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IMPROPER FERROELECTRICITY: A THEORETICAL AND
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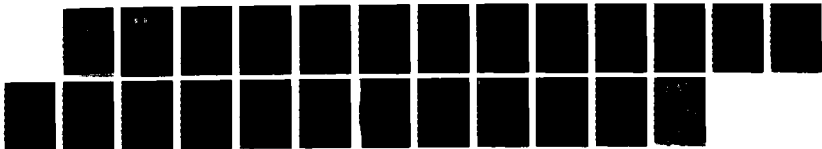
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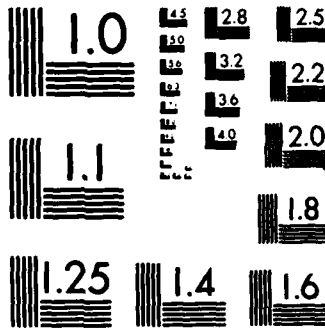
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REPORT DOCUMENTATION PAGE

2a. SECURITY CLASSIFICATION AUTHORITY		1b. RESTRICTIVE MARKINGS	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		3. DISTRIBUTION / AVAILABILITY OF REPORT	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION		7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code)		7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS	
11. TITLE (Include Security Classification)			
12. PERSONAL AUTHOR(S)			
13a. TYPE OF REPORT		14. DATE OF REPORT (Year, Month, Day)	
13b. TIME COVERED		15. PAGE COUNT	
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	
		22c. OFFICE SYMBOL	

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the theoretically-predicted lines could be made. Methods for measuring transition temperatures more precisely, ± 0.5 K, using birefringence and capacitance measurements under varying temperature and uniaxial stress, were developed. Measurements of the Raman spectra of CsZnI_4 , which behaves differently from the other materials studied so far, were completed; a complete comparison with theory awaits the completion of M-D calculations for this material.

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Improper Ferroelectricity:
A Theoretical and Experimental Study

Final Report #2

J.R. Hardy and F.G. Ullman

31 July 1987

U.S. Army Research Office

DAAG29-83-K-0080

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1. Introduction

The program over the past four years was effectively a continuation of our earlier Army-Sponsored work on "Improper Ferroelectrics". However, the emphasis on incommensurate behavior, which was the principal concern of the latter part of that program, developed into the major theme of the program of the past four years.

During this period the experimental and theoretical programs were closely coupled as our theoretical understanding evolved to reveal the true complexity of the behavior of ionic molecular crystals.

When the present work was initiated, we had proposed to extend the first-principles theoretical methods that had been applied successfully to RbCaF_3 (L.L. Byer and J.R. Hardy, Phys. Rev. B 24, 2577 (1981)) to isomorphs of potassium selenate such as the chlorozincates of rubidium and potassium (Rb_2ZnCl_4 and K_2ZnCl_4). To obtain experimental confirmation of the validity of these results, we also proposed to improve our analytical methods for deconvoluting the severely overlapped lines in the Raman spectra of these materials. An important corollary of these spectral studies is the ability to identify, within about one degree Kelvin, the actual phase transition temperatures in the laser-light-scattering volume. To this end, we proposed to develop the well-known measurement methods of birefringence and capacitance vs. temperature for use also under varying uniaxial stress.

Not only have we been successful in meeting these objectives, we have been able to go well beyond these original expectations, especially in the outcome of the theoretical work. Major elements of this were Dr. Edwardson's development of computer molecular dynamics simulation techniques to run on our VAX 725 system, and Dr. Katkanant's development of the analytical methods for deconvoluting complex Raman spectra. The specific details of these and

other developments are best summarized by the Abstracts of the various publications which we have incorporated in the body of this report with appropriate introductory and/or linking material.

The most outstanding development is that we believe we have uncovered the basic cause of incommensurate behavior both in the K_2SeO_4 isomorphs that we have studied, and in many, if not all, other insulating materials. This cause is physically quite simple; it stems from the fact that the molecular ions, (e.g., SeO_4^{2-} and $ZnCl_4^{2-}$) that constitute one (or more) components of these compounds, have their own natural shape and size. As a consequence, they tend not to fit well into the periodic lattice structure which is constrained on them by the other component ions (most commonly alkali or alkaline earth metals). A two-stage compromise results: first they form on very open basic lattices (e.g., simple hexagonal) which are notorious for their lack of stability--this tendency is also favored in these lattices by permitting large interstices between the molecular ions into which the small metal cations pack easily. Secondly, the molecular ions as a result of this packing, can undergo quite large rotations. This motion has two components: a collective rotation, i.e., a combined libration-translation which drives the formation of an incommensurate phase; and a local uncorrelated rotational disorder. In some systems, the disorder dominates and no structural change occurs; in others, the collective response dominates and disorder is absent. The K_2SeO_4 isomorphs, such as Rb_2ZnCl_4 , to which much of our effort has been devoted, show both types of behavior simultaneously, which is the main reason that they have proved so perplexing.

The incommensurate behavior arises from the imperfect helical symmetry operations present in the high temperature, most symmetric phase. Given a sufficiently strong collective rotational "drive", the associated helical arrays of molecules, effectively "uncouple" their helical backbone structure

from the constraint of exact repetition after either 2, 4, or 6 lattice translations, and adjust their pitch to relax their own internal strains due to their imperfectness. The result is a non-exactly repeating helix which appears as an incommensurate phase. This mechanism is discussed in detail in an article just submitted to Physical Review whose Abstract is included in the following Abstract summary.

2. Theoretical studies

The overall substance of these has been summarized in the Introduction: the specific work is now annotated sequentially below.

The first report of the theoretical work appeared as a Physical Review Letter on the behavior of Rb_2ZnCl_4 . Here the "bare bones" of the principles and simulations are described, along with the enunciation of the principle of "latent symmetry"

First-Principles Theoretical Explanation of Incommensurate Behavior in Rb_2ZnCl_4

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and

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(Received 20 December 1985)

We have carried out an *ab initio* theoretical study of the potential energy and molecular dynamics of Rb_2ZnCl_4 . These calculations demonstrate that the incommensurate transition in this compound is caused by the relaxation of imperfect-hexagonal spirals of highly unstable ZnCl_4^{2-} ions. This leads to angstrom-size displacements with essentially zero energy change. We argue that such "latent" (or imperfect) symmetry could be the general cause of incommensurate transitions in insulators.

This was followed by an extensive overall treatment of this system in a full paper currently under review by Physical Review B. The Abstract is reproduced below.

A PRIORI THEORY OF INCOMMENSURATE BEHAVIOR
IN Rb_2ZnCl_4

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ABSTRACT

We have performed a study of the potential energy, normal modes, static relaxation, and molecular dynamics of Rb_2ZnCl_4 using ab initio Gordon-Kim interionic potentials for intermolecular and interionic potentials. We find that the $\text{Pnam} - \text{Pna}2_1$ transition in this, and almost certainly many isomorphous systems is entropy driven and shows no soft mode behavior. This is shown to arise from the presence in this system of a large equipotential volume of phase space between the Pnam and the tripled $\text{Pna}2_1$ low temperature structure. This region arises from a major lattice instability involving large rotations and displacements and having approximately six-fold screw symmetry along the a axis. This concealed imperfect symmetry which we call latent symmetry is the basic cause of the existence of a near-tripled incommensurate phase over a range of 113 K (302 K - 189 K) between the Pnam and $\text{Pna}2_1$ phases. In this region the helicity is incommensurate with the lattice, being largely determined by the relief of intrahelical stresses. In addition, we have demonstrated by molecular dynamics that the ZnCl_4^{2-} tetrahedra are orientationally disordered, but, despite this, the helical instability remains. These findings are also related to anomalies in the observed Raman spectra and to X-ray data which confirm the presence of dynamically correlated disorder.

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While our use of computer molecular dynamics was a major component of both these papers, it was not itself the central theme; little more than the results were presented. However, the simulations have come to play a key role and their findings have been presented in full detail in a report of one study on Rb_2ZnCl_4 in the "normal", Pnam, phase just above T_i , the incommensurate transition temperature.

This report brings out, in particular, the interplay between disorder and cooperative behavior. However, it also revealed that there was some "missing factor" in the description of the ZnCl_4^{2-} units: principally their lack of rigidity. This factor, we have identified as ionic polarization.

Simulation of normal Rb_2ZnCl_4 near the incommensurate transition

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(Received 8 December 1986)

The purposes of the reported computer simulation of the normal (high-temperature) phase of rubidium tetrachlorozincate are to understand the disordered structure in that phase and to investigate the possibility that the transition, upon cooling, from the normal phase to one with an incommensurate modulation is associated with a change from the disordered structure to an ordered one. The simulation of the dynamics of 168 ions in a periodic structure begins from a slight perturbation of a structure that is determined by minimization of the potential energy within the constraints of the experimentally determined average symmetry. Rigid ions with short-range interactions described by the electron-gas model (with a qualification) are assumed. We find both zinc-induced and rubidium-induced instabilities in the chloride sublattices of the average experimental structure. The zinc-destabilized chloride ions move to a new sublattice in the simulation; however, a crude estimate indicates that this is caused by neglect of ionic polarizability and that these chlorides should either remain at their original sites or be disordered with chains of correlated positions. The rubidium-destabilized chloride ions form two-dimensional ordered networks in the disordered structure. We suggest that the inevitable freezing-out of disorder among the chains of zinc-destabilized chloride ions and among the networks of rubidium-destabilized chloride ions is the mechanism for the transition to the incommensurate phase.

In view of the important role of the Cl^- ion's polarization, and, to a lesser extent, that of the Rb^+ ion, we extended our studies to include that effect with the results described in the following abstract.

To be submitted to Physical Review B

Simulation of the Polarizable-ion Dynamics of Rb_2ZnCl_4

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The role of ionic polarizability in the near stability of the average structure of normal Rb_2ZnCl_4 is explored through constant-pressure simulation. Fifty-six ions under periodic-boundary constraints are allowed to polarize in nonlinear response to electrostatic and short-range forces. The parameter-free short-range forces are obtained from the electron-gas model. In contrast with methods based on the shell model, the present method conserves energy, includes nonlinear effects, and avoids the polarization catastrophe. These results support the hypothesis [Edwardson et al, Phys. Rev. B, 1-Jun-1987] that polarizability, rather than charge transfer, is a crucial factor in the properties of the ZnCl_2^{2-} ion and the structure of Rb_2ZnCl_4 .

We are currently extending these studies to other isomorphous systems.

Finally, in order to test the generality of our ideas, we studied BaMnF_4 , a totally different structure, and found the same general principles to hold.

Submitted to Solid State Communications

Ab Initio Explanation of the Incommensurate Phase

Transition in BaMnF_4

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ABSTRACT

Results of an a priori theoretical study of the origins of the incommensurate stability in BaMnF_4 are presented. The most unstable vibrational mode lies at $q_i = (0.32, 0.5, 0.5)$ (in fractions of the reciprocal lattice vectors for the orthorhombic lattice), while the observed value is $(0.392, 0.5, 0.5)$. These findings are interpreted in terms of our previously introduced concept of an imperfect, or "latent" symmetry which is extended into a general explanation of incommensurate behavior. A further possible consequence of this is that some strongly incommensurate systems could, in a specific and restricted sense, be novel states of matter.

3. Experimental Studies

In the experimental program, the emphasis has been on extending our previous light-scattering studies of K_2SeO_4 to its isomorphs, such as Rb_2ZnCl_4 and K_2ZnCl_4 . As mentioned in the Introduction, analytical methods had to be developed to deconvolute the severely overlapped spectra of these materials. New (for us) methods of determining the phase transition temperature in the light-scattering volume more precisely, using measurements of birefringence and dielectric constant, had also to be developed. The light-scattering studies were described in the Technical Report issued in July, 1986. Abstracts of the papers and the title page and foreword from the Technical Report are reproduced below with additional comments as needed.

The article below is a part of the Proceedings of the Fifth European Meeting on Ferroelectricity held in Benalmadena (Malaga), Spain in September, 1985. It described our first Raman-scattering measurements on Rb_2ZnCl_4 and also an application of a different analytical technique to a previously published uniaxial stress study of the soft "amplitude" mode in K_2/SeO_4 .

STUDIES OF THE PHASE TRANSITIONS IN POTASSIUM SELENATE AND SOME OF ITS ISOMORPHS

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Department of Electrical Engineering and Department of
Physics and Astronomy

J. R. HARDY, V. KATKANANT, and D. BILLESBACH
Department of Physics and Astronomy

Abstract Raman spectra of Rb_2ZnCl_4 for several temperatures from 18 K to 340 K are compared with those of K_2SeO_4 . The results support a model proposed previously¹ for the origin of the anomalous internal mode spectra in K_2SeO_4 . Previous work on the uniaxial stress dependence of the peak frequency of the amplitude mode below the incommensurate transition temperature (~ 130 K) is analyzed using a sixth degree Landau free energy expansion. The results show little deviation from previous conclusions based on mean-field analysis.

Since birefringence measurements are non-contacting and non-destructive, and proportional to the square of the order parameter, they are a powerful tool for measuring phase transition temperatures. In this work, it was possible to study the uniaxial stress dependence of the incommensurate transition temperature with good precision in this way.

**Birefringence measurements of the uniaxial-stress dependence
of the incommensurate phase transition in K_2SeO_4**

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(Received 4 February 1985)

The uniaxial-stress dependence of the incommensurate-phase-transition temperature (at 130 K) in K_2SeO_4 was measured along all three crystal axes by observation of the anomalies in the birefringence caused by the structure change. The results for the *c*-axis-stress dependence (-17.0 ± 0.2 K/kbar) agree with previous studies of other workers. This experiment has also provided the first direct measurements of the *a*-axis- and *b*-axis-stress dependences ($+3.1 \pm 0.2$ K/kbar and $+7.7 \pm 0.2$ K/kbar, respectively). Also, a value of -6.2 ± 0.3 K/kbar was calculated from these data for the dependence of the transition temperature on hydrostatic pressure. This is in agreement with hydrostatic-pressure measurements and thus confirms the reliability of the uniaxial-stress results.

These two papers are part of the Proceeding of the Sixth International Meeting on Ferroelectricity held in Kobe, Japan in the summer of 1985.

Proceedings of the Sixth International Meeting on Ferroelectricity, Kobe 1985
Japanese Journal of Applied Physics, Vol. 24 (1985) Supplement 24-2, pp. 790-792

Analysis of the Raman Spectrum of the Higher Frequency Modes of Rb_2ZnCl_4

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The stretching-region ($250\text{--}330\text{ cm}^{-1}$) internal modes of Rb_2ZnCl_4 were studied by Raman-scattering from 190 to 330 K. Four lines, peaking at about 275, 285, 295 and 304 cm^{-1} are clearly resolved below the normal-to-incommensurate phase transition (307 K in these measurements); above 307 K, the four merge into three and the 285 cm^{-1} peak is no longer detectable. The derivatives of these spectra were fitted to the derivative of an overlapped, spectrometer-corrected, four-Lorentzian lineshape. The resulting temperature dependence of the integrated intensity of the 285 cm^{-1} peak decreases by at most a factor of 3 up to 305 K whereas the square of the order parameter in this range decreases by a factor of about 50. Thus, its disappearance above 307 K is as yet unexplained.

Proceedings of the Sixth International Meeting on Ferroelectricity, Kobe 1985
Japanese Journal of Applied Physics, Vol. 24 (1985) Supplement 24-2, pp. 775-777

Effect of Uniaxial Stress on the 130 K and 93 K Phase Transitions in K_2SeO_4

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The uniaxial stress dependencies of the 130 K(T_1) and 93 K(T_2) transitions in K_2SeO_4 were determined from measurements of birefringence anomalies at T_1 , and capacitance anomalies at T_2 . At T_1 , for crystal axes defined as $c < a < b$, we obtain: $-17.0 \pm 0.2\text{ K kbar}$ for stress along "c", $3.1 \pm 0.2\text{ K kbar}$ for stress along "a", and $7.7 \pm 0.2\text{ K kbar}$ for stress along "b". Summing these three values gives the hydrostatic pressure dependence of -6.2 K kbar , close to the reported experimental values of about -6.5 K kbar . Capacitance vs temperature data, for stress along "c" only, in the vicinity of 93 K were fitted to a Curie-Weiss law to determine the transition temperatures. A value of about -25 K kbar for the c-axis stress dependence of T_2 was found.

This article will appear shortly in the Proceedings of the NATO Advanced Research Workshop on Incommensurate Structures held in Boulder, Colorado in July, 1986 and is to be published in book form by Plenum Press. It reviews some of our light-scattering studies of the internal modes of Rb_2ZnCl_4 and of the soft "amplitude mode" in K_2SeO_4 .

SOME ASPECTS OF RAMAN SCATTERING FROM A_2BX_4 COMPOUNDS*

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1. INTRODUCTION.

Since the development of ion lasers made Raman spectroscopy a routine analytical tool, it has been used extensively in studies of structural phase transitions in solids. Even though it is restricted in most cases to zero wavevector excitations, the effects of non-zero wavevector instabilities can also be evident in the spectra. It has thus also proved useful for the study of the incommensurate phase transitions that were the subject of this workshop. To illustrate how Raman scattering studies have contributed to a better understanding of incommensurate phases in ferroelectric insulators, we have selected for this article two quite different studies in which Raman scattering has provided new information about the incommensurate ferroelectrics, K_2SeO_4 and Rb_2ZnCl_4 .

First, we describe measurements of the temperature dependence of the amplitude mode of K_2SeO_4 in its lock-in phase over a range from about eighty degrees to just below its incommensurate transition, T_i , which occurs at about 130K. It will be shown that these data can be analysed by purely classical considerations with no need to invoke theories of critical behavior or to rely on partial fits to Curie-Weiss laws.

Second, we describe measurements of the internal mode spectra of Rb_2ZnCl_4 which cannot be described by conventional factor group analysis. The results support a model proposed earlier (1) to explain similar but less obvious effects in the spectra of K_2SeO_4 . The model attributes the lack of agreement with conventional analysis to orientational disorder of weakly-coupled selenate ions. An explanation for the cause of the disorder has been developed from an analysis of the dynamics of Rb_2ZnCl_4 and K_2ZnCl_4 (2).

The next two Abstracts are based on material described in much greater detail in the Technical Report, whose Abstract follows those two. The first, on K_2SeO_4 , is under final review by Physical Review B. The final draft of the second, on Rb_2ZnCl_4 and K_2ZnCl_4 , is in preparation for submission to Physical Review B.

NEW MEASUREMENTS OF THE RAMAN SPECTRUM OF POTASSIUM SELENATE*

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ABSTRACT

The Raman spectrum of K_2SeO_4 has been re-measured at 140K and 110K with neon line calibration and numerical fitting of peak frequencies to obtain ± 0.1 cm^{-1} precision. Although the results at 140K confirm the measurements of the internal mode peak frequencies reported by Unruh which appear to agree with the factor group predictions for the perfect crystal, arguments are presented to show that the orientationally-disordered selenate model still holds. Additional measurements in the incommensurate phase at 110K revealed line-splitting similar to those reported for infrared spectra; a comparison with those results is given.

RAMAN-SCATTERING STUDIES OF Rb_2ZnCl_4 and K_2ZnCl_4

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ABSTRACT

The Raman spectrum of Rb_2ZnCl_4 has been measured at 20 K, 100 K, 200 K, room temperature, and 315 K, covering all four known solid phases of this crystal. The spectra for the four highest temperatures were deconvoluted by fitting to a multi-Lorentzian function convolved with a slit transmission function. The peak frequency, full half-maximum width (FWHM), and integrated intensity for each of the deconvoluted peaks is tabulated and compared with those Raman lines calculated from the lattice dynamics for the presumed perfect crystal structures in the normal high-temperature phase, Pnam , and the higher-temperature phase of the two commensurate ferroelectric phases, $\text{Pna}2_1$. The four highest frequency lines that fall in the $270\text{-}310\text{ cm}^{-1}$ range have been studied at several temperatures in the $190\text{-}330\text{ K}$ range where they behave anomalously, compared to a similar group in K_2SeO_4 . This behavior is accounted for by the chlorozincate ion disorder and an accidental phonon degeneracy uncovered by the lattice-dynamical calculations that can, along with the disorder, permit harmonic mode-coupling. The internal modes do not change drastically with temperature; i.e., the tripling of the lattice period in the commensurate phase does not add a corresponding number of lines to the internal mode spectrum other than a few splittings, indicating the disordered chlorozincate ion

sublattice to be weakly coupled. Greater, but far from complete, splitting is found for the lattice modes. A similar study of commensurate, ferroelectric K_2ZnCl_4 shows the same general behavior.

ANALYSES OF THE RAMAN SPECTRA
OF THE INCOMMENSURATE FERROELECTRICS
 RB_2ZNCL_4 AND K_2SEO_4

INTERIM TECHNICAL REPORT

BY

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AND

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JUNE 30, 1986

U.S. ARMY RESEARCH OFFICE
CONTRACT DAAG29-83-K-0080
UNIVERSITY OF NEBRASKA-LINCOLN

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FOREWORD

Previously, a study (1) of the Raman spectrum of the incommensurate ferroelectric, potassium selenate (K_2SeO_4) was reported from this Laboratory. A qualitative model was proposed in that work to explain the universal observation, that in its paraelectric phase, there is a higher multiplicity of lines in the internal mode spectra (selenium-oxygen vibrations within the selenate tetrahedra) than predicted. The predictions came from conventional symmetry analysis of the x-ray-determined (for the selenate) $Pn\bar{3}m$ -potassium sulfate structure ($Pn\bar{3}m$). The main features of that qualitative model suggested the true structure to be slightly deviated from the inversion symmetry of the $Pn\bar{3}m$ space group as a result of small rotations (both static and dynamic) of the selenate tetrahedra out of their centrosymmetric positions. Further, it was necessary to postulate that these rotations did not possess translational symmetry but were disordered in the lattice, and that the selenate-selenate coupling was weak, in order to explain the numbers of lines observed in each Raman-scattering configuration.

More recently (i.e., since June, 1983), in addition to refining some of our measurements of the selenate spectra, we have made a detailed study and analysis of the Raman spectra of an isomorph of K_2SeO_4 , rubidium tetrachlorozincate (Rb_2ZnCl_4), also known (like K_2SeO_4), to exhibit incommensurate behavior (2,3). This experimental study paralleled (and reinforced) an intensive theoretical study of the lattice dynamics of Rb_2ZnCl_4 , to be described elsewhere, but from which calculated Raman peak frequencies were taken and are cited in

this report. (A brief preliminary report of some major results of the theoretical work has been submitted for publication (4)).

In the following sections, we describe our experimental results on Rb_2ZnCl_4 , our analytical procedures, and the results of our analysis, and we compare these results with our earlier studies on K_2SeO_4 and with the predictions of the model offered previously and described briefly above.

We also present in a second chapter some new measurements of the potassium selenate internal mode spectra, made with more precise frequency calibration, for comparison with work reported by other laboratories.

Portions of this report are being prepared for the appropriate journals. However, this material is presented also as a technical report since many of the details will be omitted in journal publications because of space limitations.

The authors are especially indebted to their colleague, Professor R. D. Kirby, for many helpful suggestions on instrumentation, and on the analysis and interpretation of the data.

In the Spring of 1984, the co-principal investigators began organizing, as guest Editors (and at their instigation), a special issue of FERROELECTRICS, dedicated to the scientific contributions of the late Issai "Lef" Lefkowitz. The contents are restricted to those areas in which Lef played an active role and contain papers by authors from many countries.

The issue appeared in April 1987, just a month after the historic American Physical Society meeting at which the "marathon" session on high-temperature superconductors was held. It is appropriate to recall, as does one section of this issue of FERROELECTRICS, that Lef was a prime mover in the encouragement of research on insulators (e.g., CuCl) as potential high-temperature superconductors. The Guest Editors' introduction to that volume of FERROELECTRICS is reproduced below.

GUEST EDITORS' PREFACE

We first came to know "Lef" Lefkowitz through his supportive role as a Program Manager in the U.S. Army Research Office and later, through working with him for a few years in our roles as Program co-Chairs for IMF-5. We kept in contact mainly by phone—more frequently throughout his last illness.

It was impossible to know Lef at all well without realizing that he had not been able to reach his personal goals in pure research; in one author's recollections (later in this issue), it is noted that Lef "never quite landed the big one", and maybe this is true. However, an examination of his publication list reveals a considerable body of work, much of it at the frontiers of the areas that attracted his interest.

In an introductory section that follows, we have collected recollections from friends, co-workers, and supervisors who were close to Lef at various major stages of his professional career. As one reads through these, it becomes more and more clear that Lef's true role was as a "catalyst"—not in the usual casual overworked sense of the word, but rather in its most frequent chemical sense—the component without which the reaction effectively does not take place. This was Lef's most abiding contribution; without his participation, so many valuable scientific contributions might not have been made.

In this sense, this volume is a tribute to Lef's ability to see the future impact of new ideas, to his ever-present enthusiasm, and to his ability to push forward those areas he recognized as being potentially important whether or not they were popular or acclaimed at the time.

We recall the old saying that the good that men do dies with them. Lef's life (as we knew it) refutes this cynical appraisal. The good he did lives on in the minds and work of those who were supported, stimulated, cheered, and inspired by him, particularly during his last years which a lesser man could have made into a tragedy. Lef made them an inspiration and ultimately his own kind of triumph—as another contributor puts it so well, "Even when Lef lost, he won."

Lef is no longer with us but his influence lives on and grows, as ever more of the seeds he planted, mature, come to fruition, and in turn, generate their own progeny.

Finally, this volume is dedicated to those who were closest to him: his wife and sons. We are especially grateful to Libby for her support and encouragement. And to Neil and Philip, may this volume add another dimension to their memories of their father.

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August 1986

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