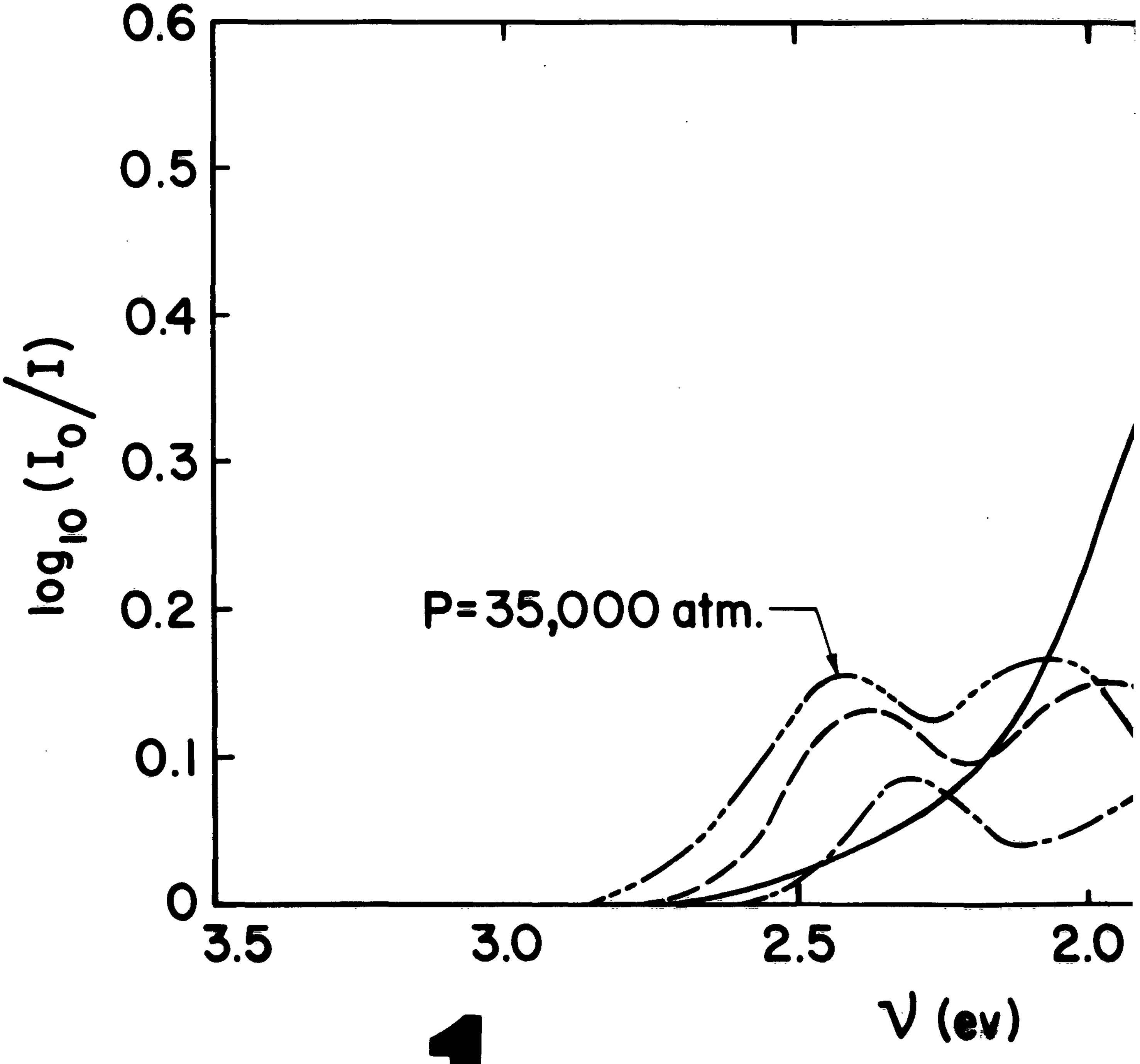

P=50,000 atm.
P=1 atm.
log$_{10}$(I$_0$/I)
0
0.2
0.4
0.6
0.8
1.0
1.2
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
ν (ev)

1

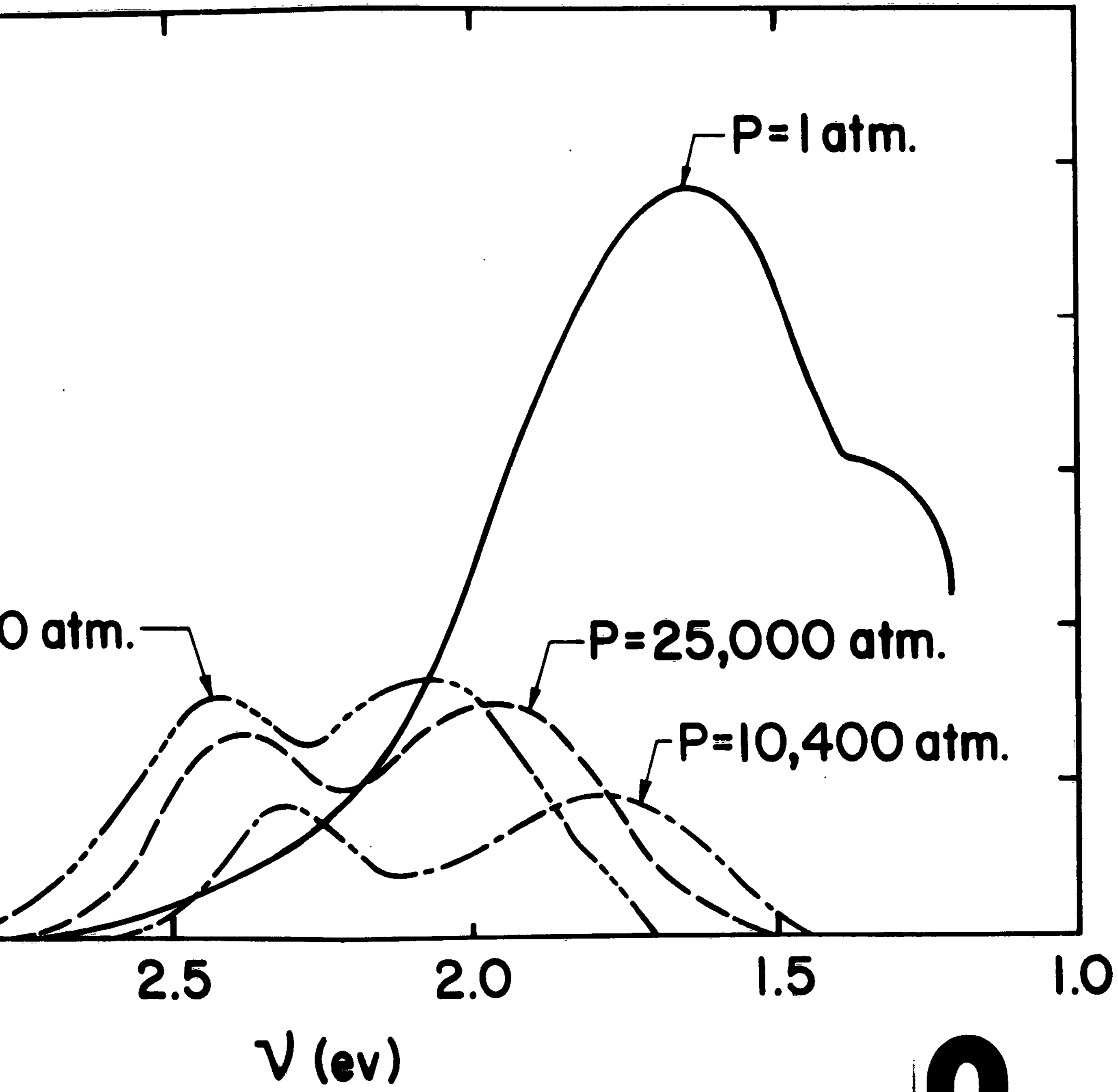


$\log_{10}(I_0/I)$
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
P=39,000 atm.
P=15,000 atm.
P=1 atm.
P=50,000 atm.
2
1

Fig. 16 The absorption spectrum of RbI. The F band (low energy peak) and the No. 3 band (high energy peak) are shown at several pressures. All measurements made at room temperature.



1



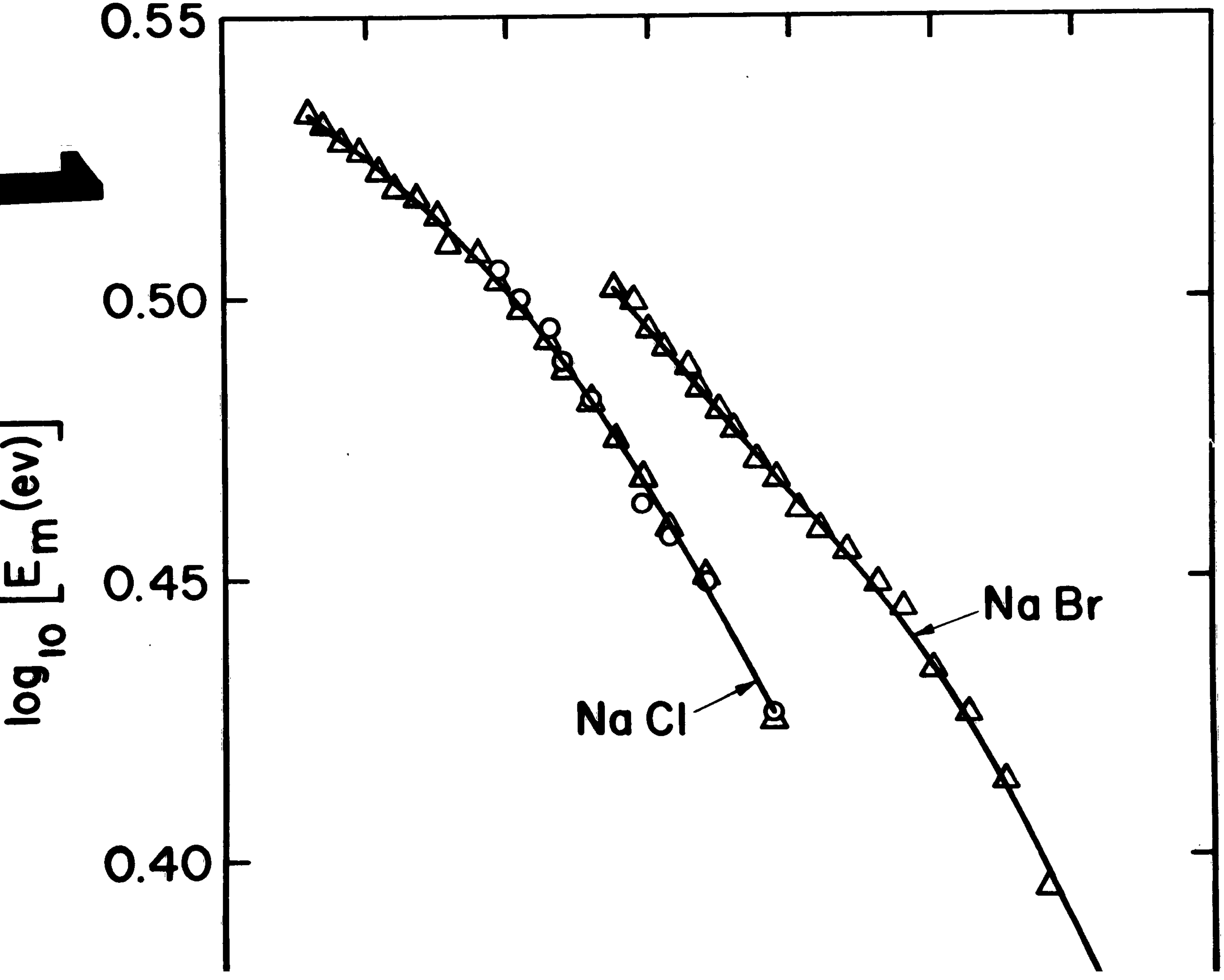
2

Fig. 17 $\log_{10} E_m$ vs $\log_{10} a$ for the F band in NaBr and NaCl

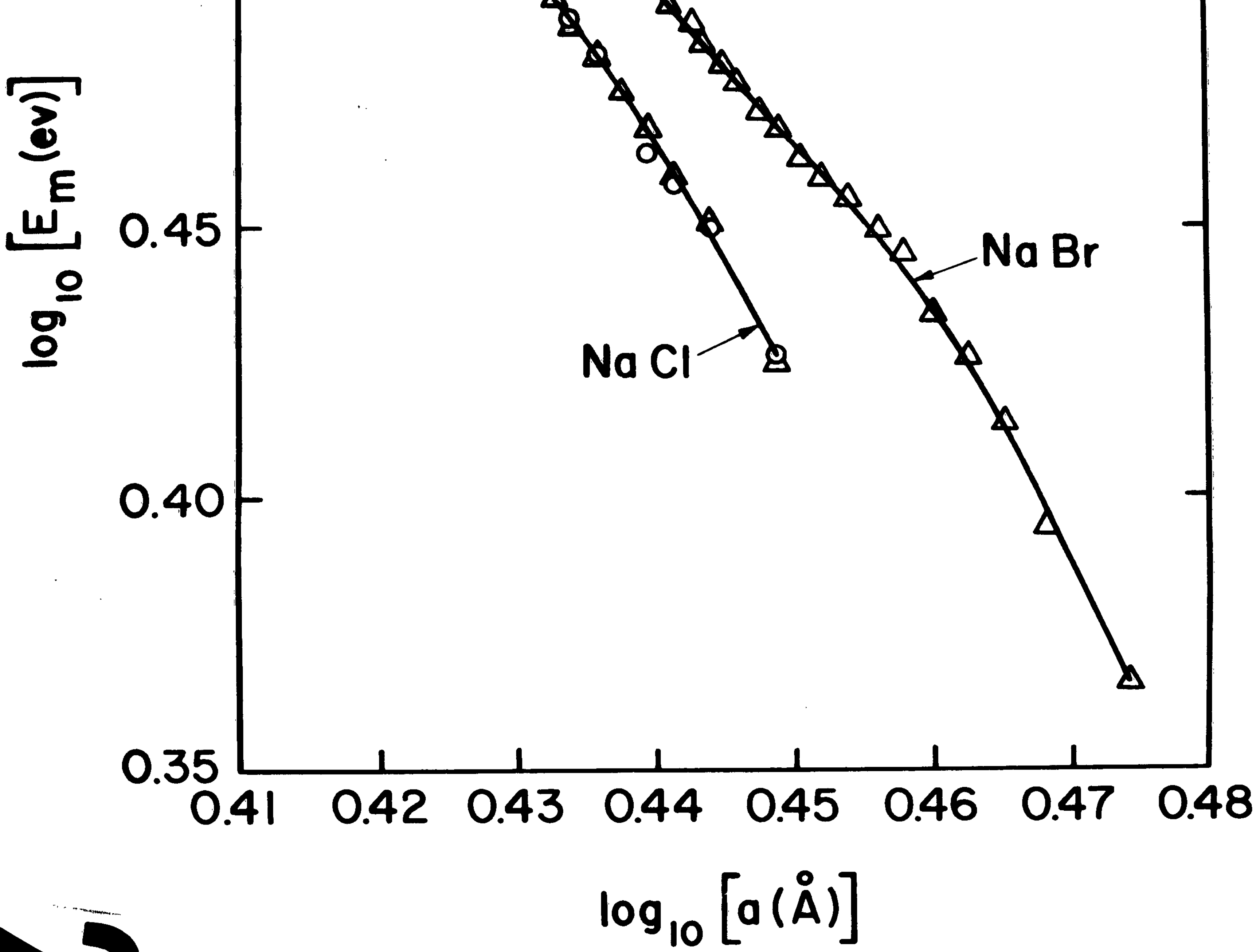
All measurements made at room temperature.

○ - NaCl:Na

△ - Eppler and Drickamer



1


log$_{10}$ [E$_m$(ev)]
0.45
0.40
0.35
0.41
0.42
0.43
0.44
0.45
0.46
0.47
0.48
log$_{10}$ [a(Å)]
Na Br
Na Cl

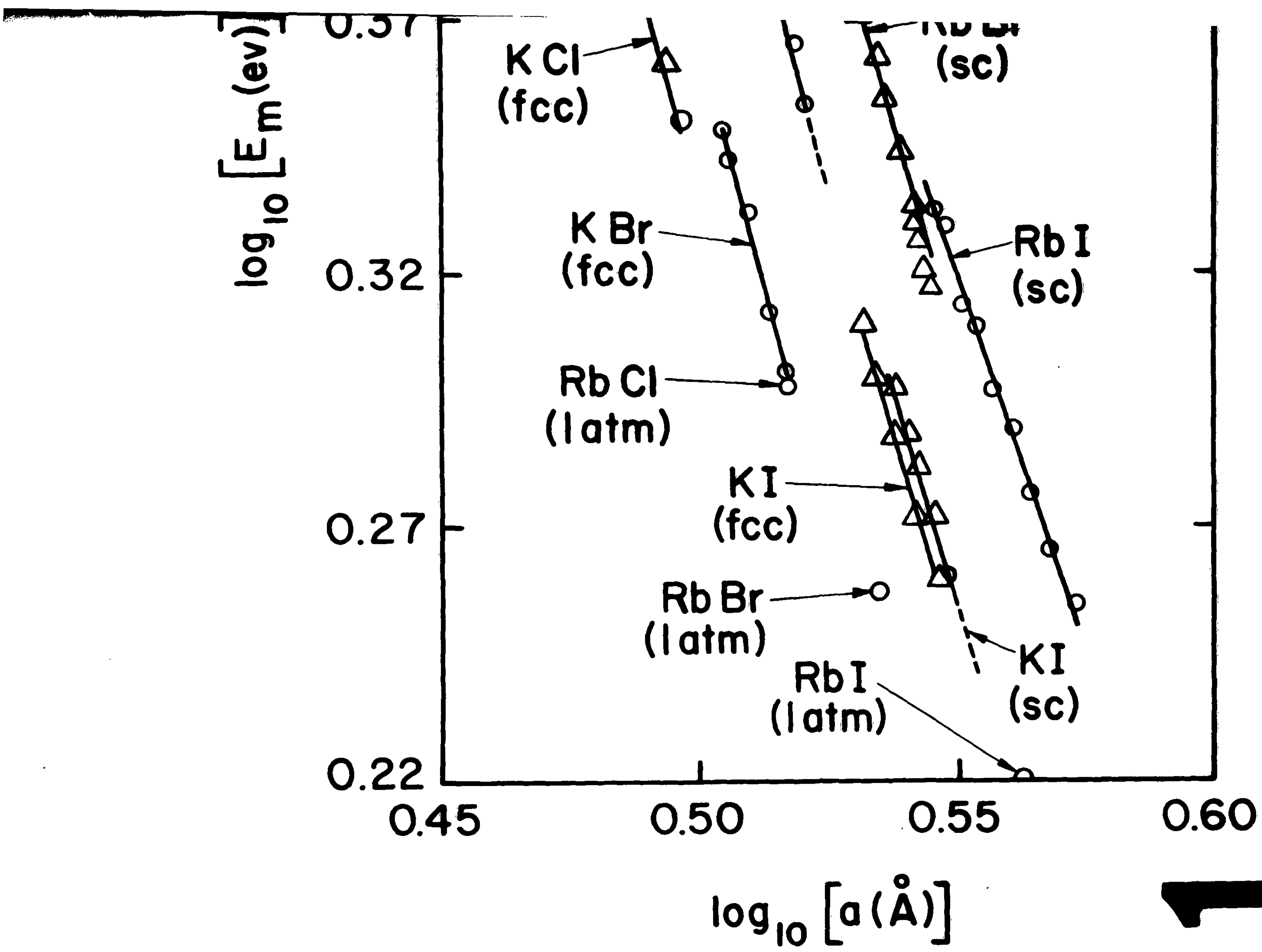
2

Fig. 18 Log$_{10}$ E$_m$ vs log$_{10}$ a for the F band in the potassium and rubidium halides.

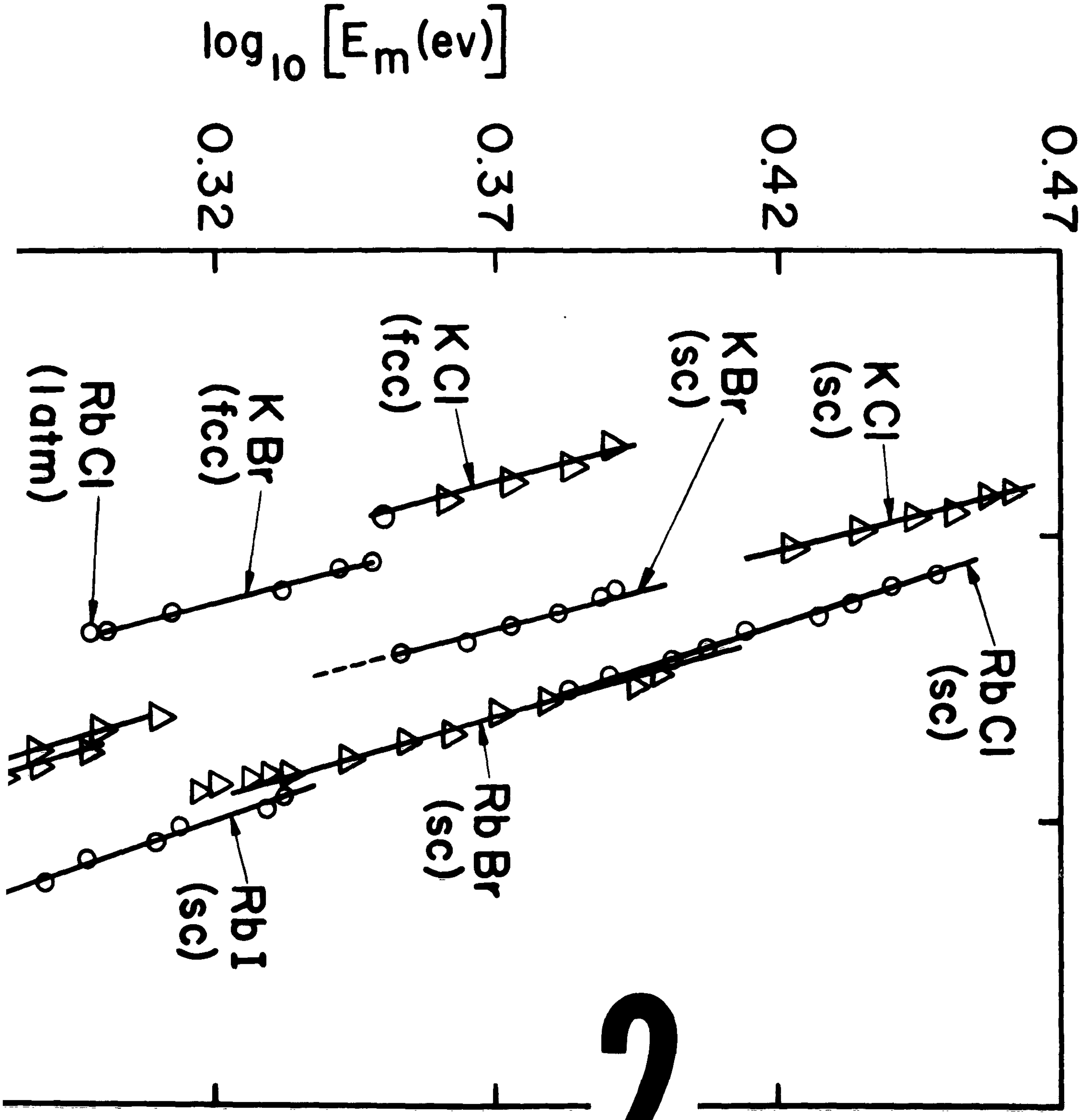
Δ - For KCl and KI, data from Maisch and Drickamer

All other data from present research.

All measurements made at room temperature.


log$_{10}$ [E$_m$(ev)]
0.37
0.32
0.27
0.22
0.45
0.50
0.55
0.60
log$_{10}$ [a (Å)]
K Cl (fcc)
K Br (fcc)
Rb Cl (1 atm)
K I (fcc)
Rb Br (1 atm)
Rb I (1 atm)
(sc)
Rb I (sc)
K I (sc)

1


log₁₀ [Em(ev)]
0.32
0.37
0.42
0.47
KCl (fcc)
KBr (sc)
KCl (sc)
RbCl (1atm)
KBr (fcc)
RbCl (sc)
RbBr (sc)
RbI (sc)

2

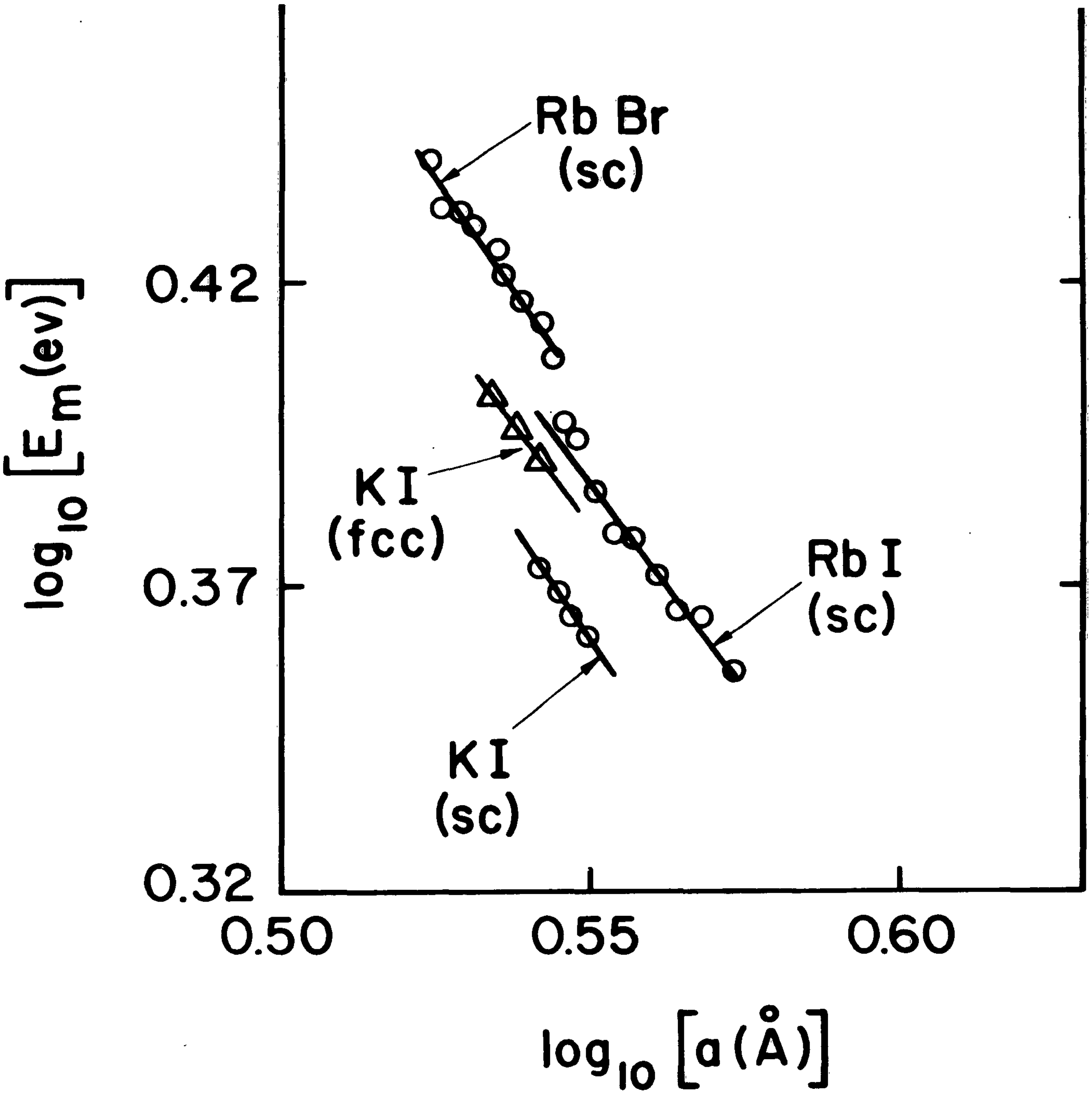
Fig. 19 Log$_{10}$ E$_m$ vs log$_{10}$ a for the No.3 band in KI, RbBr, and RbI in the CsCl (sc) structure and the No. 1 band in KI in the NaCl (fcc) structure.

○ - No. 3 band

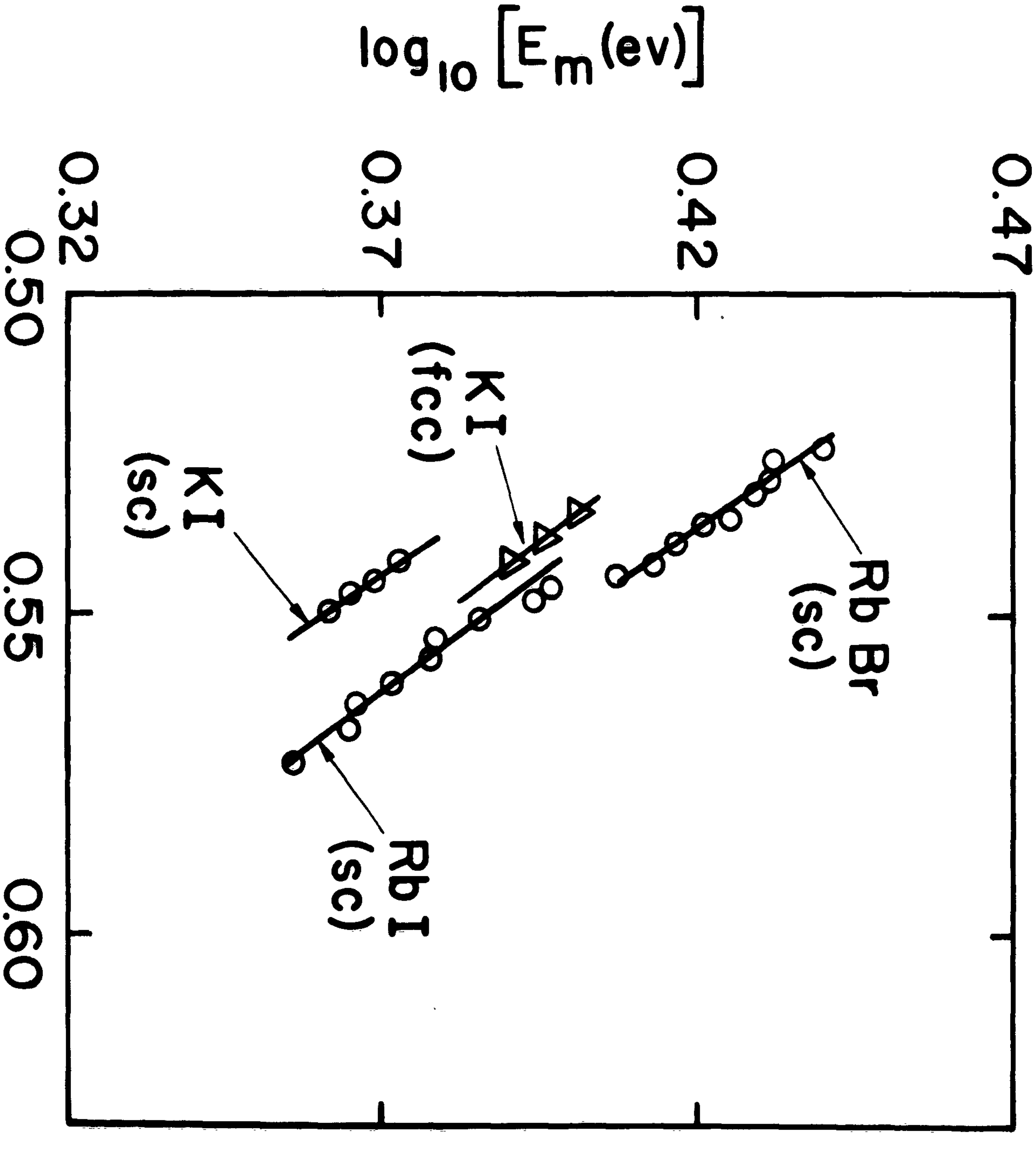
Δ - No. 1 band

KI data from Maisch and Drickamer

All measurements made at room temperature.


Rb Br
(sc)
K I
(fcc)
Rb I
(sc)
K I
(sc)
0.42
0.37
0.32
0.50
0.55
0.60
$\log_{10}[E_m(\text{ev})]$
$\log_{10}[a(\text{Å})]$

1


log$_{10}$ [E$_m$(ev)]
0.32
0.37
0.42
0.47
0.50
0.55
0.60
KI (fcc)
KI (sc)
Rb Br (sc)
Rb I (sc)

2

Fig. 20 $\log_{10} E_m$ vs $\log_{10} a$ for the F band in various alkali halide crystals. The Ivey curves are given for the crystals in the NaCl (fcc) and CsCl (sc) structures.

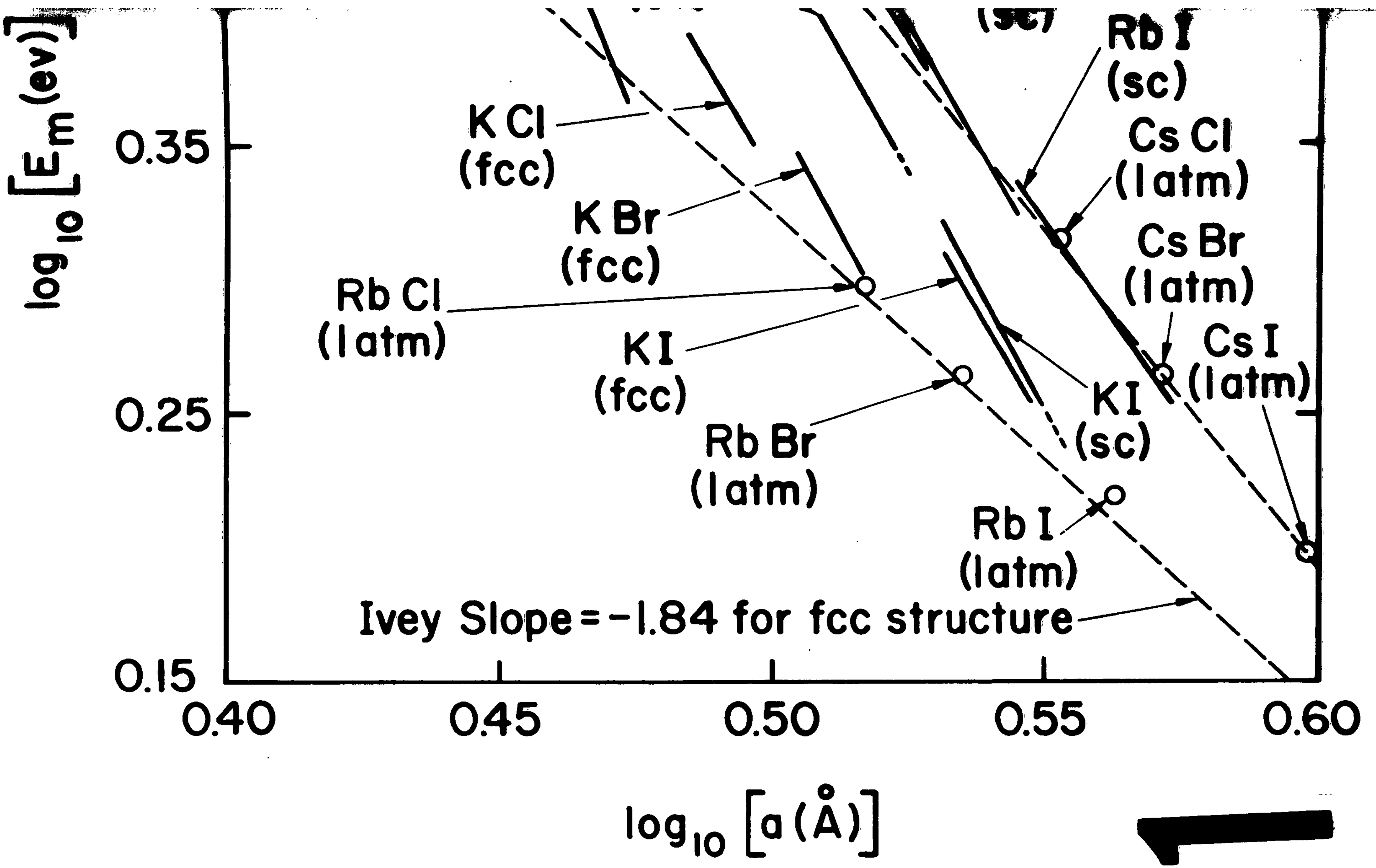
One atmosphere data for CsCl, CsBr and CsI from Avakian and Smakula.

High pressure data for KCl and KI from Maisch and Drickamer.

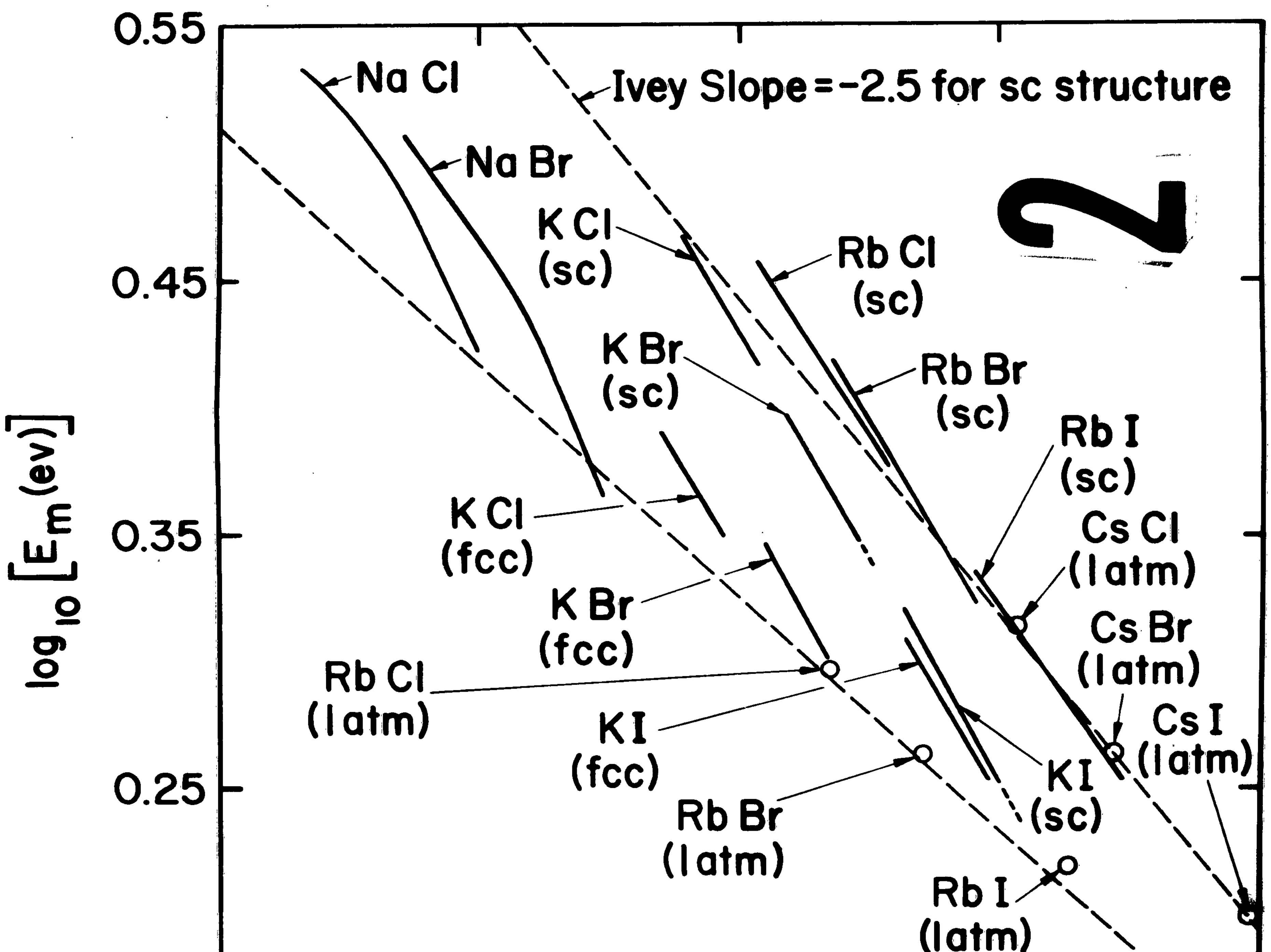
High pressure data for NaCl and NaBr from Eppler and Drickamer.

All other data from present research.

All measurements made at room temperature.


log10 [Em(ev)]
0.35
0.25
0.15
0.40
0.45
0.50
0.55
0.60
log10 [a (Å)]
K Cl (fcc)
K Br (fcc)
Rb Cl (1atm)
K I (fcc)
Rb Br (1atm)
K I (sc)
Rb I (1atm)
Rb I (sc)
Cs Cl (1atm)
Cs Br (1atm)
Cs I (1atm)
Ivey Slope = -1.84 for fcc structure

1



2

0.55
0.45
0.35
0.25
$\log_{10}[E_m(\text{ev})]$
Na Cl
Na Br
Ivey Slope = −2.5 for sc structure
K Cl (sc)
Rb Cl (sc)
K Br (sc)
Rb Br (sc)
Rb I (sc)
Cs Cl (1atm)
K Cl (fcc)
K Br (fcc)
Cs Br (1atm)
Rb Cl (1atm)
K I (fcc)
Cs I (1atm)
K I (sc)
Rb Br (1atm)
Rb I (1atm)

Fig. 21. Diagrams illustrating the method which was used to obtain the energies for the ratios calculated at the transition point. The solid lines represent the experimental curves and the dashed lines represent the extrapolations.

(A) Diagram illustrating the method which was used to determine the energies in equations (14-a) to (14-d).

$$a_1\,(\rho_1) = k_1\,\rho_1^{-1/3}$$

$$a_1\,(\rho_2) = k_1\,\rho_2^{-1/3} \qquad k_1 = (\sqrt{3}/2)\,M^{1/3}$$

$$a_2\,(\rho_1) = k_2\,\rho_1^{-1/3} \qquad k_2 = \left(\frac{M}{2}\right)^{1/3}$$

$$a_2\,(\rho_2) = k_2\,\rho_2^{-1/3}$$

(B) Diagram illustrating the method which was used to determine the energies in equations (17-a) to (17-d).

$$a_1(\rho_1) = k_1\rho_1^{-1/3} \qquad k_1 = (\sqrt{3}/2)\,M^{1/3}$$

$$a_2(\rho_2) = k_2\rho_2^{-1/3} \qquad k_2 = \left(\frac{M}{2}\right)^{1/3}$$

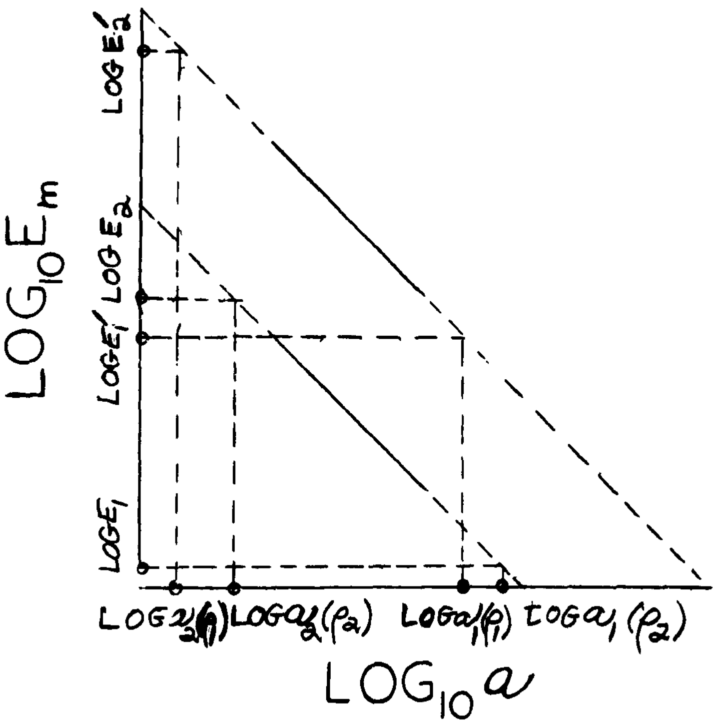


FIGURE 21-A

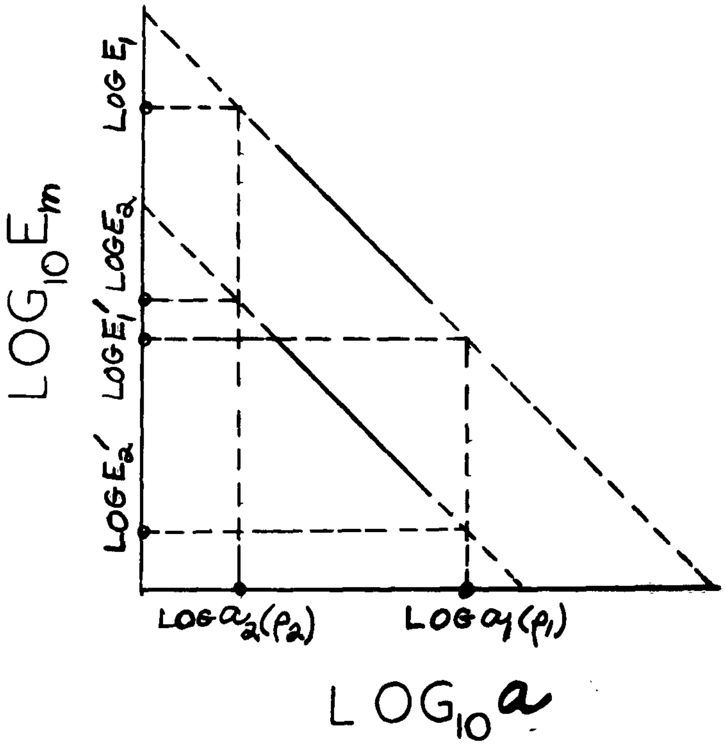


FIGURE 21-B

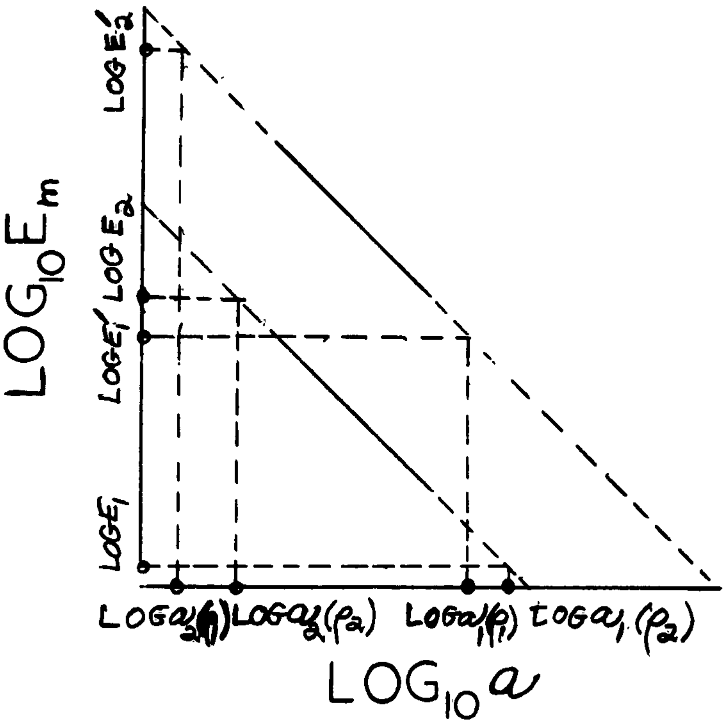


FIGURE 21-A

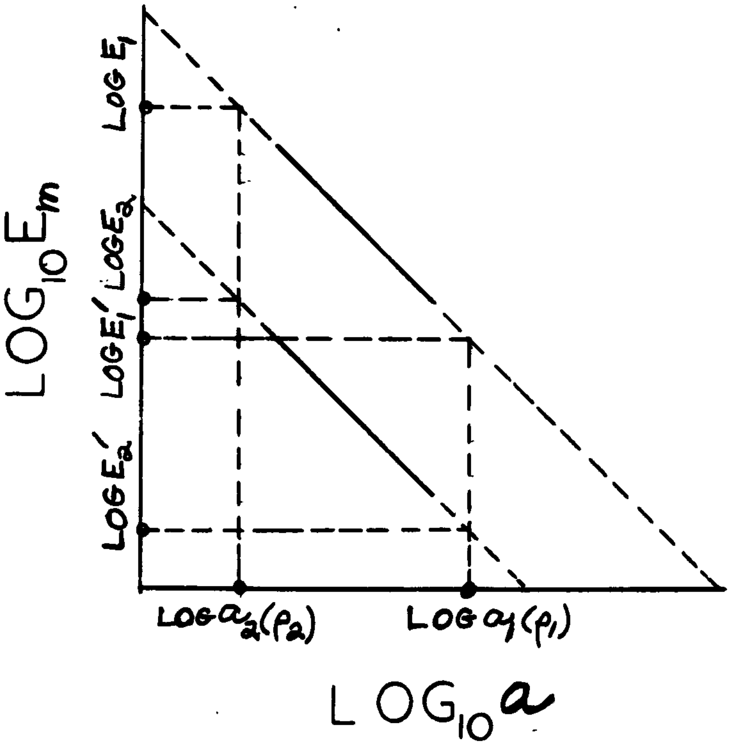


FIGURE 21-B

APPENDIX I

ESTIMATION OF ERROR

The greatest uncertainty in these experiments lies in the determination of the pressure. Several experiments were performed to determine the suitability of using Drickamer's calibration[27] for the equipment built in this laboratory. The optical transmission of the potassium halides as a function of pressure in the region of the phase transition was determined and compared to similar data obtained by Drickamer. Although individual measurements of the transition pressure showed deviations as large as ± 10%, the average values agreed very well with Drickamer's. As an additional check, a comparison was made of the spectra of several colored alkali halides observed in both laboratories. Since, as is discussed below, the error in the frequency determination is insignificant in comparison, this is essentially a measurement of the reliability of the pressure determination. The individual deviations were again within ± 10% and were distributed uniformly around Drickamer's points. The data quoted in this thesis are the averages of several runs, and so are good to better than ± 5% with respect to the calibration. However, on an absolute basis, the pressures are no better than ± 10%.

The error in the frequency determination is very small. Atomic line sources were used in the frequency calibration and the errors are almost negligible (between 0.1 and 0.01%). However, when the high pressure spectra were obtained, they were scanned at a higher speed relative to the response time of the instrument and the optical band pass was variable. Furthermore, the determination of the exact maximum of the rather wide absorption bands was difficult. As a result, the frequency measurements are good to about ± 1%.

The determination of the half-widths of the absorption bands is also affected by the finite and varying slit widths. This effect is minimized somewhat by the fact that the slits were relatively narrow in the region of the F band and by the large widths of the absorption bands. The error in these measurements is estimated to be within the range + 5 to + 10%.

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PART III

Pressure Effect on Color Centers in RbF, RbCl, RbBr, and CsI*

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Pressure Effect on Color Centers in RbF, RbCl, RbBr, and CsI

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Received (   )

ABSTRACT

The absorption spectra of the F and M centers in RbF, RbCl, RbBr, and CsI have been investigated as a function of pressure. In addition to the F and M band, the No. 3 band and some other unidentified bands have been observed. These experiments were conducted at room temperature with both electrolytically and additively colored crystals. Frequency shifts were observed under pressures up to 10,000 atm for the absorption spectra of RbCl and RbBr and up to 50,000 atm for the absorption spectra of RbF and CsI. In RbF a phase transition appears at 33,000 atm. The pressure dependence of the frequency shift in the rubidium halides is similar to that in the potassium halides.

INTRODUCTION

During the last ten years there have been investigations of the effect of pressure on the spectra of trapped-electron centers in alkali halide crystals.(1-6) Some of these experiments were run under pressures up to 166,000 atm. It was found that with increasing pressure the absorption bands shift to higher frequencies as long as no phase transition occurs. Extensive studies of KCl have been published. A plot of log ν_m versus log a gives a straight line for the F centers in KCl and various other salts (ν_m= frequency of maximum absorption, a = lattice parameter). In colored KCl the shift in frequency of the absorption band is strongest for the F band, gradually weaker for the N, M, and R_2 bands.

At the phase transition, which transforms crystals with a fcc lattice into a sc lattice(7), the frequencies of the absorption bands change discontinuously. The discontinuous shift can occur towards higher or lower frequencies, depending on the color center and the alkali halide. In Table I previously measured shifts at the phase transition are listed for most of the potassium halides. Some measurements already exist of the effect of pressure on color centers in several rubidium halides above the transition point. In this paper optical measurements on RbCl and RbBr below the phase transition are described. In addition, the F center in RbF and the F and M centers in CsI are investigated and the phase transition of RbF is determined.

EXPERIMENTAL PROCEDURE

Two different types of high pressure optical cells, both developed by Drickamer and co-workers(8,9) were used to cover the pressure range from 1 to 50,000 atm. In the cell used in the low pressure range from 1 to 10,000 atm, the pressure is hydrostatic. A 12.7mm diameter piston in the high pressure end of this cell is linked mechanically to a 76.2mm diameter piston in the hydraulic press which forms the low pressure end of the cell. The oil pressure behind the large piston is generated by a hand pump. Two sapphires 12.7mm long and 12.7mm in diameter are used as windows. The effective aperture of the windows is 6mm and the maximum path length available for the crystals is about 5mm. Freon II was used as the pressure transmitting liquid. The crystals were held in the optical path by a clamp which screwed to one of the window mounts. The crystals remained clear below the transition pressure but clouded as the transition took place. The spectra were observed with increasing pressure only, and those above the transition region were inferior in quality to those below. Although these crystals tend to regain most of their transparency at pressures sufficiently higher than the transition pressure, such pressures could not be achieved in this apparatus.

At higher pressures, the "liquid" cell described above cannot be used. A "solid" cell, in which solid samples are embedded in a disk of sodium chloride, is used up to pressures of 50,000 atm. The sodium chloride flows under pressure above 5,000 atm without cracking and transmits the pressure from a piston to the sample. Sodium chloride is used also as the windows in this cell, and is extended from single crystals into the window opening at 20,000 atm. The diameter of each window opening increases in a series of steps from the center of the cell (sample compartment) from 0.7mm to 6.1mm. The sample compartment itself is 5mm high and 3.0mm in diameter, permitting a maximum sample thickness of 2.5mm.

In operation, this cell is placed in a small hydraulic press designed to fit in the optical path of the spectrometer. The pressure is generated in the same manner as described above, the ratio of the press/cell piston diameters in this case being 11.43mm/ 3.0mm. The design of this cell permits the pressure to be raised and lowered repeatedly, but measurements are made only after an increase in pressure to insure consistent results.

Neither of the cells described above fills the entire slit with light, i.e., the f-number of each cell is larger than that of the instrument. Since the f-number of the liquid cell is much less than the f-number of the solid cell, more strongly absorbing crystals could be studied in the former cell.

High pressure cells of the above types were calibrated originally by Drickamer by means of a manganin gauge (liquid cell) and various solid-solid phase transitions (solid cell). These calibrations were checked by means of frequency shifts observed in both laboratories and found to be still applicable. The phase transition undergone by many of the alkali halides studied served as a further check of the calibration.

The absorption spectra were observed with a single beam spectrophotometer, the Beckmann IR3. This instrument had a quartz-tungsten lamp as the light source, two LiF prisms as the dispersing elements, and an RCA 931A photomultiplier as the detector. The sample optics were modified to accomodate the high pressure equipment between the exit slit and the detector. All spectra were recorded directly as percentage transmission by the use of a tape recorded slit program which took into account the various background effects, including those of the uncolored crystal and the cell.

The single crystals used in these experiments were obtained from the Harshaw Chemical Company. The CsI crystals were colored electrolytically at a temperature of 470°C and under an applied voltage of 100 V/cm. Each crystal was fused on one side to a flat strip of nickel, which served as the anode, and a hot pointed platinum wire, the cathode, was driven into the other side. Electrolysis was completed in one minute and the crystals were then quenched in air. The rubidium halide crystals were colored additively in a Pyrex tube in potassium vapor at 550°C for 2 to 3 days. The tube was cooled in air and the crystal stored in the dark. Subsequent handling of the crystals was done under weak illumination, and, in the case of RbF, under a stream of dry nitrogen.

RESULTS AND DISCUSSION

The results of the measurements for RbCl and RbBr are plotted in Figs. 1 and 2. In the pressure region below the phase transition the frequency shift of the F band versus pressure can be represented with sufficient accuracy by a straight line. In both figures, the frequencies measured previously in the pressure range from 10,000 atm to 50,000 atm(6) are extrapolated to lower frequencies into the region of the phase transition.

RbCl

The absorption of the F center in RbCl was studied by Jacobs(2) at pressures up to 5000 atm. This experiment was repeated and extended to 7500 atm, i.e., up to the point where the phase transition was first observed. The frequencies observed in this experiment agree very well with those found by Jacobs. The frequency increases with increasing pressure and changes discontinuously at the phase transition by 2250 cm^{-1} from 16,700 cm^{-1} to 19,250 cm^{-1} (Fig.1). The change of frequency (E) of the F center with lattice parameter (a) is defined by the quantity n_F(2), where

$$n_F = - \frac{\partial \ln E}{\partial \ln a}$$

The quantities n_F for several crystals are listed in Table III. In the case of RbCl, this quantity is greater below the transition than above.

RbBr

The effect of pressure on the frequency of the F band in RbBr is plotted in Fig. 2. The behavior in RbBr is similar to that in RbCl. At the phase transition the frequency changes discontinuously by 1500 cm^{-1} from 15,300 cm^{-1} to 16,800 cm^{-1}. This is considerably smaller than the corresponding jump in RbCl. The values of n_F for RbCl are listed in Table III.

Absorption curves for various pressures are plotted in Fig. 3. The first three curves, at 1 atm, 2200 atm, and 4450 atm were all observed below the transition pressure. These curves are plotted to the same scale and show a slight decrease in intensity with increasing pressure. The half-width of the band is approximately 2800 cm^{-1} and remains constant.

The bottom two curves in Fig. 3, at 6700 atm and 8900 atm, were observed in the region of the phase transition and just above the transition, respectively. Each of these curves is taken from a different experiment and is plotted to a scale different from that of the other and from that of the first three curves. Nevertheless, the general change in intensity which occurs as the crystal goes through the phase transition is fairly well represented. At 6700 atm, the crystal has become almost opaque due to the break-up of the lattice. In fact, the sample now consists of crystallites of both phases which scatter the light at their interfaces. Two F bands, F_f and F_b, are observed in the spectrum, the former belonging to the fcc structure and the latter to the sc structure. Band F_b increases in intensity with time at the expense of band F_f until, after about twenty minutes at room temperature, only band F_b remains.

In the absorption spectrum at 8,900 atm, there appear two bands in addition to the F band. The band at 20,500 cm^{-1}, the No. 3 band, has been observed previously in the spectra of KI, RbBr, and RbI(3,6). The values of $n_{No.3}$ and n_M are about the same, and it has been suggested that the No. 3 band has its origin in the M center.(6) The band at 12,600 cm^{-1} is located about 2000 cm^{-1} higher than the M band observed at one atmosphere, and its intensity is greater than that of the M band by a factor of two to three. Minomura and Drickamer(5) observed a similar increase in the intensity of the M band in KCl, KBr, and KI as these crystals changed from the fcc to the sc structure. Therefore, the band at 12,600 cm^{-1} in RbBr can be identified as the M band.

RbF

The absorption of the F center in RbF was studied as a function of pressure up to 33,000 atm. As can be seen in Fig. 4, the increase in frequency with pressure is less at higher pressures than at lower pressures. At 33,000 atm (an average of increasing and decreasing pressure readings), the crystal became opaque and cleared up only after the pressure was increased by several thousand atmospheres. The low frequency tail of an absorption band, presumably the F band, was observed on the high frequency side of the original F band at these higher pressures. Unfortunately, the absorption band itself was out of the measurable range. This behavior is similar to that of the other alkali halides which undergo the phase transformation from the NaCl type to the CsCl type structure under pressure. Since the discontinuous jump of the F band toward higher frequencies in the various crystals increases in the order iodide, bromide, chloride, a very large change in the position of the F band in the fluoride is to be expected. Accordingly, this behavior of RbF at 33,000 atm is attributed to a change in phase.

Piermarini and Weir (10) have studied the x-ray diffraction patterns of RbF at high pressure and have concluded that the fcc structure is converted to the sc structure between 9 and 15 kbar. The authors have since stated that these figures may be somewhat unreliable.(*) It is very difficult to calibrate their apparatus accurately, so that the measured pressures are uncertain. Furthermore, the reported pressures were observed with decreasing pressure, indicating that the true transition pressure was higher. There is also some uncertainty in the transition pressure reported in the present work. The transition pressures of the other alkali halides observed in the same apparatus are several thousand atmospheres higher than those observed by Bridgman.(7) However, if internal consistency in the pressure apparatus is assumed, the transition in RbF occurred at least 12,000 atmospheres above the transition pressures of the potassium halides, or between 30,000 and 33,000 atm.

CsI

The absorption of the F and M centers in CsI were studied at pressures up to 50,000 atm. Since this crystal has the sc structure at one atmosphere, no phase change, and, therefore, no discontinuities in the absorption bands are to be expected. This, indeed, is the case, as can be seen in Fig. 5., where the F and M band frequencies are plotted as a function of pressure. $\nu_m(F)$ increases with pressure but at a decreasing rate at higher pressures. $\nu_m(M)$ is constant to within the limits of the experiment. In previous investigations of the M band in other crystals,(4,5) a shift to higher frequencies, amounting to about 25% of the F band frequency shift, has always been observed. The intensity of the M band in CsI decreases with increasing pressure and disappears completely at 35,000 atm. This also differs from previous observations on other crystals.(5)

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* Personal communication.

SUMMARY

The discontinuous shift in frequency of the F center at the phase transition is given in Table II for crystals of the rubidium halides. This frequency jump is positive for all the rubidium halides but decreases going from the fluoride to the iodide. The general trend is the same for F bands in the potassium halides. The latter show an even faster decrease and the frequency jumps for KBr and KI become negative. The M bands in the potassium halides shift in the same direction as the F bands, although the shifts are much smaller.

The pressure dependence of the F bands can be visualized by a plot of logarithm of the frequency versus logarithm of the lattice constant. This gives straight lines for most of the alkali halides(3,4,5,6). The lattice parameters were calculated from Bridgman's density data(7). Fig. 6 shows the lines for RbCl and RbBr below the phase transition; a similar line is drawn for CsI which has the sc structure. The slopes, n_F, for those crystals are listed in Table III. The values of RbF and RbI at atmospheric pressure are contained in Fig. 6. They deviate from the slope at one atmosphere for the fcc structure (drawn as dashed line with $n_F = 1.89$). The corresponding slope for the sodium and potassium halides is $n_F = 1.84$.

The particle-in-the-box-model would give a slope $n_F = 2$, since the energy of the particle is inversely proportional to the square of the box diameter, i.e., to the lattice parameter(1). This model fails to explain the pressure dependence of the F band for most of the crystals. The deviation of this model is largest for the fluorides and small alkali atoms. It becomes less pronounced going from the fluorides to the iodides and from sodium to cesium where we have the largest cations and anions. The pressure dependence of CsI, with $n_F = 1.94$, agrees well with that predicted by the particle-in-the-box-model.

New bands can appear in some crystals under pressure. Of these, the origin of the No. 3 band has not been positively identified.(6) It was observed in KI, RbBr, and RbI, but not in KCl, KBr, CsCl, CsBr, and CsI.

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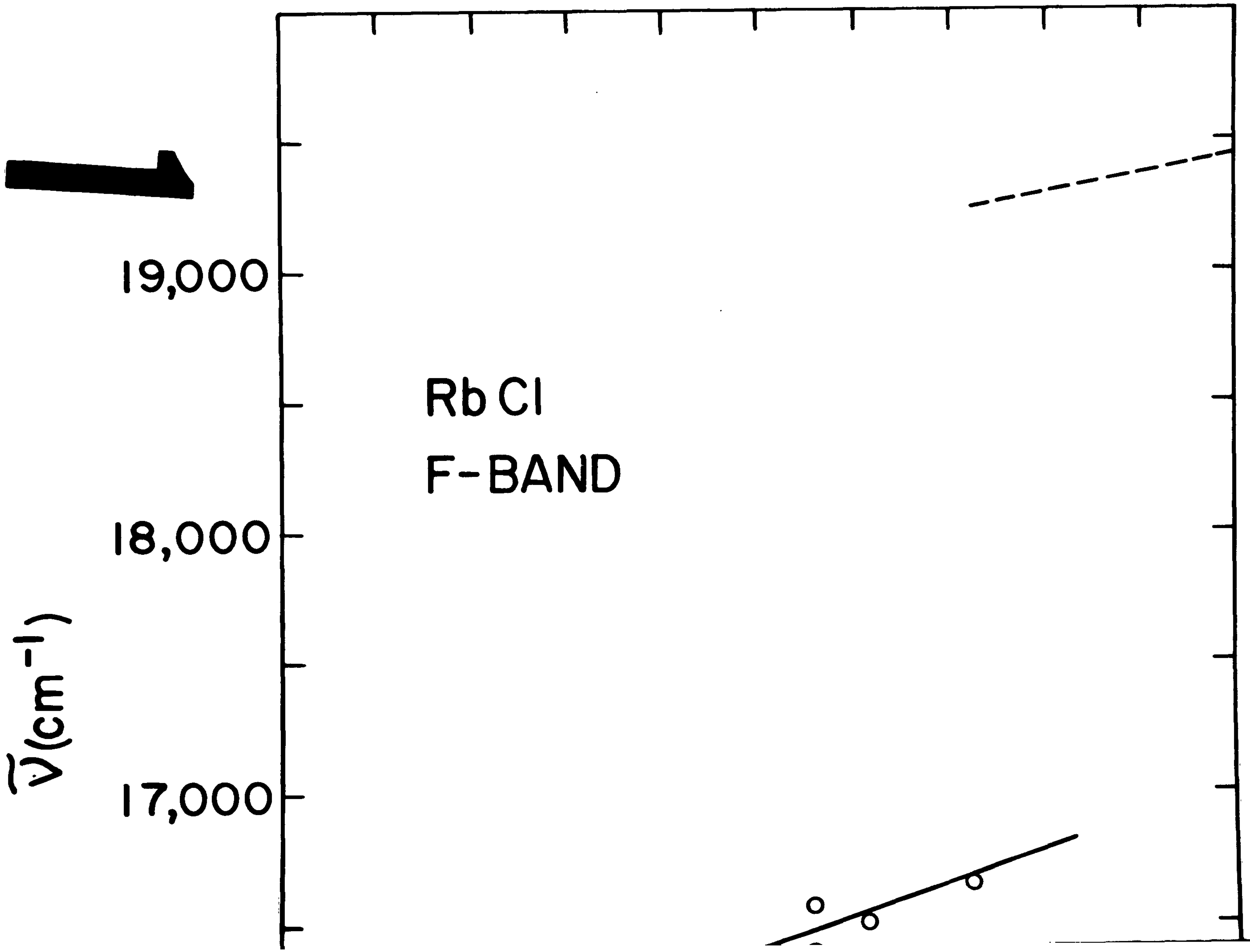
Figure 1. F band in RbCl. The measured values (O) below the phase transition lie approximately on a straight line. The dashed line above the phase transition$^{\text{(see ref.6)}}$ is extrapolated from measurements at higher pressures.



19,000
18,000
17,000
$\tilde{\nu}(cm^{-1})$
Rb Cl
F-BAND

2

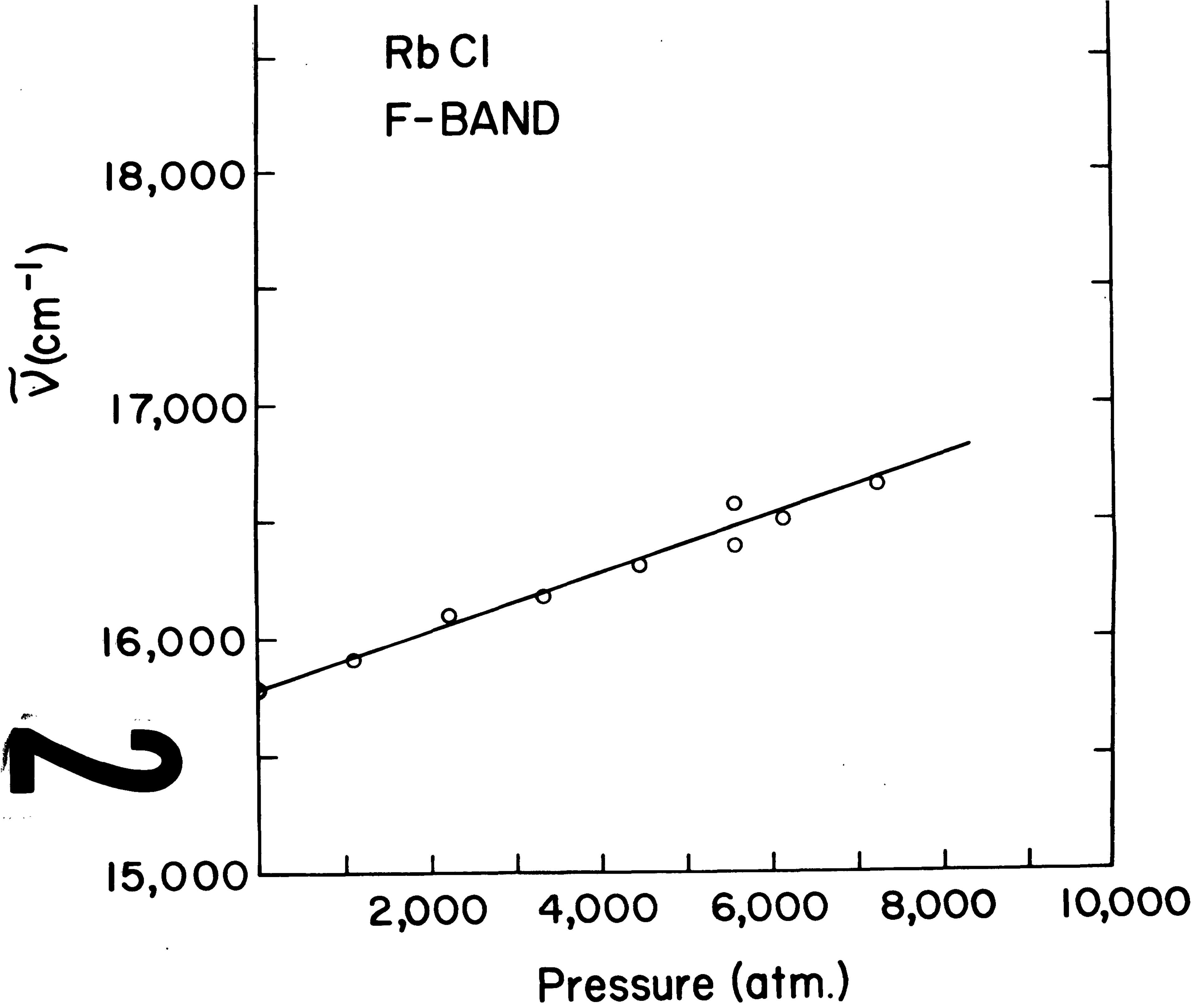
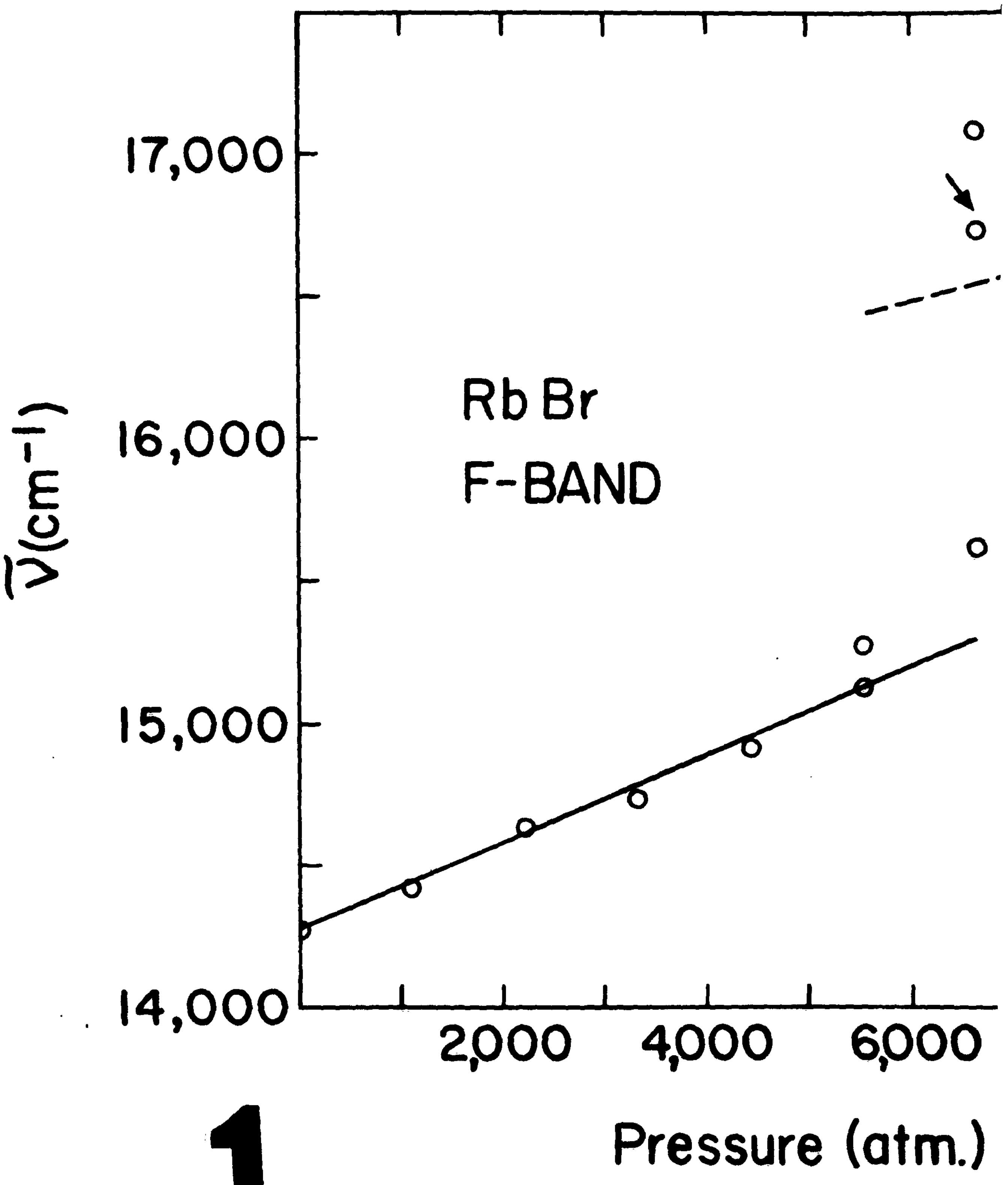
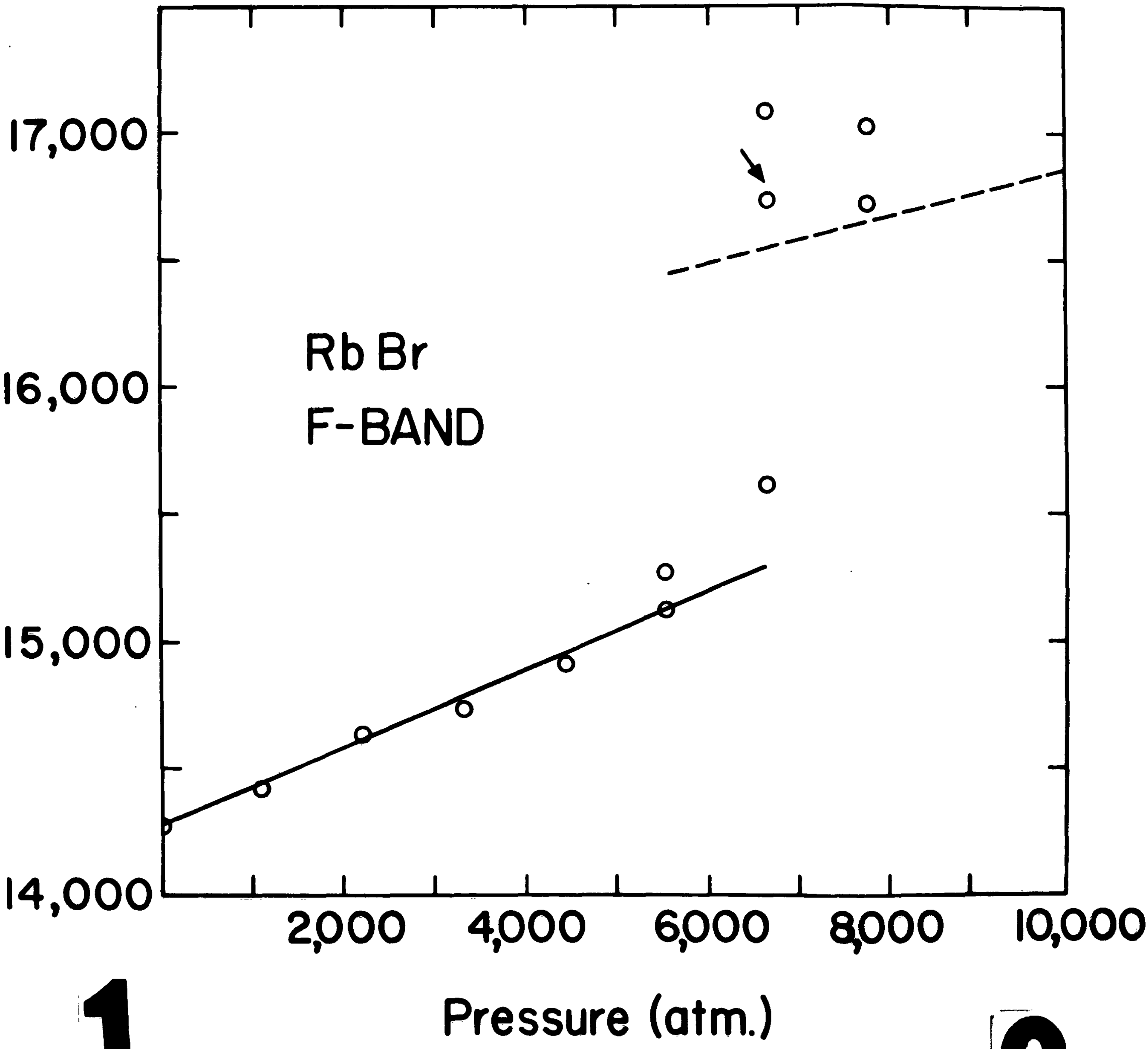

Rb Cl
F-BAND
$\tilde{\nu}$(cm^{-1})
18,000
17,000
16,000
15,000
2,000
4,000
6,000
8,000
10,000
Pressure (atm.)

Figure 2. F band in RbBr. The measured values (O) below the phase transition lie approximately on a straight line. The dashed line is extrapolated from measurements at higher pressures (see ref.6). The frequency at the phase transition corresponding to the sc lattice is marked by an arrow.



17,000
16,000
15,000
14,000
$\bar{\nu}$(cm^{-1})
Rb Br
F-BAND
2,000
4,000
6,000
Pressure (atm.)

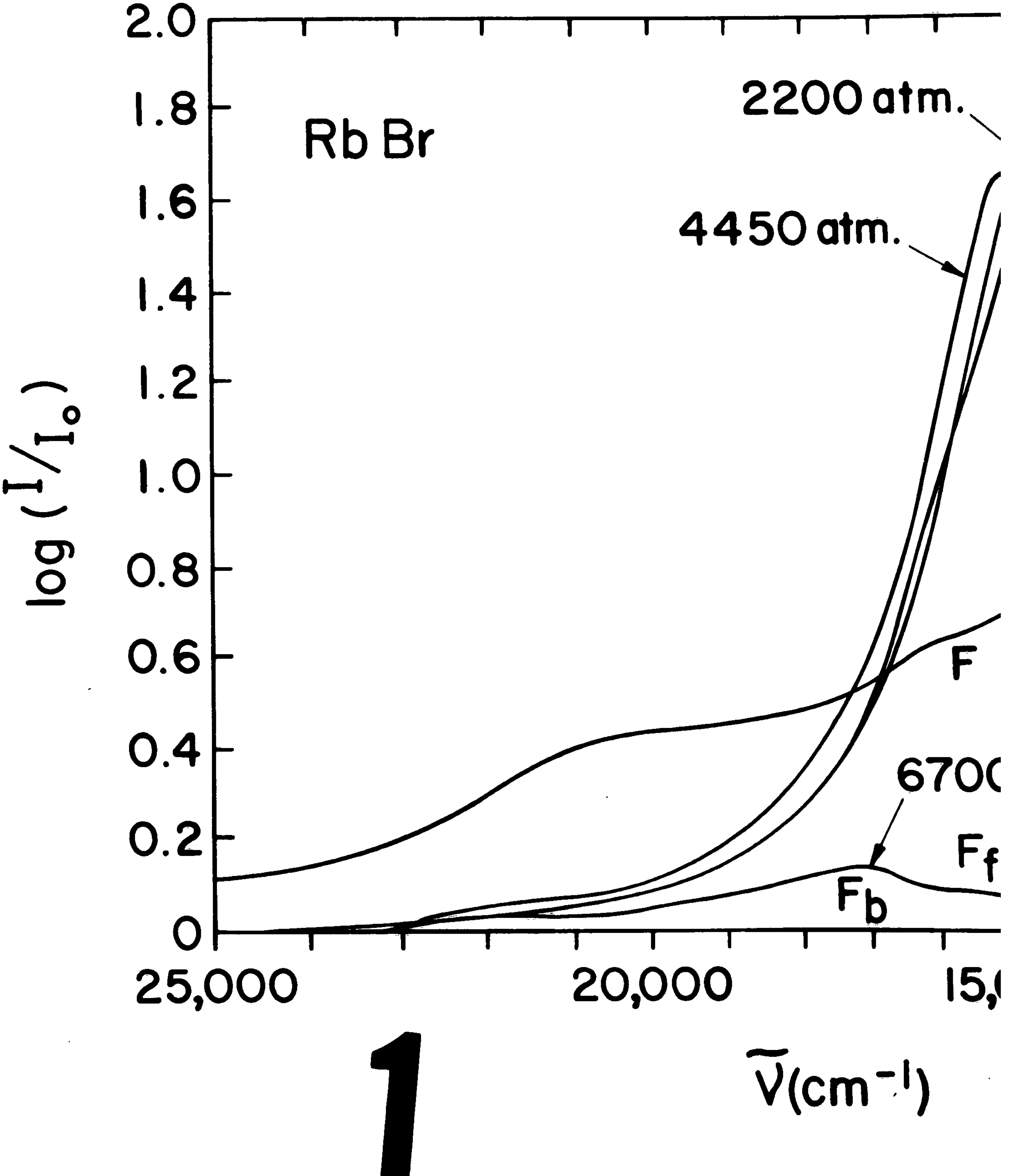
1


17,000
16,000
15,000
14,000
Rb Br
F-BAND
2,000
4,000
6,000
8,000
10,000
Pressure (atm.)

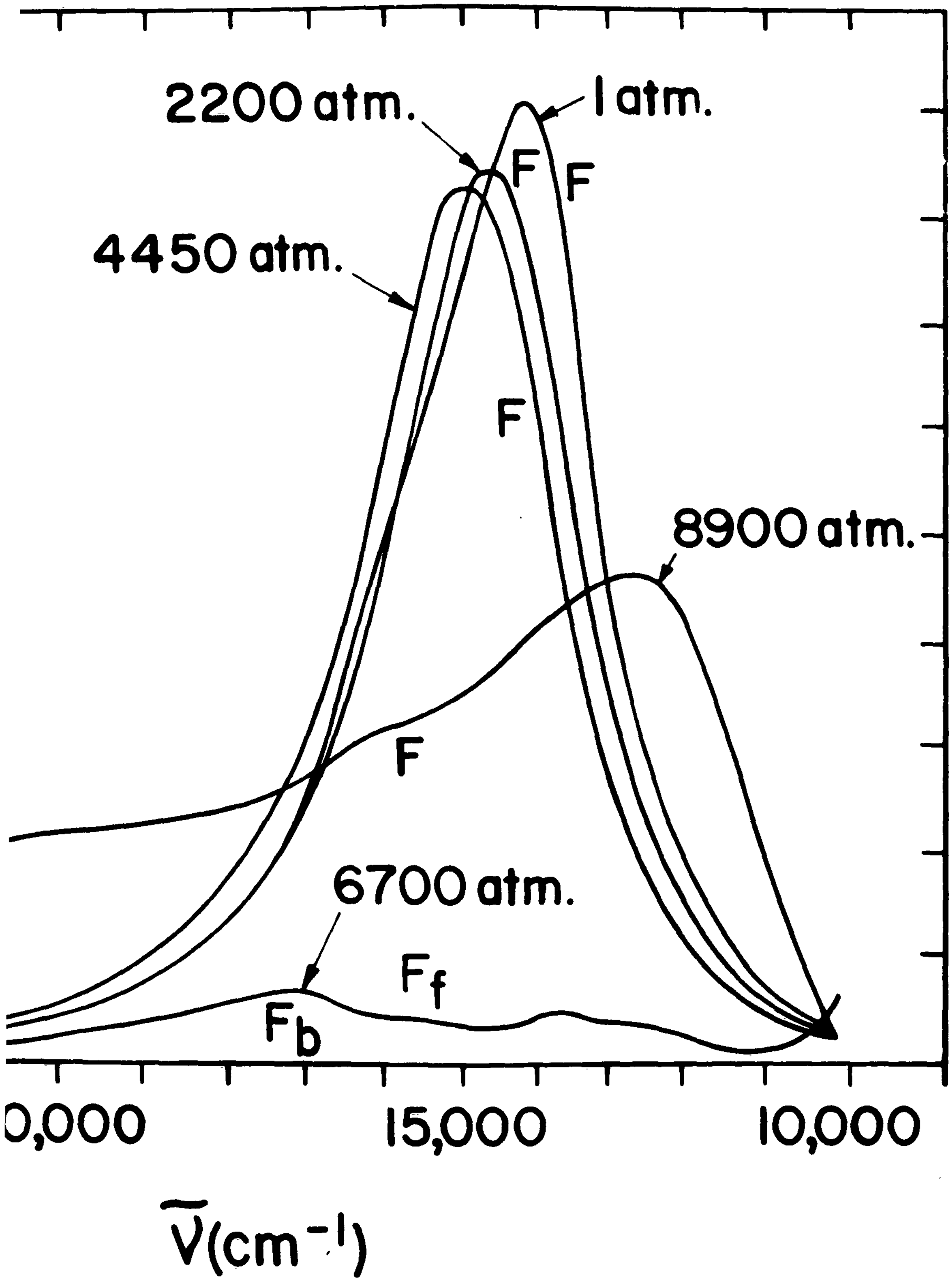
1

2

Figure 3. Absorption curves of color centers in RbBr at different pressures. The location of the F band is marked by F. The absorption curve at the phase transition shows simultaneously one F band in fcc structure, F_f, and one in sc structure, F_b.


Rb Br
2200 atm.
4450 atm.
6700
F
F_f
F_b
$\log\left({}^{I}/_{I_o}\right)$
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
25,000
20,000
15,
$\tilde{\nu}(cm^{-1})$

1


2200 atm.
1 atm.
F
F
4450 atm.
F
8900 atm.
F
6700 atm.
F_f
F_b
0,000
15,000
10,000
$\tilde{\nu}$(cm^{-1})

2

Figure 4. F band in RbF. Measurements (O) up to the phase transition.

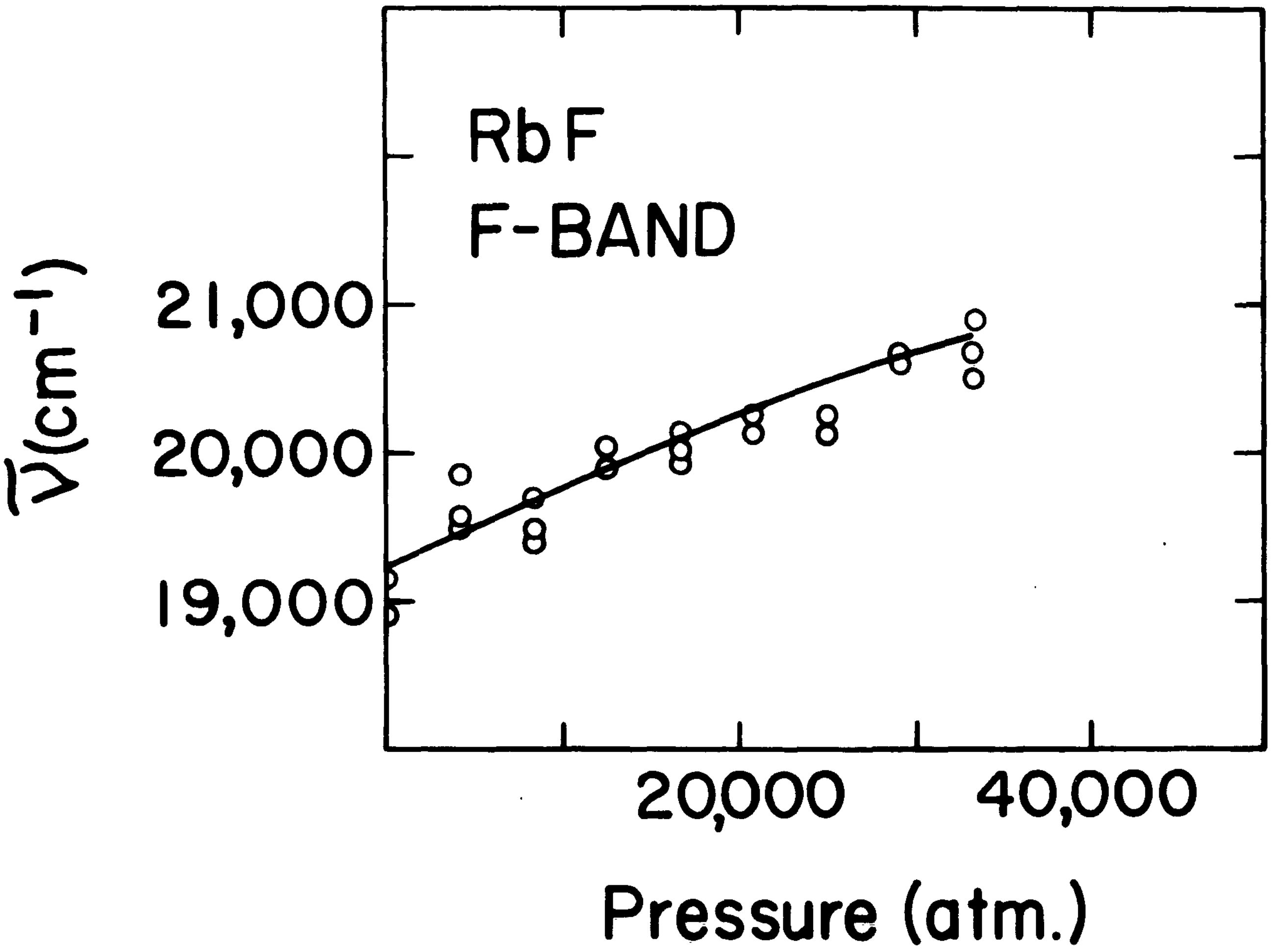

RbF
F-BAND
$\bar{\nu}$(cm^{-1})
21,000
20,000
19,000
20,000
40,000
Pressure (atm.)

Figure 5. F and M band in CsI. The frequency of the M band at 35,000 atm. is independent of pressure and the intensity becomes zero.

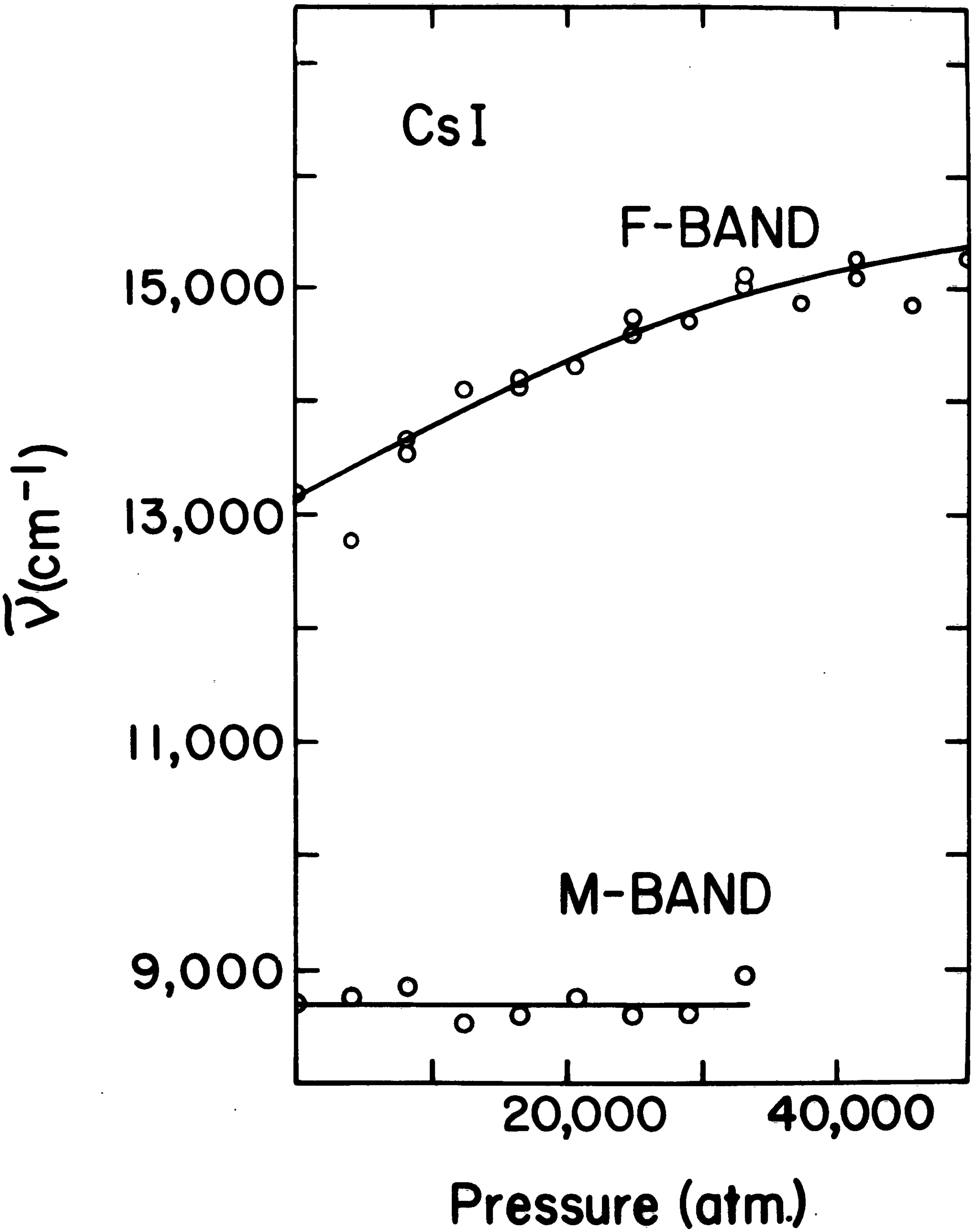
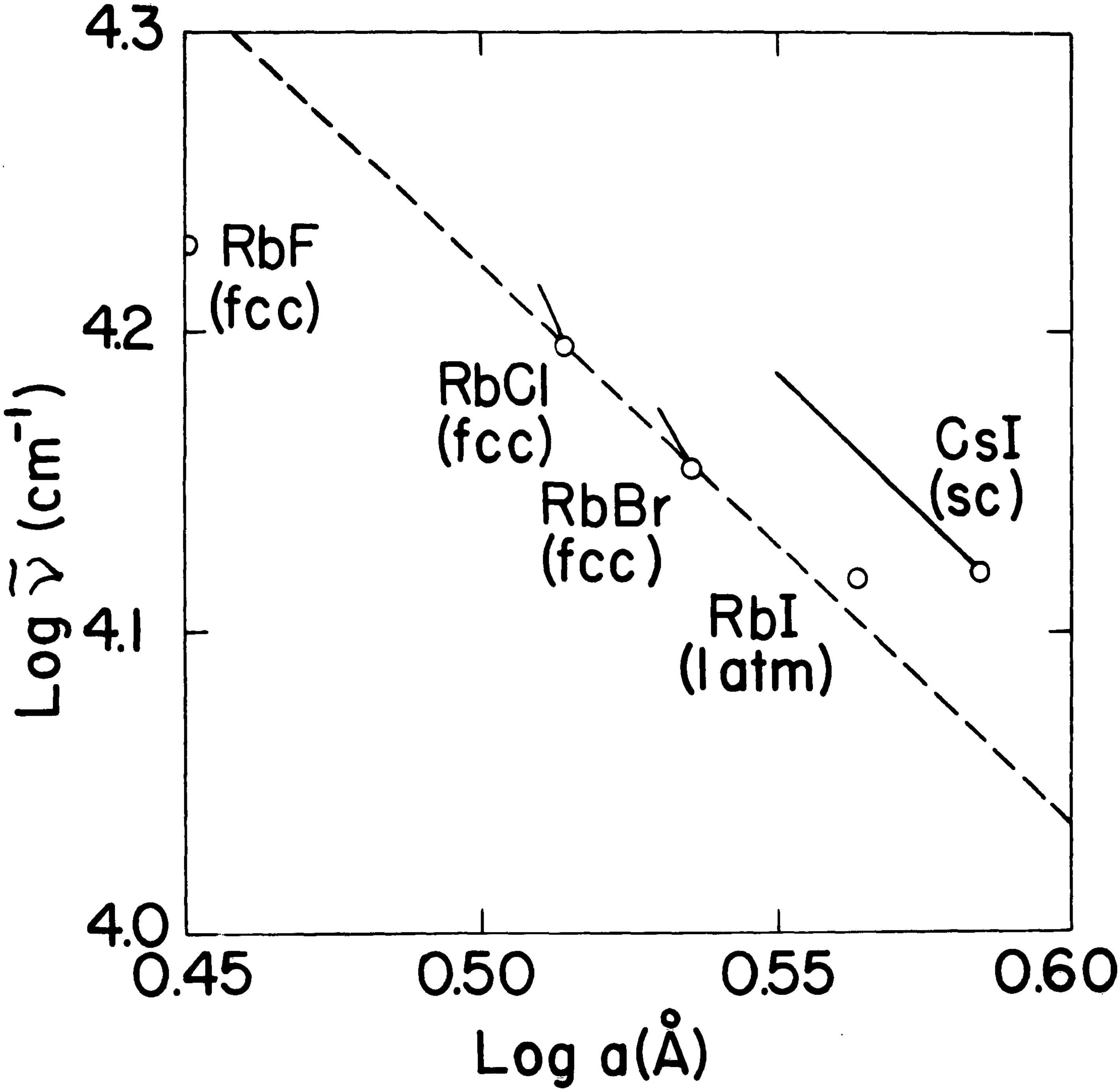

CsI
F-BAND
M-BAND
15,000
13,000
11,000
9,000
$\bar{\nu}$(cm^{-1})
20,000
40,000
Pressure (atm.)

Figure 6. F bands in RbCl, RbBr, and CsI.



4.3
4.2
4.1
4.0
0.45
0.50
0.55
0.60
Log $\tilde{\nu}$ (cm^{-1})
Log a(Å)
RbF
(fcc)
RbCl
(fcc)
RbBr
(fcc)
RbI
(1 atm)
CsI
(sc)

Table I: Frequency shift $\Delta\tilde{\nu}$ of the F and M bands at the phase transition. + sign indicates a shift to higher frequencies

$\Delta\tilde{\nu}(\text{cm}^{-1})$	KCl	KBr	KI
F	+ 680	- 420	- 2320
M	+ 50	- 250	- 860

Table II: Frequency shift $\Delta\tilde{\nu}$ of the F band at the phase transition. All shifts are towards higher frequencies. (a) Ref. 6

$\Delta\tilde{\nu}$ (cm^{-1})	RbF	RbCl	RbBr	RbI(a)
F	+	2250	1500	200

Table III: Slope $n_F \approx - \partial \ln E\ (\tilde{\nu}) / \partial \ln a\ (\mathring{A})$ of the F band for several crystals.

	RbCl	RbBr	CsI
n_F	4.77	3.79	1.94