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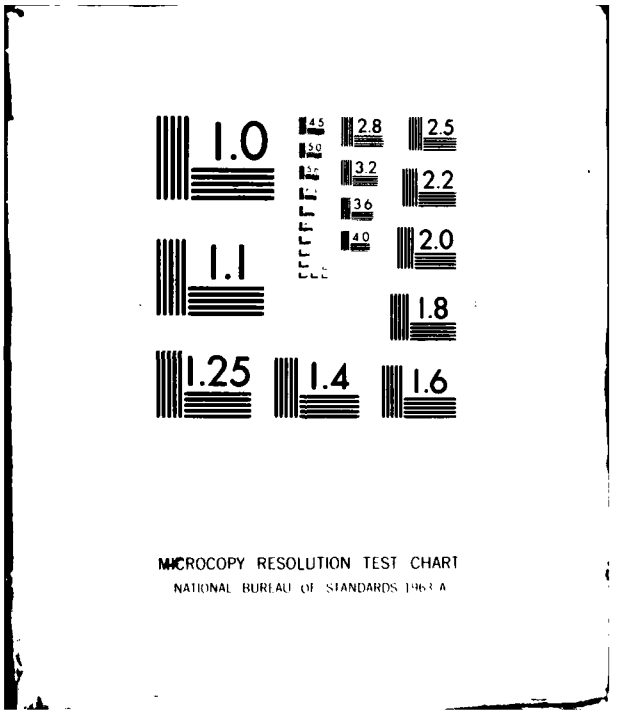
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3rd Europhysical Conference on Lattice Defects in Ionic Crystals

Dr. Lawrence Slifkin*

7 February 1980

*University of North Carolina at Chapel Hill

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The 3rd Europhysical Conference on Lattice Defects in Ionic Crystals took place at Canterbury, England, September 17-21, 1979. The topics covered included ion transport, defect configurations and reactions, dislocations and their interactions with point defects, and color centers. This report summarizes the results and discussions pertinent to all of these papers, except those dealing with color centers.

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3rd Europhysical Conference on Lattice Defects in Ionic Crystals

The 3rd Europhysical Topical Conference on "Lattice Defects in Ionic Crystals" was held from 17-21 September, 1979 on the beautiful campus of the University of Kent, overlooking the Canterbury Cathedral. The series of meetings is sponsored by the European Physical Society, and this conference also received financial support from a number of industrial, governmental, and academic organizations. Approximately half of the 270 participants came from the United Kingdom, West Germany, and France; 40 were from the remaining countries of Western Europe and about 26 were from the USA. There were also some 15 delegates from the other nations of Eastern Europe, but none or virtually none from East Germany and the USSR. In addition about 10 scientists from Latin America and some 20 from India and the Far East were in attendance.

Drs. J.H. Strange and A.V. Chadwick (University of Kent, UK) who organized the meeting did an excellent job of arranging the schedule and the facilities. As was the case in the preceding conference of this series [Berlin, 1976, (ONRL C-37-76)], the material fell rather neatly into two main headings: (1) color centers, including optical and related electronic properties of point defects, and (2) ion transport and dislocations (i.e., the primarily non-electronic phenomena of lattice imperfections). Thus, except for the plenary lectures, there were always two simultaneous sessions. This report deals with the second of these two streams: phenomena related to the atomic structure, migration, and reactions of point defects, and their interactions with dislocations, boundaries, and surfaces. All of the papers, along with some of the discussion, are to be published by the *Journal de Physique*, as one of its "Colloque" series, and should appear during the winter of 1979-80.

Fast Ion Conductors

The opening plenary lecture by W. Hayes (Oxford Univ., UK) dealt with the so-called "superionic" materials, and especially beta-alumina and the fluorites. He pointed out that the calculation of Wang, Gaffari, and Choi, which attributes the high conductivity and low activation energy in beta-alumina to replacement motions by the excess monovalent cation, appears to be well-established experimentally. In particular, one would therefore like to compare the usual non-stoichiometric material with the near-stoichiometric beta-alumina, which has not been heretofore available. Hayes described a method of preparing material with virtually no excess of the monovalent cation, by first exchanging the Na^+ with NH_4^+, heating to drive off NH_3 and H_2O, and then re-exchanging with Na^+. In this new, stoichiometric material, the conductivity is considerably reduced, as predicted. Also, detailed spectroscopic studies allow indentification of the sharp far-IR lines that replace the broad absorptions of the non-stoichiometric alumina; in particular, this work indicates that earlier interpretations of Raman spectra were incorrect. Also, Hayes' results do not corroborate the presence of H_3O^+, suggested previously for some hydrogen-beta-aluminas.

With regard to the fluorites, Hayes described the application of a variety of techniques—Raman scattering, Brillouin scattering, specific heat measurements, neutron scattering, and calculations of point defect energies—to obtain information on the structure and the concentration of Frenkel defects in the high-temperature, superionic phase. Whereas the defect concentration never exceeds about 3% in $SrCl_2$, in PbF_2 this concentration reaches some 40%; the difference can be understood in terms of the greater dielectric screening in the latter compound. The effect of doping with trivalent rare earth was also studied.

Although one might expect that the resulting excess positive charge would suppress the anion vacancy concentration, actually the doping lowers, it does not raise, the superionic transition temperature. This can be understood in terms of the binding of a second interstitial fluoride ion to the solute ion.

W. Schröter and J. Nölting (Göttingen, FRG) described calorimetric measurements on the specific heat anomaly associated with the superionic transition in several fluorites. From the excess specific heat at the beginning of the transition, one can deduce the enthalpy and the entropy of formation of the anion Frenkel defect. Then, from the integrated specific heat anomaly, one can obtain both upper and lower limits to the Frenkel defect concentration in the disordered state. For example, for $SrCl_2$, this yields H_f = 2.67 eV, S_f = 21k, and a concentration of defects above T_c lying between 7 and 12 percent. F. Bénière (Univ. Rennes, France) pointed out in the discussion that these values were consistent with his data on tracer diffusivity and ionic conductivity. (see below). P. Bendall (Oxford Univ., UK) presented results of HADES calculations on point defects in $SrCl_2$, with results that were in fairly quantitative agreement with experimental enthalpies. Calculations on monovalent cation dopant indicate the interesting possibility that the solute can occupy either substitutional or interstitial sites, and hence could be self-compensating at the lower temperatures, if thermodynamic equilibrium could be reached. Molecular dynamics simulation of defect migration in CaF_2 was reported by M. Dixon and M. Gillan (Oxford and Harwell, UK). Their results for high temperatures gave a residence time for the anion vacancy about 15 times the flight time, and yielded jump frequencies somewhat lower than the high-temperature experimental values.

The layered superionic compound Le_3N was the subject of two papers. R. Messer, H. Birli, and K. Differt (Stuttgart, FRG) studied the NMR of both ^7Li and ^{14}N, observing the temperature dependences of quadrupole splitting, line width, and spin-lattice relaxation time. Unlike earlier work, single crystals were used in this experiment. The results are consistent with an ionic model, with extrinsic cation vacancy migration along the basal plane at low temperatures (and sensitive to hydrogen concentration), and additional modes of lithium jumps at higher temperatures. Calculations for intrinsic Li_3N and beta-alumina, using HADES, are being performed by J. Walker and C. R. Catlow (University College, London), but it is not yet clear how close these results will be to experiment.

A. Lundén, (Chalmers Univ., Gothenburg, Sweden) described studies made on mixed sulfates in which the $SO_4^=$ ion rotates above a transition temperature. It is interesting that the heat and volume change of this solid state transition are each much larger than the corre-

sponding quantities for the melting that takes place at still higher temperature. One interesting question is why virtually all cations, whether large or small, whether monovalent or divalent, have such large diffusivities (of the order of 10^{-5} cm^2/s) in the rotator phase. On the basis of a variety of experiments involving ion transport, Brillouin scattering, X-ray and neutron scattering, Lundén proposes a "paddle-wheel" mechanism for cation diffusion: the rotation of the sulfate ion causes fluctuations in the saddle-point energy, and thereby assists translation of the cation. (Presumably, one manifestation of this would be an unusually weak isotope effect for diffusion.) The dynamics of the cation jump in alpha-AGi was studied by K. Funke, A. Höch, and R. Lechner (Göttingen, FRG), by means of quasielastic neutron scattering from a single crystal. To preclude the phase transition (and hence destruction of monocrystallinity) that takes place upon cooling to room temperature, the crystal was carried from Göttingen to Grenoble (the site of the neutron spectrometer) in a special van equipped with a furnace (they literally transported hot goods across the frontier ... I wonder whether there were customs problems). The anistropy observed in the narrow quasi-elastic line confirmed the tetrahop model for the jumps of the Ag^+. A calculation of jump kinetics possibly related to this type of compound was given by A. Lidiart and R. McKee (Harwell and Oak Ridge). These authors were concerned with the effects of interstitial ions interfering with one another, especially when there is a net attraction between them. One finds, for example, a deviation from he Nernst-Einstein equation. No experimental application of such calculations has been pointed out, as of now.

Calculations of Point Defect Parameters

A review of the HADES method for calculating energies of point defect configurations in ionic crystals was presented by C.R. Catlow. This work, largely centered at Harwell and London, has had a great impact in the interpretation of a wide range of experimental results. At the time of the Berlin meeting, several objections were raised that because the model does not include thermal vibrations, the calculated energies are not exactly the same as the experimental enthalpies; this difference is now apparently accepted by the Harwell-London group. As an example of the power of the technique, Catlow showed calculations of point defects and crystallographic "shear planes" in non-stoichiometric oxides, and was able to answer the question as to why some compounds show one type of defect and some the other: to stabilize the planar defect, the lattice must permit a very large (0.3-0.4A) relaxation of the cation. Hence, one understands the correlation between dielectric coefficient and the existence of these shear planes.

An extension of the HADES procedure to defects of various charges in ZnO was reported by W. Mackrodt and co-workers (ICI and Univ. of Manchester, UK). The calculated energies of neutral, singly-, and doubly-charged vacancies and interstitials agree well with those deduced from mass-action analysis of experimental data by Kröger. The calculations indicate that in stoichimetric ZnO, it is the singly charged state of the defects that dominates; that in reduced ZnO, the neutral oxygen vacancy dominates; and that doping with trivalent cation is compensated by both vacancies and interstitials.

A calculation of the volumes of formation of point defects, now refined to include the effective pressure produced by coulombic forces, was outlined by R. Bauer and R. Leutz (Stuttgart, FRG). They conclude that the net relaxation about a Schottky defect in the alkali halides is outward, in agreement with both experiment and the phenomenological model of Varotsos and Alexopoulos, but disagreeing with earlier microscopic calculcations which, apparently, are wrong. This in itself poses an interesting question, since there is no obvious error in the earlier calculcations. Bauer's calculations also predict that there should be a strong inward relaxation about a divalent cation. The temperature-dependence of the formation enthalpies was also investigated and was found to be determined by the dependence of the elastic moduli on temperature, again in qualitative agreement with earlier arguments of Gilder and Lazarus and of Varostsos. In the present work, application of the theory to silver bromide predicts that the increase in the slope of the conductivity Arrhenius plot at high temperatures should be 0.135 eV, in rough agreement with the somewhat larger experimental value found by Friauf.

Another paper on the curvature of the Arrhenius plot, this one phenomenological and thermodynamic, was given by P. Varotsos and K. Alexopoulos (Athens, Greece). They argue that the heat capacity of the defects must be several times larger than that per atom, and that this must give rise to curved Arrhenius plots of conductivity and diffusion, as demonstrated for the silver halides by Friauf and by Batra and Slifkin. They also showed that the defect-formation enthalpy produced by a HADES procedure is less than the experimentally determined enthalpy by the product $Tv\beta B$, where v is the defect-formation volume, β its volume thermal expansivity, and B the reciprocal of its compressibility—each of these factors being considerably larger than the corresponding values per atom for the perfect crystal.

A. Allnatt (Univ. of Western Ontario, Canada) discussed thermodynamic calculations of radial distribution functions for heavily-doped AgCl, at concentrations at which neither the mass-action law now the Debye-Hückel screening theory is accurate. He finds that the concentration of defect pairs is lower, and the concentration of triplets is higher, than obtained from the mass-action law.

R. Friauf (Univ. of Kansas) presented a mean-field theory to deal with the anomalous, excess ionic conductivity in the silver halides at high temperatures. He has been able to get a qualitative fit to experiment for the case of AgCl, but not a very good fit for AgBr, for which the anomaly is larger. The use of 3-body interactions to calculate the individual formation energies of the Frenkel pair components in the silver halides was discussed by F. Granzer and co-workers (Frankfurt, FRG). These calculations predict surface potentials (relative to the deep interior of the crystal) which agree reasonably well with their data from surface potential measurements on AgCl, but again the agreement for AgBr is less satisfying (of course, all of the complications are exaggerated in AgBr).

Analysis of Conductivity and Diffusivity

Diffusivities are most commonly determined from measurements of large-scale mass transport. The special capabilities of magnetic resonance as a microscopic probe of ion motions, however, were reviewed by J. Spaeth (Paderborn, FRG). He emphasized the enormous range of scale of jump times that can be explored by this technique (eleven powers of ten) and the fact that magnetic resonance can see motions that do not give rise to long-range mass transport. He also discussed the use of magnetic resonance methods to deduce defect structures and to study optically excited states of defects.

P. Jacobs (Univ. of Western Ontario, Canada), described a number of applications of the HADES procedure to defect formation and mobilities in various halide materials. With these parameters, he could fit quantitatively the diffusivity of F^- in BaF_2, measured by Figueroa, Strange, and Chadwick; the conductivity data of Friauf's group on silver halides; and a variety of tracer-diffusion results of Batra, taken on the silver halides.

Jacobs and L. Acuña presented detailed new data on the ionic conductivity of KCl: pure, Sr^{2+} -doped, and SO_4^{2-} -doped. They conclude that it is not possible to account for all of the conductivity and tracer diffusion (from Bénière, et al.) data in terms of the usual Schottky defect model. On the other hand, HADES calculcations of the energies of formation and migration of both cation and anion interstitial indicate that these defects must make a non-negligible contribution at high temperatures. Including this additional mechanism, and using the HADES parameters for the interstitials, it is now possible to fit all of the data quite satisfyingly. (An independent corrobation of the existence of some interstitials is provided by the earlier observation of Fuller that the diffusivity of Cl^- in Kl:Sr goes through

a minimum as a function of strontium concentration; the small rise at higher concentrations could be understood in terms of a mass-action enhancement of the concentration of interstitial chloride ions). Among the parameters that emerge from the data fit are the migration energies of the two types of vacancies, and, contrarary to predictions of the Harwell-London group's calculations, these two energies are found to be unequal (the anion vacancy has a migration energy which is 0.16 eV larger than that for the cation vacancy). This suggests that such calculations are probably a bit less accurate than might otherwise appear. Even larger—much larger—values of the anion vacancy migration energy were reported by J. Cook and J. Dryden (CSIRO, Sydney, Australia), who quenched various alkali halides doped with oxide or sulfide. The anion vacancy migration kinetics was measured in two ways: from the decay of the quenched-in excess conductivity, and from the activation energy for conductivity at temperatures so low that the vacancies could not migrate to the solute ions. For NaCl and KCl, the resulting energies are 1.20 - 1.23 eV, in contrast to Acuña's and Jacobs' 0.84 eV and Bénière's value from diffusion of 0.85 eV. Dryden pointed out that his data refer to a low-temperature regime, whereas the other results were obtained at high temperatures. If, however, the explanation rests on this circumstance, then the situation must be very interesting indeed.

Another experiment on time-dependent conductivity, this time with undoped KCl, was described by R. Bennett and W. Fredericks (Oregon State). They find that, after cooling from high temperature, the conductivity at around 475°C decreases with time, requiring more than 10 hours to reach its final value. These results were quantitatively explained in terms of an excess of Schottky defects and the diffusion of vacancy pairs (formed from the excess, quenched-in vacancies) to sinks.

A detailed study of NaI, including ionic conductivity and self-diffusion of both cation and anion, was presented by D. Kostopoulos, K. Reddy and F. Bénière (Athens, Madras, and Lannion, resp.). For temperatures well below the melting points, the Arrhenius law is well obeyed, and the data can be analyzed to give the formation and migration parameters of the Schottky defects. Although the formation energy and the cation migration energy agree rather well with the HADES results of Catlow et al., the experimental value for the anion migration energy is substantially above the theoretical one. An interesting feature emerges from the high-temperature results: for temperatures within about 30° of the melting point, the conductivity and both diffusivities rise anomalously above the Arrhenius extrapolations, all showing an excess of about 50% at the melting point. This behavior can be interpreted in terms of the model of Varotsos and Alexopoulos as due to effects of anharmonicity on the defect-formation-free energy. Chemical interdiffusion of NaCl-KCl in the low temperature range of the miscibility gap was described by L. Bonpunt, N. Chanh, and Y. Haget (Bordeaux-Talence, France). In such a case, one observes a Kirkendall effect similar to

that seen for intermetallic diffusion, but with the complication that in the ionic crystals electric fields may build up, and the steady-state flux of cation vacancies must equal that of the anion vacancies. It was found that the compositions of the border phases are not those of the equilibrium-phase diagram, and that the interdiffusion coefficient versus composition goes through a maximum.

K. Becker (Bochum) showed how one could analyze nuclear-spin relaxation data on doped AgBr to obtain the frequencies with which the cation vacancy exchanges with silver and with the solute. For AgBr:Na^+, the resulting diffusivities agree well with Batra's tracer data. For AgBr:Li^+, the NMR results predict a solute diffusivity much greater than the substitutional component of silver self-diffusion (a somewhat suprising conclusion).

Nevertheless, the Li^+ cannot be diffusing interstitially, since increasing the vacancy concentration by doping with cadmium also increases the jump frequency of the Li^+. A quite different type of experiment was presented by S. Rushbrook Williams and L. Barr (Paisley College, Scotland), who measured the release into vacuum of bromine when crystals of AgBr and $PbBr_2$ are irradiated with ultraviolet. After an initial period during which the release rate is constant (i.e., the accumulation increases linearly with time), the process then goes over into a $t^{\frac{1}{2}}$ regime. The linear regime involves several tens of monolayers, and the authors speculate that the sub-surface ionic space charge may be involved. The $t^{\frac{1}{2}}$ process appears to involve diffusion, perhaps of photoholes to the surface. The temperature-dependence of the rate constant for the $t^{\frac{1}{2}}$ regime is complicated: while the rate constant increases with an activitation energy of 0.16 eV for $PbBr_2$, in the case of AgBr it goes through a maximum near to room temperature. No explanation for what is going on is yet available.

Several papers dealt with divalent and trivalent halides. M. Bénière (Paris VI and Lannion, France) have applied their consistently careful techniques to $SrCl_2$, measuring the ionic conductivity and both self-diffusivities in the intrinsic range below the disordering transition to the superionic state. Comparison of the various results gives a temperature-independent Haven ratio of 0.85 for the anion, suggesting a contribution from some type of interstitial mechanism, in addition to the dominant vacancy mechanism. In contrast to hese results, A. Chadwick, F. Kirkwood, and R. Saghafian (Univ. of Kent) presented conductivity data on $SrCl_2$ variously doped with both mono- and tri-valent solutes which gave an energy of formation of the anion Frenkel defect which is about 0.7 to 1.0 eV lower than deduced by Bénière, et al. and by Schröter and Nölting (see previous discussion), although agreeing with the prior HADES calculation of Catlow, et al. This work also agrees with theory on the value

of the migration energy of the anion vacancy, but gives a much higher value for the interstitial migration energy. K. Wapenaar (Utrecht) interpreted his measure-of-conductivity of alkaline earth fluorides heavily doped (many percent) with U^{4+} in terms of the extensive formation of defect clusters. Lithium-doped MgF_2 which has the anisotropic rutile structure, is being studied by J. Toulouse and A. Nowick (Columbia Univ.). They have employed a wide variety of techniques—conductivity, diffusion, and internal friction—to demonstrate that, at least at the lower temperatures, the Li^+ forms a dumbbell defect: two Li^+ ions per cation site, as predicted from HADES calculations by James and Catlow. At higher temperatures, this defect dissociates into a substitutional and an interstitial Li^+; hence the solute is self-compensating. The Columbia workers have been able to determine the various formation-, association-, and migration-activation energies involved. Electrical studies of PbI_2, doped with either mono- or tri-valent solutes, were analyzed by T. Hagihara et al. (Osaka Univ., Japan) to obtain activation energies for the various types of jump of both anion and cation vacancy. G. Jaroszkiewicz and J. Strange (Univ. of Kent) presented NMR data on ion motion in the layered compound LaF_3, and showed how one could reconcile the relatively complicated NMR results with the much simpler behavior exhibited by the conductivity, in terms of the anistropic motions of the fluorides. An NMR study of the antifluorites formed by the oxides and sulfides of the alkali metals, by M. Mousa, Y. Oei, and H. Richtering (Bochum), gave data on cation jumps which have thus far not been reconciled with the small amount of conductivity data which does exist; the details of the diffusion mechanisms are thus not yet sorted out.

Turning now to diffusion and ionic conductivity in oxides, studies of the diffusion of oxide ion in Cu_2O were reported by F. Perinet, S. S. Barbezat, and C. Monty (CNRS, Bellevue, France). In this non-stoichiometric material, the dominant defect is the cation vacancy, and oxygen is the slow component. The work discussed here used a SIMS analysis for ^{18}O, at various temperatures and partial pressures of external oxygen gas, and demonstrated that the anion migrates as the singly charged interstitial. In cobalt-deficient CoO, tracer diffusion measurements of cation self-diffusion as a function of oxygen partial pressure, by N. Peterson and W. Chen (Argonne), indicate that the dominant mechanism is via a singly charged cation vacancy at high $P(O_2)$ and via a doubly charged vacancy at low pressures. Other possible interpretations were eliminated by the demonstration that the isotope effect (found to equal 0.56) is independent of $P(O_2)$.

Tracer experiments on Ni-diffusion in pure and Al-doped NiO, discussed by A. Atkinson and A. Hammou (Harwell & Grenoble), gave dependences on T and $P(O_2)$ for the doped specimens which could not be understood in terms of a simple defect model, and which indicated a large effect of solute-vacancy association and precipitation. Anion self-diffusion in NiO,

again using SIMS detection of ^{18}O, was reported by M. Meyer et al. (CNRS, Bellevue); the results were consistent with earlier isotope exchange data, showing that there was no significant artefact introduced by the ion implantation techniques employed in the present experiment. This conclusion is important, because ion implantation methods in diffusion studies could be quite useful in a variety of systems.

D. Norris (Berkeley Nuclear Labs.) discussed the relation between the thermomigration behavior of oxide ion and the defect structure in such non-stoichiometric materials as the mixed uranium-plutonium oxides. B. Cales and P. Abelard (Orléans, France) described complex impedance measurements on yttira-stabilized ZrO_2 and on forsterite, which they interpret in terms of the Honscher phenomeno-logical model, in which the complex dielectric permittivity is represented by a power law in the frequency. For both oxides, a critical frequency was found, at which the exponent changes abruptly. A discussion of the motion of cations in dehydrated zeolites was presented by R. Schoonheydt (Heverlee, Belgium).

Impurity-Vacancy Complexes in Halides

The effect of addition of F^- on solute-vacancy complexes in NaCl:Pb was described by D. Pinatti and M. deSouza (Univ. de São Paulo, Brazil), using both ionic thermocurrents (ITC) and UV spectroscopy. The association of fluoride with lead produces three new ITC peaks in the quenched material. From the annealing behavior of the ITC and the UV peaks, the authors suggest that some fluoride ions actually occupy the same site as the associated Pb. In $SrCl_2$ doped with alkalies, M. Jacquet and M. Bathier (Univ. de Clermont) found that the activation energy for the ITC peak or the dielectric loss decreases with increasing size of the dopant, from 0.35 eV for Na^+ to 0.26 eV for Rb^+. A similar, but more extensive, experiment on rare-earth doped BaF_2 was reported by E. Laredo, D. Figueroa, M. Puma (Univ. Simon Bolivar, Caracas, Venezuela). After correcting the slightly broadened ITC peaks for a gaussian distribution of activation energies (due to dipole-dipole interactions), their plot of activation energy for reorientation of the complex versus radius of the trivalent rare earth showed a smooth curve, with a pronounced maximum at samarium (which, perhaps not coincidentally, has about the same radius as does the host cation). These authors also showed that plastic deformation could produce an additional, very large ITC peak. The broadening of ITC peaks because of dipole-dipole interactions was studied in more detail, in rare-earth-doped CaF_2 and SrF_2 by H. den Hartog (Univ. Groningen, the Netherlands). As the concentration of dopant is increased above about 0.01%, the ITC peaks broaden, with the second-nearest-neighbor peak broadening more than that due to the nearest-neighbor dipole; there is also an increase in the ratio of the concentrations of the former to the latter. Similar effects

are also seen in the EPR spectra. The interactions between the dipoles appear to involve elastic as well as coulombic forces.

Aggregation and Precipitation of Solute-Vacancy Complexes

J. Wright (Univ. of Wisconsin) presented some very informative results on laser spectroscopy of $CaF_2:Er^{3+}$, in which one could selectively excite a nearest- or next-nearest-neighbor complex, or various aggregates, such as dimers and trimers of different configurations. The concentration of a given defect complex is then monitored by the luminescence which its excitation elicits. He could explain the puzzling experimental phenomenon that the concentration of cubic Er^{3+} centers becomes anomalously high at high concentrations of dopant; this comes about because dimers tend to pick up an extra interstitial F^-, thereby converting dipolar complexes into free solute ion (this is thus very similar to a suggestion put forth earlier by Crawford). Wright's conclusions were verified by J. Fontanella et al. (US Naval Acad. and Case Western Reserve Univ.), who performed dielectric relaxation experiments on CaF_2 double-doped with two different rare earths. They were able to identify one of the peaks as arising from the dimer, and their results agreed well with those from the laser-stimulated luminescence. They also have done experiments under hydrostatic pressure, and find evidence that the compressibility of the defect is about ten times that of the bulk material.

Two theoretical papers dealing with aggregation were given at Canterbury. J. Corish and J. Quigley (Dublin, Ireland) used the HADES program to evaluate the binding of dimers, trimers, etc. in alkali halides doped with divalent cation. They find that large-solute radius favors the nearest-neighbor dimer, while small-solute radius favors the next-nearest-neighbor dimer. Also, their value of the binding energy of the trimer suggests that this is the route taken during aggregation to the Suzuki phase. In a different type of approach, E. Lilley (Univ. of Sussex, Brighton, UK) carried out a computer simulation of aggregation kinetics, and concluded that the dominant process leading to the decay plateau is the third-order formation of trimers. He showed that when the initial supersaturation of complexes is not too high, the data can be fit to an Unger-Perlman 2nd-order plot, even when the main product is the trimer. This calculation is similiar to one recently done by G. Dines.

The morphology of Suzuki-phase particles in doped NaCl was observed by A. Guerrero, E. Butler, and P. Pratt (Imperial College of Science and Technology, London), using transmission electron microscopy. With Mg-doping, where the lattice misfit is large, they see the elastic strain and the "debris" which surrounds the particles, but with Cd-doping, where the misfit is small, there are not misfit dislocations. In the systems studied by the Imperial College group, the second-phase particles looked to be square, in projection. In contrast to this, P. Bertoldi, R. Capelletti, F. Fermi, and V. Graveris (Parma, Italy) analyzed the

time-dependence of photoluminescence and optical absorption due to Suzuki-like phase in Kcl:Pb, and found the kinetics to correspond to the growth of rods. This conclusion was corroborated by thermal conductivity studies of the same system by M. Locatelli, E. Zecchi, and R. Capelletti (CEN-Grenoble, and Parma). TEM studies of precipitates in NaCl:Sr, by I. Bhagavan Raju, H. Strecker, and H. Strunk (Stuttgart, FRG) revealed both platelets and rods that are not Suzuki phase; in NaCl:Cd, however, they see Suzuki-phase particles that, in projection, are square. An X-ray study of the perfection of various natural and synthetic alkali halide crystals, by Z. Morlin et al. (Lab. for Cryst. Phys., Budapest, Hungary) revealed the presence of many weak reflections that could be related to various types of solute aggregate, such as Ca-O-Ca. Morlin stated that his survey indicates that the very best NaCl crystals are natural ones from a particular salt mine in Poland.

Y.Chen, M. Abraham, J. Boldu, and V. Orera (Oak Ridge) summarized their work on "microgalaxies" of $(Li)^\circ$ centers that can be thermally formed in lithium-doped MgO crystals. The $(Li)^\circ$ center acts as an electron acceptor, but cannot completely ionize within a microgalaxy because of the large potential difference that would be built up if all of the holes were lost. Dielectric loss experiments on this system, done by J. Crawford and D. Eisenberg (Univ. of N. Carolina), give such an intense peak that the authors propose that the microgalaxies must be greatly elongated, presumably along dislocations. The observed activation energy, 0.6 - 0.7 eV, is consistent with the ionization energy of the $(Li)^\circ$ center. They also reported measurements of the effects of annealing, which indicate that the oxygen intake during formation of the centers must take place via dislocations.

Two papers were concerned with formation of metallic colloids. This topic has been extensively studied in alkali halides, as a final product of annealing additively colored crystals, but the papers at Canterbury dealt with other types of processes. M. Treilleux and G. Chassagne (Lyon, France) implanted alkali metals into crystals of MgO, annealed, and then observed colloids via transmission electron microscopy. With implanted Li, the particles are fcc if smaller than 200 A, and bcc if larger. The Li particles are easily nucleated, and are coherent with the MgO matrix. With implanted Na, nucleation is also easy, and there is a partial coherence. With K, however, nucleation is more difficult, the particles are incoherent, and they have a broad distribution of sizes. Implantation of Na in NaCl and Ca in CaF_2 was studied by V. Orera and F. Modine (Zaragoza and Oak Ridge), with the goal of learning something about the electronic properties of the small particles by means of magnetic circular dichroism. For Na, the results were consistent with an effective mass equal to that of the bulk metal, but for Ca, the fitting of the data required a very large mass ($m^*/m_e = 2.4$), which was attributed to the effect of a large hydrostatic pressure exerted by the matrix.

Dislocations and Plasticity

In a review lecture, J. Castaing (Bellevue, France) surveyed the particularly new effects that arise in ionic crystals, in contrast to the case of metals. For example, in addition to elastic terms, the energy of the dislocation and its interaction with other defects must include coulombic and polarization terms. Also, in cases such as Al_2O_3, the Burgers vector is very large, causing the energy-per-unit length to be large also, and producing brittleness at low temperatures. Castaing showed that, in addition to the more common conservative dissociation along the glide plane, one could also observe climb dissociation perpendicular to the glide plane. Several of the following talks gave examples of these two types of dissociation; in Y_2O_3 (R. Gaboriaud and M. Boisson, Poitiers); and in spinel (R. Duclos, N. Doukhan, and B. Escaig, Univ. Lielle; and P. Veyssiere, S. Kirby, and J. Rabier, Univ. Poitiers and US Geol. Survey). In Y_2O_3 crystals, there are two regimes of deformation: at low temperatures and high stress, Gaboriaud and Boisson find anisotropic deformation, easy glide and dislocation dissociation within the glide plane; at high temperature and low stress, a different set of dislocations, dissociated out of the glide plane, is active. Duclos et al. worked with nearly stoichiometric spinel, and studied the effect of varying the tensile axis, using stress-strain experiments (there is a yield stress with a [110] axis, but not with [100]), creep (at a constant strain rate with [100] but an accelerating rate with [110]), and TEM (one sees loops after [110] compression and climb dissociation after [100]). The experiments on spinel by Beyssiere et al. emphasized the low-temperature regime. For a particular orientation of the specimen, the flow stress does not decrease monotonically with increasing temperature, but shows three regions: at lowest temperatures, the dislocations are not dissociated and the flow stress decreased with increasing T; at somewhat higher T, the flow stress begins to rise as climb dissociation becomes more extensive; at higher T, the dislocations are now in equilibrium, and the flow stress begins to fall once again.

Optical birefringence microscopy of YAG crystals, showing the effect of long-range strain fields of both dislocations and inclusions, was reported by S.Y. Shu, Z.-Z. Ke, and D. Fong (Nanking, China). The dependence on composition of the critical-resolved-shear stress in mixed Kcl-KBr single crystals was discussed by T. Kataoka and T. Yamada (Osaka, Japan). They find that at very low temperatures (approaching liquid helium temperature), addition of either KBr to KCl or vice versa, produces solution softening for the first few percent of colute, and then the usual hardening at higher compositions, with the stress going as $c(1 - c)$. These results could be understood in terms of the assistance of solute ions in overcoming the Peierls barrier at low temperatures and low-solute concentrations; at higher values of T or c, the flow is not Peierls limited, and solute interactions become a barrier.

M. Puls and C. So (Whiteshell Nuclear Res. Est., Pinawa, Man. Canada) presented some calculations of the interactions of dislocations and complexes of point defects, such as the Fe^{3+}-vacancy-Fe^{3+} in MgO. There is both an elastic interaction and also a repulsive force if the dislocation tries to shear the complex. The difficulty with this sort of work is that the results are very sensitive to the choice of interionic potential, so it is not surprising that the theoretical values do not agree with experimental ones. A very interesting application of NMR to the dislocation-point defect problem was outlined by W. Alsem and co-workers (Groningen and Dortmund, FRG). They observe the effect of compression of NaCl on the spin-lattice relaxation time. From the dependence of T_1 on strain rate, they conclude that the average spacing between obstacles encountered by the moving dislocation is 0.6 microns—apparently forest dislocation in high-purity NaCl—and the average v velocity is about 2 cm/s. In NaCl:Ca, the distance between obstacles decreases with increasing solute concentration, and increases with increasing temperature. Upon removal of the stress, T_1 immediately recovers, demostrating that the effects observed are not due to excess point defects generated by the deformation.

M. Matrai et al. (Res. Lab. for Cryst. Phys., Budapest) gave an analysis of the effects of dislocations on the optical absorption of F-centers in various alkali halides. The effect of dislocations on cathodoluminescence of MgO, subjected to various oxidation and reduction anneals, was reported by S. Datta, I. Boswarva, and D. Holt (Imperial College, London). They used a scanning electron microscope, and found some emissions which are localized at slip bands (thus extending earlier work of T. Turner). From the effects of various types of anneal, they conclude that a strong, blue deformation-induced band is probably due to an aggregate of ferric ion with one or more vacancies.

Boundaries

Three papers dealt with grain boundaries and surfaces. D. Wolf (Argonne) has made calculations on the stability of coincidence twist boundaries in cubic materials such as NiO. He finds that coulombic interactions dominate, and there is a great amount of ion relaxation. None of the possible coincidence boundaries are stable, according to these results; the fact that Valluffi has experimentally prepared such boundaries suggests that there must be some difference between the two. A variety of experiments on diffusion along the grain boundary of a KBr or NaCl bicrystal was discussed by L. Harris (Univ. of New South Wales). Contrary to earlier reports, the cation migration along the boundary is very much greater than for the anion. Harris provided much evidence that the grain-boundary effect is due mainly to the presence there of precipitates of residual impurities, and is not sensitive to the physical structure of the boundary itself. Calculations of the energies of (110) and (111) surfaces of various fluorite-type crystals, reported by P. Tasker (Harwell, UK) were found to agree reasonably well with experimental cleavage energies. Tasker also described the inward relaxations, and the resulting rumpling, that takes place at the surface.

Charged Dislocations and Surfaces

R. Whitworth and V. Petrenko (Univ. of Birmingham, UK and Acad. Sci., Chernogolovka) presented experimental results and analyses of the fascinating effects of ionic and electronic charge, and of illumination, on the plastic properties of the II-IV compounds. These materials are less ionic than are the alkali halides, are semiconductors, and can shear on several different types of planes (called the "glide plane" and the "shuffle plane", and with choice of cation or anion layer on top). One can distinguish between the various possibilities by measurement of the sign of charge flow during shear, the effects of doping to make the material n- or p- type, and the effects of band-gap illumination (which can double the magnitude of the charge density along the dislocation). The charge densities are so large (tenths of an electronic charge per atom length) that the dislocations cannot be in thermal equilibrium and must sweep up electronic charge during their motion. An effect of ionic charge on the surface of crystals of AgCl was reported by L. Slifkin et al. (Univ. of N. Carolina). With doped crystals, a very weak solvent distinguishes between the relatively rapid dissolution of the compensating space-charge region (several 100's of A) and the remaining bulk; the space-charge region can be reformed upon aging long enough to allow for solute diffusion. Another effect of surface charge was found by M. Yacaman and J. Hirth (Univ. Nat. Auton. of Mexico, and Ohio State Univ. USA), who studied the morphology of sublimation spirals (the inverse of growth spirals) on alkali halides, using the gold-decoration technique. Application of a longitudial electric field during sublimation converts square spirals into rhombic ones, increases the step heights, and nucleates vacancy clusters; all of this could be interpreted in terms of the effect of the field on the charged kinks. A. Kessler (Stuttgart, FRG) considered the effects of space-charge and electrode material on charge transport in CdF_2. It is possible to get electron injection, with the formation of small particles of Cd inside the crystal; one then finds that even with blocking electrodes, a steady current can be drawn. Also, these particles give rise to a second thermally-stimulated-depolarization peak, in addition to the usual space-charge peak. Finally, M. Georgiev et al. (Sophia, Bulgaria) showed that the Poisson-Boltzman equation has periodic solutions, for the case of minimum free energy. This allows for the possible existence of large-scale (on the order of 100's of A, the Debye length) superlattices, in which the net charge density is periodic. Georgiev did not specify the physical conditions which might favor such a structure, but did relate his solutions to the well-known Suzuki phase precipitates (although, here the periodicity length is only a few A); he thinks, nevertheless, that such structures may well be more general in doped ionic crystals.