AD-A037 950 OFFICE OF NAVAL RESEARCH LONDON (ENGLAND) F/G 20/2
LATTICE DEFECTS IN IONIC CRYSTALS: REPORT ON THE BERLIN CONFERE--ETC(U)
FEB 77 L M SLIFKIN, J H SCHULMAN
UNCLASSIFIED ONRL-C-37-76 NL

1 OF 1
ADA037950

END
DATE
FILMED
4-77

(12) FG.

ONR LONDON CONFERENCE REPORT

ONRL C-37-76

OFFICE OF NAVAL RESEARCH

BRANCH
OFFICE
LONDON
ENGLAND

LATTICE DEFECTS IN IONIC CRYSTALS: REPORT ON THE 1976 BERLIN CONFERENCE

L.M. SLIFKIN* and
J.H. SCHULMAN

22 FEBRUARY 1977

*University of North Carolina, Chapel Hill

UNITED STATES OF AMERICA

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

⑭ 1. REPORT NUMBER
ONRL-C-37-76

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

⑥ 4. TITLE (and Subtitle)
LATTICE DEFECTS IN IONIC CRYSTALS: REPORT ON THE 1976 BERLIN CONFERENCE (1976),

5. TYPE OF REPORT & PERIOD COVERED
Conference

6. PERFORMING ORG. REPORT NUMBER

⑩ 7. AUTHOR(s)
L. M./ Slifkin, Univ. N. Carolina, Chapel Hill and
J. H./ Schulman

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Office of Naval Research, Branch Office, London
Box 39, FPO New York 09510

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS

⑪ 12. REPORT DATE
22 February 1977

13. NUMBER OF PAGES
23

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
⑫ 26p.

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

LATTICE DEFECTS
POINT DEFECTS
DISLOCATIONS
OPTICAL PROPERTIES OF SOLIDS
COLOR CENTERS
LUMINESCENCE
THERMOLUMINESCENCE
RADIATION DAMAGE
RADIATION EFFECTS
ION TRANSPORT
DIFFUSION
CONDUCTIVITY
ALKALI HALIDES
SILVER HALIDES
ALKALINE EARTH HALIDES (cont'd)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Salient problems and recent progress in the study of lattice defects in ionic solids were covered by excellent tutorial reviews and numerous contributed papers. This Report gives a general overview of the meeting and briefly summarizes a large fraction of the papers.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

265 000

4B

Item #19 (Cont'd)

ALKALINE EARTH OXIDES
X-RAY STUDY OF DEFECTS
E-MICROSCOPE STUDY OF DEFECTS

ONRL C-37-76

LATTICE DEFECTS IN IONIC CRYSTALS: REPORT ON THE 1976 BERLIN CONFERENCE

The 2nd Europhysical Conference on "Lattice Defects in Ionic Crystals" was held in West Berlin on 30 August - 3 September 1976, under the auspices of a number of international, European and German organizations. The Conference attracted about 200 participants, most, as would be expected, from the Federal Republic of Germany, with France as the next highest contributor, followed by about 15-20 participants each from Great Britain and the United States. Although the site of the Conference was apparently chosen to encourage participation of scientists from the USSR and the Eastern Bloc countries, they were conspicuous by their extremely small representation. The absence of participants from East Germany was particularly evident, even Professor J. Teltow of East Berlin, one of the Conference's scientific advisory committee, being among the absentees.

The large number of papers (about 150) necessitated the use of parallel sessions. However, the organizers of the Conference, headed by Professor F.W. Felix of the Hahn-Meitner Institut für Kernforschung, Berlin, did a remarkable job of unifying the meeting by means of well-chosen topics for the plenary papers, all of which were presented with a high standard of tutorial excellence. Despite the very full schedule of papers, an atmosphere of deliberateness was achieved, with plenty of opportunity for discussion immediately after the papers in the sessions themselves and during the various breaks. Even the social events seemed to promote these kinds of discussion, one of the events being a leisurely boat trip on the Spree for a visit to the Hahn-Meitner Institut. Here the assembled group was introduced to the activities of the Institut by short talks and a guided tour through its facilities and laboratories.

The Proceedings of the Conference are to be published by the *Journal de Physique*. The price and publication date are not known at this writing, but the Proceedings should appear reasonably soon in view of the rigid demands put on the authors for the submission of manuscripts. Nevertheless, the present report may serve to give a preliminary glimpse of the wealth of material discussed. The material in the Conference can roughly be divided into two parts: the electronic properties of point defects (primarily those properties implied by the terms color centers and luminescence) and what may be called the ionic and structural properties of defects (point defects and dislocations). Although there were separate sessions entitled "Color Centers" at the Conference, it appears, from the nature of the papers given, that this historically important topic may no longer be singled out as an entity unto itself, but will be merged instead with other topics that constitute the study of defects in crystals. Indeed, although the 1977 International Conference on Defects in Insulating Crystals to be held in Gatlinburg, Tennessee next October is chronologically a member of the 20-year-old series of Color Center Conferences, it will have the same broad scope of the Berlin Conference, of which color centers comprise only a part.

On the point-defect side, the main problems dealt with at the Berlin Conference were transport phenomena and defect-defect interactions (for example, aggregation of defects). As for dislocations, in ionic crystals one has a new phenomenon due to their electrical charges in addition to the sort of mechanical properties generally considered in non-ionic substances. Surprisingly, there was very little on the mechanical aspects of dislocations in comparison to the large amount of work reported on point-defect transport phenomena. Also the two-dimensional effects (grain boundaries, free surfaces) received almost no consideration at Berlin; this is especially curious since these interfaces must, in general, be electrically charged in the case of imperfect ionic crystals and hence should display a number of interesting and unique phenomena.

A major impression made by the Conference is that defects in solids--particularly the area of ion transport phenomena in ionic crystals--is a vigorous and productive activity in Europe, in contrast to the situation in the United States, which seems to have suffered a decline in the status of this field of research over the past several years.

In the summary of papers given below and organized by topic, the plenary papers are grouped with the contributed papers in the same field, as nearly as possible.

Point Defects in General

The opening lecture was given by A. Guinier, of Orsay, under the provocative title "Can We 'See' Lattice Defects in Crystals". He contrasted microscopy, which gives a direct image, with diffraction, which gives a pattern related to the average environment of the atoms. In principle, if one had first determined the structure of defects in ionic crystals, the perturbed electronic energy levels of these defects could then be calculated, thereby predicting the properties of color centers; in practice, color center spectroscopy developed first, and we are just now catching up with the structural end of the problem.

For ionic crystals, direct microscopy is much more difficult and restricted than it is in the case of metals. Field-ion techniques, for example, are simply inapplicable to non-conductors, and electron microscopy is quite difficult and so far has been fruitful only in several special cases. One of these cases is the study of dislocations produced in irradiated alkali halides, by L. Hobbs and colleagues, discussed later in this report. Other examples illustrated by Prof. Guinier are the electron microscopic images of crystallographic shear planes in non-stoichiometric V_2O_5 and Nb_2O_5 and the actual observation of single vacancies in V_7S_8. This latter case, however, is exceptional, and one cannot generally see a random distribution of vacancies: microscopic techniques usually show primarily only the extended defects, such as dislocations. Another difficulty that arises in the attempt to study ionic crystals by transmission electron microscopy is the damage produced by the electron beam itself. This can be exploited, of course, in studies of radiation damage, but can be a nuisance in other types of inquiry.

In contrast to microscopy, which—in favorable cases—gives images of individual extended defects, diffraction experiments yield information about the average atomic environment of an ensemble of localized, point defects. Whether one is using x-rays, electrons, neutrons, or possibly other beams, it is necessary to assure an adequately large intensity of the scattered wave, and also to employ wavelengths less than about 1 Å in order to have high enough resolution. In any case, it is the weak, diffuse scattering outside the Laue spots which signals the presence of defects in an otherwise perfect crystal (one must subtract the thermal diffuse scattering which is present even in the absence of point defects). It is not possible to deduce the structure of the defect directly from the scattering, but one must instead compare the predictions of various models with experimental results. The sensitivity of the method is now such that concentrations of one part in 10^3 to 10^4 can be detected, thanks to more powerful sources of x-rays, such as rotating anode tubes, and more efficient detectors (such as a slit detector, in which the height of a resulting pulse is related to the position along the slit at which the photon entered). A promising new source is the synchrotron, which gives an intense and continuous radiation.

One thus appreciates that microscopy and diffraction are complementary techniques. And, in a sense, one can "see" lattice defects.

J. Peisl (Ludwig Maximilians Univ., Munich) carried the theme on further, discussing in detail the extraction from x-ray scattering experiments of information about the structure of defects in crystals. The defects are "visible" both because they disturb the lattice periodicity and also because they cause lattice relaxation over a substantial volume, thereby changing the average value of the lattice parameter. Since the defects are generally present only in very small concentrations, it is permissible to analyze the results in terms of the relatively simple kinematical theory of x-ray scattering. Thus, the shift in the positions of the Bragg peaks gives the change in lattice parameter, which in turn yields the size of the defect. One also can measure an attenuation of intensity (a sort of static Debye-Waller factor) within the peaks and an increase in the diffuse scattering, which is the scattering produced by the defects themselves. The magnitude and symmetry of the lattice parameter change enables one to determine the complete strain tensor of the defect, and thereby define and characterize it. In additively colored NaCl, for example, it was thereby possible to deduce the volume of the F-center (0.6 atomic volumes); in radiation colored NaCl, on the other hand, one sees additional effects arising from the interstitial halogen that is produced along with the F-center.

The diffuse scattering is related to the Fourier transform of the displacement field about the defect and the interference between fields in the case of nearby defects (as with a close vacancy/interstitial pair). The anisotropy of the scattering reveals the symmetry of the defect. Further, an examination of the dependence of the intensity of the diffuse scattering on distance in the reciprocal lattice provides a check that the scattering really originates from point defects.

As further examples of the power of the technique, Peisl described the determination of the symmetry of the interstitial halogen in alkali halides; the observation of clustering of defects (manifested by the increase in intensity that comes about because in the cluster the defects scatter coherently) upon annealing (clusters were found to contain 100-200 defects); and elucidation of the site of a defect from determination of locations in the reciprocal lattice of scattering minima. Peisl visualized the eventual emergence of an "x-ray defectography" which would allow one to "zero-in" on the structure of defects.

In another general plenary lecture, H. Schmalzried (Technical Univ. of Hanover) reviewed several chemical aspects of point defects in ionic crystals. In this approach, the defect is considered as a chemical species, present in a highly dilute solution in the matrix, which serves as the reaction medium. One can then apply standard chemical thermodynamics and kinetics to discuss the rate constants of processes in homogeneous systems and the microscopic transport in macroscopically inhomogeneous systems. For example, in Ag_2S, the variation of the chemical potential of the silver ion with deviation from stoichiometry is similar to an acid-base titration curve, and, in fact, can be obtained by coulombic titration. As another example, the effects of dissociation of solute ion-vacancy complexes in AgBr doped with a divalent cation can be analyzed as with similar processes in aqueous solutions. In non-stoichiometric Fe_3O_4, the diffusivity of Fe as a function of the iron-to-oxygen ratio passes through a minimum: at high oxygen pressures, the large concentration of cation vacancies dominates the diffusion, while on the other side of the minimum one has a large effect of interstitial cations; a conventional solution model works quite well for compositions not too far off stoichiometry. In the case of non-stoichiometric CoO, however, the behavior is highly non-ideal. Lastly, Schmalzried considered the attainment of defect equilibrium during a reaction at the crystal surface, relating the rate of the reaction to the diffusivity and concentration of the defect.

Ion Transport

There were a substantial number of papers dealing with ion transport in crystals. An invited lecture by E. Sonder (Oak Ridge) focused on one set of practical reasons for studying these processes in high-temperature insulators such as oxides: our present ignorance is so great that it is difficult to design and assess a number of advanced energy generation systems. Among these systems are ceramic fuel elements for high-temperature fission reactors, blades for high-temperature gas turbines, components of controlled thermonuclear reactors, and magnetohydrodynamic generators. In all of these systems, high temperatures are coupled with other extreme conditions, such as very large gradients of temperature (which induces a preferred direction of ion migration). At present, we know very little about mass transport in these materials, even in the absence of supplementary perturbations, such as variations in composition and driving forces due to electrical and thermal gradients.

Many papers dealt with the study of ion transport by means of the electrical conductivity—and usually in systems much easier experimentally than those discussed by Sonder. C. Murthy and P. Pratt (Imperial College, London) discussed the reliability of the defect formation and migration parameters which are extracted from a computer program for the least-square fitting of the ionic conductivity versus temperature. Using data taken by other investigators on KCl and two distinct computing routines, they obtained sets of parameters with differences as great as 25%. This comes about because the minima in the multi-dimensional space which the computer is exploring are actually rather flat. Murthy and Pratt hence concluded that such analysis could not be made to yield significant results unless some of the parameters were constrained to fit other types of measurement also, such as tracer diffusion and/or careful and independent determination of solute concentrations. In the discussion from the floor, P. Jacobs pointed out that the ionic conductivity data actually show non-random deviations from the best fits, implying further that the simple model itself which is assumed in the analysis is inadequate. Studies of the ionic condictivity of LiH and LiD were reported by P. Varotsos, (Univ. Athens). For these substances, the Debye temperatures are very high and very isotope-dependent: 851 K for LiH and 638 K for LiD. One expects to find very large isotope effects and substantial deviations from linearity in the Arrhenius plot of the ionic conductivity, and this expectation was indeed borne out. The curvature at high temperatures of the log (conductivity x T) versus 1/T was attributed to anharmonic effects; at low temperatures, on the other hand, well below the Debye temperature, the attempt frequency becomes temperature-dependent, and gives rise to further curvature. For LiH, Varotsos found the migration activation energy for the cation vacancy to be 0.53 eV, the entropy of migration to be near zero, the Schottky formation energy to be 2.50 eV, and the formation entropy to be about 16k. For LiD, these parameters had almost the same values, but the conductivity versus temperature was somewhat below that for LiH. Experiments on the migration and equilibration of cation vacancies in NaCl and KCl in the presence of large temperature gradients were described by A. Rahman and D. Blackburn (The Open Univ., UK). An analysis of the ac conductivity in the presence of grad T, along with data on thermoelectric power, enabled one to draw the following conclusions: (1) the lifetime of vacancies is sufficiently long that local equilibrium is not attained in the presence of a thermal gradient; (2) this lifetime corresponds to a mean free path of about 12 microns; (3) the cation heat of transport in both substances is a bit greater than the activation energy for the migration of the cation vacancy, and increases slowly and linearly with increasing temperature. A. Laskar, D. Foster, and K. Wagner (Clemson) reported work on KN_3 and RbN_3 which indicates that the major defect is of the Schottky type and that transport is via the cation vacancy.

The transport properties of the alkaline earth halides continue to present challenges. P. Jacobs and S. Ong (Univ. Western Ontario) discussed the ionic conductivity of nominally pure and doped CaF_2. Because of difficulties at high temperature involving reaction with oxygen, these workers analyzed data only at relatively low temperatures (below 1000 K). They deduce that the Frenkel defect formation energy is 2.73 eV, the migration energy of the interstitial fluoride is 0.78 eV (a value lying a bit on the low side of the range of previously reported results), and that the anion vacancy migration energy is either 0.38 or 0.47 eV (this choice of two rather well-defined numbers is unusual!). V. Carr, A. Chadwick (Univ. Kent), and D. Figueroa (I.V.I.C., Caracas), working with BaF_2, also reported difficulties with high-temperature data: reaction with water and/or oxygen apparently produces a surface layer. Their analysis is therefore largely based on data taken at rather high frequencies, around 500 kHz. As the temperature approaches the phase transition point, the conductivity shows an excess in the concentration of point defects. Also, the halide interstitial is found to be more mobile than the anion vacancy only above about 800 K. The reaction between oxygen and BaF_2 and CaF_2 was also investigated by V. Levitskii, A. Hammou, and M. DuClot (Univ. St. Martin d'Heres, France), using a variety of techniques. They measured the increase in the concentration of anion vacancies as oxide ion is substituted for fluoride, therby causing the ionic conductivity to increase. They did not find the "anion liquid state" that was earlier reported by O'Keeffe. M. Maitrot and R. Madru (Univ. Lyon) measured the conductivity of CaF_2 at very low frequencies, down to 0.001 Hz, largely to explore space-charge effects. They have seen three different relaxations, one of which is a diffusion effect and another is an electret effect which is almost independent of the nature of any impurity present.

Several of the divalent fluorides, such as those of Sr, Ba, and Pb, show a diffuse transition at high temperatures to a very highly conducting phase. These have been examined by M. Dickens, W. Hayes (Oxford), and M. Hutchings (Harwell), using neutron scattering to gain information about the lattice dynamics, defect concentration, and diffusive processes. As one approaches the phase transition, there are substantial changes in the breadths of lattice modes, but neither any large anomaly in lattice parameter nor a pronounced increase in concentration of Frenkel defects in the anion sub-lattice.

R. Friauf (Univ. Kansas) gave a survey of the means whereby various experiments on ionic conductivity, diffusion, drift effects, and isotope effects can be collectively analyzed to give a detailed picture of transport processes in AgCl and AgBr. The analysis indicates an anomalous increase in the concentration of Frenkel defects at high temperature, apparently associated with a decrease in the defect formation energy. This temperature dependence of the formation energy was confirmed by experiments using the diffusion of sodium ion as a probe for the concentration of cation vacancies, as reported by A. Batra and L. Slifkin (Univ. North Carolina). They also described studies of diffusion of transition metal ions in AgCl, which can be quantitatively understood in terms of crystal field effects, and studies by J. Dutta and D. Golopentia on the kinetics of aggregation of manganese-vacancy dipoles in AgCl--these latter show that the order of the kinetics can be either second or third, depending on the degree of supersaturation. The growth of colloidal silver specks in 100 Å microcrystals of silver halides was discussed by C. Marquardt, J. Giuliani, and R. Williams (US Naval Research Lab, Washington, DC). The microcrystals, imbedded in a glass matrix, were excited by a laser pulse, and were then observed for several tens of microseconds by means of time-resolved optical absorption spectroscopy and ESR. It was found that there is no growth of colloidal silver below 130 K; above 150 K, the growth time is approximately 7 μsec, almost independent of temperature. The very small dependence of growth rate and colloid size on temperature indicates that the interstitial silver ions involved are on the surface, not inside the bulk of the microcrystal. The temperature and pressure dependence of the ionic conductivity of the high-pressure fcc phase of AgI was described by B. Baranowski, E. Bowling, and A. Lunden (Chalmers Univ. and Polish Academy of Sciences). The activation volumes were found to depend on pressure, and the values of the energies of formation and migration of the cation defects were quite different from those of the (possibly) related materials AgCl and AgBr.

For many years, the curvature of the high-temperature portion of the intrinsic region of the Arrhenius plot for the ionic conductivity of the alkali halides has been analyzed in terms of a small contribution from anion vacancies, jumping with a rather large activation energy. Recent experiments by Beniere *et al*, however, have shown that in KCl the two types of vacancy move with almost the same activation energy. At this Berlin Conference, the results of a detailed theoretical study of point defect energies in the alkali halides were summarized by a group working at Harwell: C. Catlow, J. Corish, K. Diller, P. Jacobs, and

M. Norgett. A shell-model treatment showed that for all of the fcc alkali halides, the migration energies for the cation and anion vacancies are essentially equal to one another, both in the case of isolated vacancies and also as components of vacancy pairs. These authors concluded that the high-temperature curvature of the Arrhenius plot may perhaps be due to the onset of a contribution from a cation interstitialcy mechanism. The entropies of formation of lattice defects were discussed by F. Beniere (Lannion, France), who used simple models to relate them to other physical parameters of the material. There is a question, however, in such treatments as to whether inclusion of a greater number of lattice modes might not change the results considerably. The problem of the creation and migration of defects on the crystal surface was addressed by W. Mackrodt and R. Stewart (Imperial Chemical Industries, Runcorn, England). For MgO, for example, they find that: the formation energy on the surface can be greater or less than in the bulk, depending on the orientation of the surface; the migration energy is less on the surface than in the bulk; and the binding energy of the vacancy pair is greater on the surface because of a smaller effect of lattice polarization. The diffusion paths for the migrating cation in a number of ionic crystals were discussed by P. Guerin and A. LaForgue (Univ. Reims). Their calculations omitted the effects of polarization, which perhaps accounts for the fact that the values of the activation energy obtained were always much higher than the accepted experimental ones. Also, they conclude that the migration path is a curved one for NaCl and for a number of other materials, whereas the Harwell group find that the path is straight for all of the alkali halides.

Several papers were presented on radio-tracer diffusion experiments. Concentration-dependent diffusivities of divalent calcium and strontium, simultaneously diffused into high-purity NaCl, were measured by H. Machida and W. Fredericks (Oregon State Univ.). The migration activation energies of the solute-vacancy complexes were found to be 0.85 eV (Ca) and 0.93 eV (Sr), while the binding energies of the complexes were determined to be 0.75 and 0.67 eV, respectively. Comparing the present results with earlier ones on other solutes, one concludes that in NaCl the solute-vacancy binding energy is larger for transition ions than for alkaline earth solutes, but that it does not correlate well with ionic radius. The effects of a grain boundary--in this case a 10° (100) tilt boundary--on cation self-diffusion in NaCl were explored by L. Harris (Univ. of New South Wales). The literature contains many conflicting reports on this phenomenon, and Harris' work points to a likely explanation: the cation migration along the grain boundary is very sensitive to thermal history and impurity content, largely because of the formation precipitates along the boundary, even for solute concentrations well below the bulk solubility limit at the temperature of the experiment. Further observations of this peculiar precipitation effect are cited in the account of a paper by Wentz *et al*, below. The heats of transport of Sr and Mn in KCl were discussed by S. Rushbrook-Williams and A. Allnatt

(Univ. Western Ontario). When the effective heats of transport, determined from the solute concentration gradient established by a thermal gradient, are corrected for the solute-vacancy association energy, the values which were obtained were about 6 and 3 eV for Mn and Sr, respectively, considerably larger than the activation energy for diffusion.

The use of nuclear magnetic resonance (NMR) in diffusion studies was the basis of papers by H. Richtering, K. Becker, and H. Hamann (Univ. of the Ruhr) and by R. Gordon and J. Strange (Univ. Kent). Richtering *et al* discussed primarily the diffusion of cuprous and cupric ions in AgCl and AgBr. For the cuprous ion, the diffusivities are lower than the tracer values by about two powers of ten, presumably because the NMR technique looks mainly at substitutional Cu whereas the tracer experiment is dominated by the tiny fraction of copper that is interstitial. Gordon and Strange used the NMR technique to study the diffusion of fluoride ion in BaF_2, an experiment of especial importance because the absence of a suitable isotope makes difficult any accurate direct tracer measurement of this quantity. The NMR diffusivities obtained were about twice as large as those inferred from the ionic conductivity. This discrepancy could possibly be due to errors or to the presence of an additional mechanism seen only by the NMR (e.g., motion of a neutral defect).

Complex Defects and Aggregates

The properties of many complex defects, and the aggregates formed by them, are still largely unknown. Since many of the simpler complexes have a dipole moment, their properties and concentrations can often be monitored by the ionic thermocurrent (ITC) method, which is essentially a low-temperature depolarization experiment. One such experiment, on lead-doped KCl, was discussed by R. Capelletti and A. Gainotti (Univ. Parma). During aging, as the concentration of lead-vacancy complexes decreases, one sees the build-up of a new ITC peak, located at a temperature higher than that of the Pb-vacancy complex. This new band really represents a superpositon of relaxations, with an effective activation energy of about 0.7 eV. Its appearance is correlated with the onset of light-scattering, and it was proposed to have originated from Maxwell-Wagner polarization at the surfaces of particles of a Suzuki phase. The 0.7 eV-activation energy may then be identified as the migration energy of the cation-vacancy in the new phase. These conclusions were strengthened by results of experiments on the low-temperature thermal conductivity of the same system, reported by M. Locatelli (CEN-Grenoble), who could analyze his results to conclude that the new phase observed by Capelletti had particle sizes of several hundred Å. The ITC technique was also used by J. Winter and K. Rossler (Jülich) to study phase transitions in ammonium halides and compounds of the form R_2MX_6, which contain dipolar defects when heated or irradiated. Sharp peaks are found at the transition temperatures, and these should somehow be related to the lattice dynamics at the transition.

Various dipolar complexes in alkaline earth fluorides doped with trivalent erbium were studied by means of dielectric relaxation by D. Jones, J. Fontanella (US Naval Academy), and C. Andeed (Case-Western Reserve Univ.). The effects on peak height of thermal history and addition of oxygen to the specimen made possible some tentative identifications of several of the large number of peaks. It was also reported that the effective migration energy of the anion vacancy is 0.87 eV; this value, however, is about 0.4 eV larger than that obtained by Jacobs, and it perhaps includes the association energy of an oxygen-vacancy complex. Nearest- and next-nearest-neighbor complexes in rare-earth-doped alkaline earth halides were studied by J. Crawford and G. Matthews (Univ. North Carolina), using ITC to measure the ratio of concentrations of the two types of defects in specimens that have been equilibrated at various temperatures. For SrF_2, the simple model fits the experimental data rather well, and one can state that the nn complex is more tightly bound than is the nnn complex by 0.046 eV; also, the ratio of the dipole moments that is obtained differs greatly from that predicted by the unrelaxed point ion model, showing that there is a large difference in relaxation between the two species. In the case of CaF_2, however, the situation is apparently more complicated than encompassed by the simple model. M. Jacquet, A. Gervais, and M. Bathier (Univ. Clermont, France) presented a series of experiments on $SrCl_2$, doped with both monovalent and trivalent solutes, and studied by means of ITC, conductivity, and EPR. The migration activation energy of the interstitial chloride was found to be 1.0 eV, a value too high to allow much conductivity from this defect. For the anion vacancy, however, the migration energy is only 0.34 eV; also, the binding energy of the complex formed between an alkali ion and an anion vacancy was found to be 0.49 and 0.45 eV for Na and K, respectively.

An interesting effect on conductivity and dielectric loss during the redissolution of the Suzuki phase particles in aged LiCl:Mg was reported by Y. Al-Jammal and E. Lilley (Univ. Sussex). If the previous cooling rate of the sample had not been too slow, then upon re-heating to some constant high temperature, the conductivity rises above the equilibrium value, goes through a maximum, and then decays to the final equilibrium value. This effect appears to be associated with a difference in molar volume between host matrix and the precipitated phase, thereby releasing an excess of vacancies during dissolution.

For a number of years, there has been a controversy over the mechanism of aggregation of impurity-vacancy complexes in alkali halide crystals, evidence being available that the process is of second order (forming dimers), and also other evidence that it is of third order (to form trimers). A. Kessler (Stuttgart) discussed dielectric loss measurements on calcium-doped NaCl which demonstrate that aggregation of solute to dislocations can greatly influence the results, especially if the total concentration of solute is not very large as compared to that required to saturate the dislocations. Kessler's data indicated that the bulk process is via a second order mechanism. The discussion from the floor, however, demonstrated that this controversy is still not settled. A related experiment, by Hartmanova and Vlasak, is discussed below. For AgCl heavily doped with cadmium, the processes of aggregation and precipitation were studied by a variety of methods (ITC, conductivity, small angle x-ray scattering, and light scattering) by M. Wentz, K. Ledjeff, K. Zierold, and F. Granzer (Frankfurt am Main). The results show that after the early stages of aggregation of the cadmium-vacancy dipoles, particles of Suzuki phase are formed. The number of dipoles within the precipitate increases, vacancies are injected into the crystal, and eventually there is a change of phase to particles with a higher concentration of $CdCl_2$. Although at high initial concentrations of Cd in the bulk, the resulting precipitates are approximately spherical, one sees needle-like precipitates to form along the dislocations even at very low bulk concentrations.

Off-Center and Axial Ions

Off-center defects were the subject of two papers from the University of Utah. The first, by J. Wahl, A. Gongora, and F. Lüty, dealt with a determination of the dynamics of jumping of the fluoride defect in several bromides and iodides; dielectric loss and time-dependent Kerr effect were employed. In the second, U. Holland and F. Lüty showed how the application of hydrostatic pressure could induce Ag, Cu, and Li defects to shift from an off-center to a central site. This increase in pressure also lowers the barrier between the off-center sites, observed--of course--before the pressure has become so high as to render the off-center sites unstable.

The properties of a novel set of compounds, the alkali hyperoxides, MO_2 were reviewed in an invited paper by W. Känzig (ETH, Zurich). These compounds have an NaCl-like structure, but with an anion, $(O_2)^-$, which has an axis and a magnetic moment. The cohesive aspects of the hyperoxides are in many ways similar to those of the halides: (1) the compressibility depends similarly on lattice parameter; (2) the mass-corrected reststrahlen frequencies are similar; (3) all of the various phases of these compounds show about the same Raman frequencies, indicating that the binding of the peroxide ions has not changed very much; and (4) the far IR reflection is what one might expect for an alkali halide when account is taken of the possibility of ordering of the anion. It is the varied assortment of ordering possibilities of the anion that make these materials so interesting. Also, there is the possibility of magnetic ordering as well as structural, and the two types of order must interact. Throughout, it is the elastic interaction which dominates. Känzig outlined the rich variety of phenomena displayed by these materials: antiphase structures, various types of magnetic behavior, extreme anharmonicity of the rotational dynamics of the anion, and a large number of phase transitions.

Radiation Effects

The present status of our understanding of the production of lattice defects by ionizing radiation in alkali halides was evaluated in an invited paper by N. Itoh (Nagoya Univ.). The especially interesting feature of this process is that energy possessed by the electronic system is converted into energy for mass transport of the anions to form a Frenkel pair. About ten years ago a mechanism was proposed independently by D. Pooley and H. Hersh, in which the electron's recombination with a self-trapped hole (V_k-center)--or in other words, the decay of a self-trapped exciton--produces the Frenkel pair. An important part of the evidence for this view was the observation that radiative recombination and non-radiative decay are complementary to each other, and it is the latter which parallels the formation of Frenkel pairs. Itoh discussed the evidence that the precursor to the F-center is not the luminescent state of the self-trapped exciton, but is instead a higher-energy excitation. The problems connected with the de-excitation step, the dynamic motion of the interstitial, and its interactions with other defects were considered in the light of experimental information on the effects of temperature and the presence of other defects and impurity ions. Finally, the large trapping cross sections for interstitials to form higher-order aggregates were described.

This aggregation of defects was also considered, *inter alia*, by L. Hobbs (Harwell), who surveyed the general topic of the formation of more complicated structures from a high concentration of point defects in an ionic crystal, often resulting in extended defects. In addition to the aggregation of F-centers, he discussed: the formation of crystallographic shear planes in oxygen-deficient transition metal oxides; the formation of a defect in oxygen-excess FeO, in which an interstitial ferric-ion is surrounded by a tetrahedron of cation vacancies (amusingly enough, exactly the same center was found to form in halogenated AgCl:Fe some years ago, by Pilbrow, Hayes, and Slifkin); the aggregation of divalent cation in MX to form the Suzuki phase; the stabilization of the anion interstitials in irradiated alkali halides, with the needed extra space provided by a dislocation loop; and the clustering of trivalent cation-interstitial fluoride complexes in the fluorites.

There has already been a great deal of research on the spontaneous recombination of close Frenkel pairs in metals, where the interactions are primarily mechanical. In ionic crystals, one must also expect electrostatic and chemical bonding interactions. The theory for this process was outlined by K. Rossler (Jülich). For substances of the type A_2BX_6, the theoretical value for the recombination radius is 5 to 8 Å, agreeing with experiment. For such oxides as HfO_2 and Fe_2O_3, virtually all cations manage to get back to substitutional sites after irradiation. For the alkali halides, he concluded that the recombination radius is between one and one-half of the lattice parameter.

An experimental study of neutron-induced defects in potassium halides, along with a computer simulation comparison, was reported by F. Felix, M. Muller (Hahn-Meitner Inst., Berlin), and K. Rossler (Jülich). The concentrations, properties, and stabilities of the irradiation-induced defects were monitored experimentally by measurements of the diffusivity and of the activation energy for diffusion of the argon that is also produced. Of especial interest was the role of the energy of the incident neutron beam. For example, with low-energy neutrons, the defects are produced in small zones and have high rates of recombination. In a related paper, B. Graneli and M. Muller (Hahn-Meitner Inst.) presented work on a combined sectioning and gas-release study of diffusion and trapping of argon in neutron-irradiated KCl. Here, the main interest was on the effect of the annealing of the traps during the diffusion measurement.

The release of stored energy in alkali halides upon warming up after an x-irradiation at 10 K was measured by R. Balzer and P. Schrey (Darmstadt). Some ten different peaks could be resolved in the energy release versus temperature run; these were correlated with changes in the optical absorption of color centers. It was thereby possible to assign the peaks to recombinations of various configurations of charged and uncharged Frenkel pairs. The question of how the H-center is stabilized after creation of the Frenkel pair was considered by G. Guillot and A. Nouailhat (Inst. of Applied Sciences, Lyon). They studied the growth kinetics of F-centers, during electron irradiation, as a function of added impurity, which acts as a trap for interstitials and nucleates clusters, thereby inhibiting recombination. For impurity concentrations exceeding 10^{16}/cc, this process is much more important than is homogeneous stabilization by formation of bi-interstitials. A computer simulation of recombination and trapping of Frenkel pairs in LiF was described by A. Van den Bosch (SCK/CEN-Mol).

Several papers dealt with the formation of larger defects--dislocation loops and colloid particles--upon irradiating alkali halides. A. Kawamata, B. Hibi, and K. Yada (Tohoku Univ.) followed the formation of loops during observation in the beam of a 100 kV-transmission electron microscope. Inside the large interstitial loop which soon appears, they find the growth of a second, smaller loop, perhaps of the vacancy type. Their results show that energetic electron irradiation creates approximately equal numbers of Frenkel defects on both sub-lattices. Such loops can also be studied by diffuse x-ray scattering, and H. Spalt (Darmstadt) showed that the nature of the loops, their size, and whether or not clusters are also present are all dependent on the irradiation conditions, such as the nature of the irradiating beam. U. Jain and A. Lidiard (Harwell) gave a theory for the growth of metal colloid particles during high-temperature irradiation of alkali halides. This process depends on the fact that not all Frenkel pairs recombine, but that some interstitials can aggregate to loops, leaving an excess of anion vacancies to aggregate, ultimately forming metal colloids. It is interesting that the net imbalance of these various processes produces colloids only over a relatively narrow range of temperature; also, not surprisingly, the results are quite sensitive to dose rate. The model presented by Jain and Lidiard was shown, within the uncertainty of several of the parameters involved, to be capable of reproducing the experimental observations. That a similar effect occurs in the alkaline earth halides was demonstrated by R. Alcala and V. Orera (Univ. Zaragoza, Spain), who analyzed the resulting optical absorption bands in terms of the Mie theory, correcting for the pressure exerted on the metal particles by the surrounding matrix. For CaF_2, their results give the sum of the anion vacancy migration energy plus half the Frenkel formation energy to be 2.05 eV, if one can neglect the temperature-dependence of such parameters as the interfacial energy.

Defects produced upon annealing crystals of KI which had previously been irradiated with deuterons or alpha particles were studied by L. Chassagne, J. Serughetti (Univ. Lyon), and L. Hobbs (Harwell). They followed the formation of colloid particles both by optical absorption and by electron microscopy--both in transmission, which showed that most colloid particles formed in the stopping zone of the bombarding ion, and by replication, which showed the formation of small extrusions on the surface. The inclusions were identified as fcc K metal, formed epitaxially. Also, there were inclusions and bubbles believed to be KH and He, respectively. Dislocation loops were also found, and these were seen to be distributed to depths much greater than the ranges of the bombarding ions, apparently because of ionization-produced Frenkel defects. A. Berthault (CEA-Montrouge) presented data on Li colloids produced in LiH which had been gamma-irradiated and then annealed. The distribution of particle sizes as a function of dose and annealing history was followed by analysis of the resulting inhomogeneously broadened EPR line.

The effects of implanting MgO with sodium and potassium ions were described by P. Thevenard (Univ. Lyon). When the crystals are heated to 600°C, a colloid band begins to develop. These particles were shown to contain at least about 50 atoms. Similar experiments on LiF, by J. Davenas, A. Perez, and C. Dupuy (Lyon), showed that at temperatures well below room temperature, small complexes of alkali atoms are formed; upon warming to near room temperature, these aggregate and give rise to much larger particles. C. Terras (CEA-Montrouge) measured the effects of gamma irradiation on the elastic constants of LiH, and particularly the recovery processes that take place upon subsequent annealing. Both cavities and precipitates can form, grow, and decay, and the evolution of the state of the system depends on a number of variables, such as the irradiation temperature and the dose. For example, if the irradiation temperature were 90°C, then a 400°C anneal causes the dissolution of the small cavities present; if, however, the original irradiation temperature were well above 90°C, then annealing causes the large cavities that are present to agglomerate into stable clusters. The sputtering of alkali halides by high-energy (up to 300 keV) ions at temperatures up to 300°C was found by J. Biersack and E. Santner (Hahn-Meitner Inst.) to proceed by a Pooley-type mechanism, rather than via collision cascades. Thus, the halogen is primarily removed, the alkali following by evaporation; also, the process has a 0.2-eV activation energy, the yields depend on electronic stopping power, and are very much higher than would be produced by collision cascades. B. Neidhart, B. Stojanik, R. Lauer, and K. Bachmann (Darmstadt) discussed experiments on the release during warm-up of various ions that had been implanted in different crystals. The resulting kinetics are apparently somewhat obscure.

A novel method of looking at point defects in crystals such as CaF_2 was described by H. Ackermann, D. Dubbers, H. and M. Grupp, P. Heitjans, and H. Stockmann (I.L.L.-Grenoble). Polarized ^{20}F nuclei are produced by capture of polarized neutrons. The NMR of these nuclei is then detected by means of the polarization of the subsequent beta decay. The presence of a neighboring defect is manifested through the quadrupole interaction with the resulting electric field gradient. One sees a recombination occurring with quite low activation energy, which is assigned to close pairs. From relaxation time studies, one can obtain the diffusion coefficient of the ^{20}F nuclei; the resulting activation energy, about 2 eV, is that for intrinsic interstitial fluoride diffusion. This is quite strange, since the temperature range is such that the crystal is in the extrinsic region, and it is not clear why the spin system should be relaxed by intrinsic but not extrinsic defects. In another discussion of effects of nuclear reactions, H. Muller and S. Martin (Univ. Freiburg) gave data on the various species that are formed in mixed crystals of K_2ReBr_6-K_2ReCl_6 when a nuclear reaction produces bromide ion recoils. The recoil ions can in turn produce bromide vacancies, and a variety of products then result.

The trapping of photocarriers after exposure to light can be studied by means of the spectral distribution of the luminescence and by glow curves. Experiments of this sort, on nominally pure and also cadmium-doped AgCl, were carried out by W. Polzin, W. Assmus, and F. Granzer (Univ. Frankfurt am Main). Complementary ESR experiments showed that the self-trapped hole (Ag^{2+}) is stable only up to about 60 K; hence, whereas the self-trapped hole may be the dominant luminescence center at low temperatures, it cannot be important above 60 K. The luminescence at these higher temperatures was found to be very sensitive to the thermal history of the crystal. In the Cd-doped samples, it is likely that a Cd-rich second phase is responsible for the shift to longer wavelengths of the luminescence of the doped crystals. Exposure to ultraviolet also produces specks of Ag metal, and these appear to be very efficient traps for photocarriers, thereby dominating the thermal glow curves.

Dislocations

The Conference offered several papers on atomistic calculations of the structures of dislocations and several others on the mechanical properties induced by dislocation motion in ionic crystals, but unfortunately a conflict prevented the authors from hearing many of these. H. Strunk (MPI-Stuttgart) presented the results of a transmission electron microscopy study of bromide-doped NaCl that had been deformed into the easy glide stage; the function of the bromide was to prolong stage I. By using high accelerating voltages for the electron beam, and by keeping the specimen below 18 K, it was possible to obtain micrographs without producing excessive radiation damage. Strunk found that, if the concentration of bromide was below about 0.1%, the screw dislocations frequently had pronounced cusps, dragging edge dipoles; in this case, the flow stress was probably determined by the bowing of loops between jogs. With increasing concentration of bromide, however, the screws become smoother, and the stress is now limited by elastic interaction between dislocations. The mobility of dislocations in several alkali halides was investigated at very low temperatures (down to 4 K) by E. Gutmanas (Technion, Haifa). He measured the velocity, by means of pulse loading and etch pits, as a function of stress, purity, temperature, and dislocation orientation. In particular, the temperature dependence of the mobility is quite startling: at very low temperatures, the mobility decreases with increasing temperatures. At higher temperatures, the mobility begins to increase, but it does not go as a simple Boltzmann factor. In general, the screws were less mobile than the edges. It could be concluded that the yield stress at low temperatures is limited by the multiplication of dislocations, and not by their mobility.

Because the jogs of dislocations in ionic crystals must maintain a separate equilibrium with each type of point defect in the bulk of the crystal, these dislocations generally carry an electrical charge, the sign and magnitude being dependent on temperature and impurity content of the crystal. This situation thus gives rise to a variety of phenomena: production of potential differences across inhomogeneously deformed crystals, effects of moving and static dislocations on ionic conductivity and diffusion, enhanced solute segregation, and--amusingly enough--the photographic process. In particular, the conductivity of a deformed specimen evolves as follows: during deformation, there is a large excess conductivity; when deformation is stopped, the conductivity excess drops to a small but positive value, which gradually decays, and eventually becomes negative (i.e., a long time after the deformation the conductivity is less than it was originally). A straightforward model which accounts for all of these observations, as well as several other transient effects, was presented by R. Whitworth (Univ. Birmingham). He showed that the increase during deformation was not due to the production of additional vacancies by moving jogs, as had originally been thought, but rather is due to the effect of the electric field on the mobility of the charged dislocations. The small excess conductivity remaining just after the deformation stops is due to vacancies which have been swept away from compensating divalent solute ions, and the final drop is due to the ultimate removal of some of the bulk vacancies by trapping at jogs on the newly created dislocations. This final decrease is too large to be accounted for by the observed dislocation density, and must therefore be due to a large concentration of debris which is not seen in etch pit studies. Some of these conclusions are in conflict with a paper of A. Toth and J. Sarkozi (Tech. Univ. Budapest). These authors indented doped NaCl crystals and deduced the charges carried by the moving dislocations from the potential difference that developed between crystal and indentor. In particular, they were concerned with whether the dislocation can sweep up vacancies from solute-vacancy complexes. In various runs, the ratio of free-to-bound vacancies was varied by varying the dopant concentration, the thermal history, and the temperature of measurement--and for all of these the measured charge was directly proportional to the concentration of free vacancies, independent of the amount of complex present. These results thus contradict those of Whitworth given above. During the discussion, in an attempt to resolve this conflict, some doubts were expressed as to the validity of the methods employed by Toth and Sarkozi, but the question remains unresolved.

The kinetics of the segregation of a solute to fresh dislocations were investigated by M. Hartmanova and G. Vlasak (Acad. of Sciences, Bratislava) in NaCl doped with strontium. The loss of Sr was followed by the time-dependent decay of ionic conductivity after deformation, and the results were analyzed by means of the Cottrell-Bilby model, which predicts an accumulation at the dislocation which increases at $t^{2/3}$ for times that are not long enough for a back-diffusion flow to be appreciable. It was found that the present results could indeed be fitted to such kinetics if one ignored the first 3½ hours (at 500°C), during which there appeared to be some sort of incubation process. This is strange, however, since the Cottrell-Bilby model should hold best for the very short times, and it does not include any nucleation step. Thus, here too, questions remain.

Color Centers, Luminescence, and Related Topics

The sessions labeled "Color Centers" covered a variety of topics, some of which merge naturally with some of the other sessions of the Conference. Thus, the very lively topic of production of lattice defects in the alkali halides, a central "color-center" issue and the subject of a plenary paper by Itoh, has already been covered in this Report under the heading of "Radiation Effects" and might equally well have been considered an inaugural talk of the Conference sessions having either one of these headings. Also included under "Color Centers" were luminescence, optical studies of activator centers and complexes, color-center growth kinetics, models of centers, theory of electronic structure of centers, and even a few practical applications. The following selection of papers for mention is by no means totally representative, therefore.

An outstanding review of interstitial centers in alkali halides was given by D. Schoemaker (Univ. Antwerp) in a plenary lecture which he entitled "Games People Play With Interstitials". Starting from a description of the H-center (a form of interstitial halogen, X, existing as essentially an X_2^- molecular-ion occupying a single anion lattice site in the pure alkali halides, Schoemaker described the rich variety of modified H-centers that one can form by doping the crystal with foreign halogen, alkali, or other impurity ions. These modified H-centers--some consisting of mixed halogen molecule-ions (e.g., ClF^- rather than Cl_2^-), others consisting of H-centers formed near impurity alkali ions--are often more themally stable than the normal H-center, and they display an interesting variety of orientations with respect to the lattice as well as different symmetries and vibrational motions. When halogen interstitials are trapped at cation impurities, the resulting H-center is symbolized by the subscript "A", and the impurity is indicated in parenthesis, viz., $H_A(Na^+)$ (which can be formed in KCl:Na). Halogen interstitials can also be trapped by pairs of nearby impurity cations, symbolized by H_{AA}, these centers occuring at heavy dopings with the impurity cation in question. Interstitials can also exist which involve both foreign cations and foreign anions, such as the <110>-oriented $BrCl_2^=$ configuration, a $H_A(Na^+)$-type center formed in $LCl:Na^+:Br^-$. In general, H_A centers have lower symmetry than H-centers; thus, the H-center in KCl is oriented along the <110> direction, while the axis of the $H_A(Na^+)$ center makes an angle of 5.7° with <110>, giving the possibility of four distinguishable $H_A(Na^+)$ centers in $KCl:Na^+$. The description of all the different configurations of H-centers left little time for a discussion of their properties, but Schoemaker did mention the optical orientation of H-centers by polarized light. Indeed, the symmetry of the H-center was first determined by W.D. Compton and C.C. Klick by this method even before its actual configuration was demonstrated by the ESR studies of W. Känzig and T.O. Woodruff. All in all, Schoemaker's lecture demonstrated the astonishing progress that has been made since Känzig essentially revolutionized the concept of trapped-hole centers by his pioneer ESR work in the 1950s.

A paper by Lüty (Univ. Utah) and S. Morata (now at Inst. de Energia Atomica, São Paulo) revealed a new fundamental hydrogen-bearing defect ("H_x^-") in the alkali halides ("H" meaning hydrogen in this case, not the H-centers discussed in the previous paragraph). This defect can be created in many different ways in crystals containing OH^-, SH^- or H^-, starting with photolysis or x-irradiation. One of the controlled ways to make it is from OH^--bearing crystals. One photodissociates the OH^- at low temperature, creating interstitial hydrogen centers (H_i), and then illuminates with light in the H_i absorption to form H^- and an H-center (i.e., a X_2^- at a single anion site--this is where the alphabet-soup of color-center nomenclature unfortunately gets confusing!). A study of the formation kinetics of the new center shows that it is formed by the reaction of a mobile X_2^- (i.e., a mobile H-center) with a hydrogen-bearing defect, perhaps an interstitial hydrogen, H_i. The new defect shows no electronic absorption but can be detected by a single sharp local-mode band at about 1120 cm^{-1} in KCl, with a perfect $\sqrt{2}$ H → D shift when OD^- is used instead of OH^-. No model can yet be assigned to the defect.

D. Durand and F. Lüty (Univ. Utah) described their studies on order-disorder transitions in mixed alkali halides-cyanides. The CN^- ions in the alkali salts rotate rapidly at high temperatures and average out their non-spherical features to give a pseudo-alkali-halide behavior. On cooling there are phase transitions into higher orientational ordering of the CN^- elastic and electric dipoles. This ordering can be observed by Raman-effect studies. Since the alkali cyanides are completely miscible with the alkali halides, a systematic study can be made of the onset of CN^--ion interaction effects starting from the case where the CN^- concentration is low and the CN^- is an isolated impurity.

Ionic reorientation of impurity-vacancy (IV) dipoles was discussed by S. Benci, R. Capelletti, F. Fermi and M. Manfredi (Univ. Parma), who showed that it could take place even at very low temperatures when the IV dipoles absorb light; i.e., when the Pb^{++} of a Pb^{++}-vacancy defect in KCl is raised to an electronically-excited state by illumination into a Pb^{++} absorption band. The effect occurs because electronic excitation lowers the energy barrier for ionic diffusion. The reorientation efficiency in the electronically-excited state is thermally activated, but it is still appreciable even at 78 K because of the increased lifetime of the excited state. KCl:Pb shows three radiative lifetimes in the temperature range 78-300 K, two of which are independent of temperature and the third increasing by a factor of 100 when the temperature decreases to 78 K. In response to a question, Capelletti stated that the group intends to repeat the work using polarized light which would permit further detailed probing of the orientation of the Pb^{++}-vacancy complexes. (For other work by the Parma group, see the section above on "Complex Defects and Aggregates".)

A. Rascón and J.L. Alvarez-Rivas (Junta de Energía Nuclear, Madrid) studied the thermoluminescence (TL) of alkaline-earth doped KCl after RT x- or γ-irradiation. Ca^{++}, Sr^{++}, and Ba^{++} each produces its own set of glow-peaks. The pre-exponential factors and activation energies of these peaks were obtained, and all were found to obey first-order kinetics. The magnitude of the frequency-factors found, 10^2-10^5, which is the same as those found for the annealing of F and V (226 mμ) centers, implies that one is dealing with mass motion rather than simply electron-hole recombination. The authors propose, therefore, that the TL involves the release of mobile Cl° atoms from traps followed by their reaction with F centers, at which time e-h recombination occurs and light is emitted.

O. Thiebaud, J.J. Pilloud, M.A. Aegerter and C. Jaccard (Univ. de Neuchâtel) investigated the phosphorescence observed after x-raying CsI:Na (emission peak at 420 mμ) and CsI:Tl (emission peak at 560 mμ) at low temperature. Below 50 K the decay time of this phosphorescence is independent of temperature and arises from the tunneling of an electron on the impurity (Na° or Tl°) to a V_k center trapped near the impurity. Thus, the sequence of x-ray production of defects and the subsequent tunneling process is:

$$2I^- + Na^+ + \xrightarrow{(h\nu_x)} I_2^- + Na^\circ$$

$$I_2^- + Na^\circ \xrightarrow{\text{(tunneling)}} (I_2^=) + Na^+ \longrightarrow 2\ I^- + Na^+ + h\nu_{420\ m\mu}$$

The decrease of luminescence due to the suppression of tunneling by high magnetic fields ($\leq$6T) was investigated for both dopants and was observed for CsI:Na but not for CsI:Tl.

J.L. Pascual, F.J. López, F. Jaque and F. Agulló-López (Univ. Madrid), investigating the kinetics of F-center coloration in NaCl doped with various divalent cations, showed that there is no correlation between the efficiency of F-center coloration and the concentration of vacancies or impurity-vacancy dipoles during the first stage of dipole aggregation, whereas there are a number of processes ($Pb^{++} \rightarrow Pb^+$, and $Mn^{++} \rightarrow Mn^+ \rightarrow Mn^\circ$) which do depend on the state of aggregation of the impurity.

A. Nouailhat, E. Mercier and G. Guillot (Inst. Nat'l des Sciences Appliquées, Lyon) studied exciton and host-sensitized luminescent impurity-ion luminescence in alkali halides as functions of temperature between 4 and 78 K and of the F-center concentration produced by irradiation. Making use of their earlier finding that the exciton emission is quenched by F-centers (or more accurately by interstitial centers formed along with the F-centers), they were able to show that only hot excitons created by UV excitation can diffuse at low temperatures.

G.W. Dean, S. Dannefaer, B.V. Sovelev and B.G. Hogg (Univ. Winnipeg) presented the results of their study of positron annihilation in 16 alkali halides using both lifetime measurements and Doppler broadening. The theoretically-predicted lifetime of 10^{-9} sec for e^+ trapped at F-centers was confirmed in all Na^+, K^+, and Rb^+ chlorides, bromides and iodides. F-centers in fluorides, however, are not effective traps for e^+ in alkali halides, the lifetime not being affected. This cannot be explained by the lower binding energy between the e^+ and the F-center in these salts, which although lower than in the other halides, is still of the order of 1 eV.

A scheme for information storage by $F \rightarrow X_k$ (colloid center) conversion (rather an old idea conceptually but apparently now covered by a Hungarian patent) was described by R. Viszka, S. Tökés, P. Kolin, and K. Rahsanyi (Res. Lab. for Crystal Physics, Hungarian Acad. Sci., Budapest). In this scheme F-centers are formed by ionizing radiation in highly pure (M^{+2}- and OH^--free) NaCl. These centers are thermally stable below 215°C, but can be bleached by F-band light at room temperature to form colloid, or "X_k", centers whose absorption band peaks at 580 mμ, well separated from the peak of the F-band at 450 mμ. Reading is performed non-destructively with X_k-band light. The information can be cleared by a "moderate" dose of ionizing radiation (electron bombardment). Writing speed and other quantitative information were not given.

In two papers by A.E. Hughes and his AERE, Harwell, colleagues L.S. Welch, S.C. Jain, and G.P. Pells, studies of defects in CaO were described, with emphasis on the F, F_A, F^+ and $F_A{}^+$ centers in CaO:Mg^{++}. The F-center (two electrons trapped at an $O^=$-vacancy) in pure CaO luminesces with a peak at 600 mμ on excitation with 400 mμ light. The authors report that the same excitation of a similarly prepared CaO:Mg^{++} crystal also produces a new emission band which peaks at about 690 mμ. Polarization, lifetime and other measurements suggest that this longer-wave emission comes from an F_A-center (two electrons trapped at an $O^=$-vacancy which has a Mg^{++}-ion nearest neighbor). Excitation in the F absorption band gives both emissions with a cross-over in intensity at about 60 K, the F-emission predominating below this temperature. The activation energy for the $F \rightarrow F_A$ energy transfer is about 0.05 eV. A preliminary search for the absorption band of the F_A-center suggests that it peaks near 450 mμ.

The F^+- and $F_A{}^+$-centers (one electron trapped on $O^=$-ion vacancy) in CaO are of interest because of their high production efficiency (10^5 eV/F^+ or $F_A{}^+$) and the unexpectedly high ratio of $F_A{}^+/F^+$. Hughes has shown that the latter observation cannot be due to a lowering of the $O^=$ displacement threshold because of the presence of an adjacent Mg^{++}. The high efficiency of production of both $F_A{}^+$ and F^+, and the fact that they can be produced by any kind of ionizing radiation, suggests that they are formed by electron trapping at pre-existing $O^=$-vacancies, a large fraction of which are sited next to Mg^{++} impurities. In pure CaO crystals prepared from the melt, cloudy sections are obtained which Hughes believes to be due to voids formed by vacancy condensation; in the Mg^{++}-doped CaO, he believes that the $O^=$-vacancies become associated with the impurities instead.

Two interesting defects were observed by ESR at room temperature in x-rayed synthetic $CaCO_3$:Li by G. Bacquet and L. Youdir (Univ. Paul Sabatier, Toulouse) and J. Dugas (Univ. Mohammed V, Rabat, Morocco). Both of these involve CO_3^{-3}. In the first defect, which is stable at least up to two months at RT, the CO_3^{-3} is associated with an interstitial Li^+. The symmetry axis of the (CO_3^{-3}-Li^+) center is parallel to the crystallographic <111> axis. In the second defect the CO_3^{-3} is associated with two Li^+ impurity ions located on the <111> axis; one of these is in an interstitial position and the other in a substitutional position, the substitutional Li^+ being much more remote from the CO_3^{-3} than the interstitial Li^+.

Because of its application in radiation dosimetry the thermoluminescence of LiF has been the subject of scores (perhaps even hundreds) of papers dealing with the preparation of "good" TL LiF or attempting to deduce models of the trapping and luminescent centers. It is generally agreed that the best commercial dosimeter-grade LiF contains Mg and Ti (and perhaps Si) as intentional dopants. A paper by R. Nink and H.-J. Kos (Physikal.-Tech. Bundesanstalt, Berlin) described a new way to prepare LiF with better TL properties than one finds in commercially available "dosimeter-grade" material. The dopants used by Nink and Kos are the same, both in kind and concentration, as those found in commercial "TLD" LiF. However, the new preparative method gives LiF with a dosimetrically-useful peak at 190°-200°C, but with little or no low-temperature TL peaks (which are disadvantageous features of the conventional dosimeter-grade LiF) even when the material is slowly cooled from the melt. The preparation method is to make, first, a highly Ti-doped premelted LiF as an intermediate. This is diluted to the optimum Ti concentration by grinding it up with LiF doped only with the other constituents, and then a single crystal is grown by the Czochralksi method in argon. By contrast, one-step growth of a crystal from a LiF charge containing the correct concentration of dopants, without making use of an intermediate high-Ti-concentration premelt, led to TL properties resembling those of the normal commercial "TLD" LiF. Not only are the TL dosimetry properties of the new LiF (called LiF "B") superior to those of conventional "TLD" LiF, but the absorption spectra (both before and after irradiation) are quite different for the two types of material. The authors refrained from speculating on the reasons for the differences in behavior or on models of the centers.

A paper by M.C. Wintergill, P.D. Townsend and F. Cusso-Perez (Univ. Sussex) considered still another impurity in TLD-grade LiF, namely, oxygen. (Vacuum-grown LiF:Mg:Ti has poor Tl, according to these authors.) They tested the hypothesis that the Ti^{+3} or Ti^{+4} built into the crystal is charge-compensated by substitution of F^- by $O^=$. They studied the TL as well as the absorption emission spectra of a wide range of LiF:Mg:Ti samples which were further ion-implanted with oxygen and titanium. They concluded that the enhancement of the TL produced by oxygen implantation in high-Mg and high-Ti LiF, as well as the spectroscopic changes produced, support the proposal of a [$Ti^{+4} \cdot 3O^{-2}$] defect complex.