Dipolar Complexes in KCl Resulting from 1.5-MeV-Electron Bombardment*

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The dielectric relaxation behavior of KCl crystals after exposure to 1.5-MeV electrons has been studied by means of the ionic-thermocurrent (ITC) method. At least four ITC relaxation peaks at 125, 145, 160, and 195 K are observed over the range from 80 to 200 K after irradiation at 260 K. The temperature of irradiation is found to have a strong influence on both the form of the ITC spectrum and the total amount of polarization. The production of dipolar defects, assumed to be responsible for the relaxation, is highest for irradiations in the range 200–260 K and it is rather small for exposures at 150 and 300 K. Once produced, the dipolar defects are relatively stable but they can be nearly completely removed by a 400-K anneal. The effect seems to be intrinsic in nature since the total polarization builds up linearly with exposure after the F center has substantially saturated and since it is essentially the same for high-purity crystals from several ingots. Assuming that unit dipoles are responsible for the ITC spectrum, the initial rate of formation is 0.05 times the initial rate of F-center production. Since it is difficult to conceive that such a variety of stable dipoles can be constructed from anion Frenkel defects, it is concluded that defects on the cation sublattice also result from the irradiation. It is shown that the yield of dipoles is at least an order of magnitude higher than can be expected to result from direct displacements induced by electron-ion collisions. The same types of defects may be precursors for the crystallographic voids and dislocation loops observed by electron microscopy in heavily irradiated alkali halides.

INTRODUCTION

Lattice defects produced by ionizing radiation in alkali halides are known to have important effects on a wide variety of their physical properties and a vast literature on the optical and paramagnetic behavior of irradiated crystals has accumulated.[1-3] In this paper we shall describe studies of a qualitatively different property affected by irradiation, namely, dielectric polarization.

Some time ago in their study of the relaxation of dc polarization in NaCl, Sutter and Nowick[4] observed that x irradiation at room temperature introduced a substantial time-dependent polarization current while at the same time suppressing the steady-state dc conductivity. The polarization current was not substantially altered either in magnitude or time dependence by prolonged optical bleaching in the F band, whereas it could be largely removed by annealing at 119 °C. Subsequently, Krasnopevtsev[5] investigated dielectric loss of electron- (0.5–1 MeV) bombarded KBr and observed two peaks in the loss-tangent (tanδ) vs reciprocal-temperature plot. The lower-temperature peak was found to shift to higher temperature with increasing frequency and otherwise behaved like a Debye-type dipolar relaxation. The high-temperature peak, whose position is independent of frequency, is evidently associated with the annealing of the contribution of the enhanced conductivity to the dielectric loss, since electron bombardment is observed to increase this property and it is observed to recover toward its preirradiation value at the temperature of the peak. Additional studies of dielectric loss in NaCl, KBr, and KI exposed to x rays or energetic protons by Annenkov,[6] generally substantiate the results of Sutter and Nowick.

The results just cited suggest that ionizing radiation is capable of creating in alkali halides dipolar imperfections which can be polarized by an applied electric field. Moreover, since the dc relaxation behavior observed by Sutter and Nowick does not correspond to a single relaxation time, it is apparently controlled by a series of overlapping exponential processes. The annealing behavior and the fact[6] that no polarizable component is introduced in NaCl if the irradiation is carried out above 110 °C indicate that the defects responsible for the polarization are altered or destroyed by annealing in this temperature range. Finally, it is noted that the polarization current seems to be completely independent of radiation-produced changes in ionic conductivity since the latter appears to recover at a different annealing temperature.

In this paper we describe an investigation of dielectric polarization and its relaxation in KCl exposed to 1.5-MeV electrons. Polarization relaxation was measured by means of the ionic-thermocurrent (ITC) technique, a technique first developed and exploited by Bucci and co-workers.[7] In essence, the ITC method measures the displacement current I_d as a function of temperature as the frozen-in polarization of a system of dipoles, previously polarized at a higher temperature and cooled under an applied field, relaxes during warming at a linear rate. The process is analo-

gous to a thermoluminescent glow curve I_d corresponding to the luminescent intensity. Since in most cases interaction between dipoles can be neglected, the kinetics is exactly first order. The shape and position of the peak in the I_d-vs-T curve yields the activation energy and frequency factor for reorientation of the dipole, and the total area under the curve gives the magnitude of the polarization at the temperature of the application of the electric field. In addition to the much greater sensitivity of this method compared to the ac dielectric-loss method, an important advantage is its ability to resolve relaxation processes arising from sets of dipoles with only slightly differing reorientation energies. In view of Sutter's and Nowick's observation[4] that the radiation-induced polarization is characteristic of overlapping processes, this advantage could prove beneficial. To aid in correlating radiation-induced changes in polarization behavior with another extensively studied index of radiolysis, measurements of optical-absorption spectra were made on the same specimens during the course of the experiments.

At the outset it was anticipated that the polarization effect would be of secondary importance relative to F-center production. This was found to be true since the initial F-center-production rate was 18 times as great as that for dipoles for any reasonable dipole model. However, whereas the yield of F centers tends to saturate at high doses, the polarization does not. Hence this property may be an even better index of the degree of radiolysis in alkali halides than the F-band amplitude for large exposures. Our results suggest that a substantial yield of defects is produced on the cation sublattice in addition to the familiar anion-sublattice disorder. The excitonic defect-creation mechanism,[8] thought to produce anion Frenkel pairs, does not seem capable of producing cation-sublattice damage directly. The latter may result from some other direct ionization processes, yet unknown, or it may be a product of the final stabilization process for the anion damage products. Direct production of cation Frenkel pairs seems quite unlikely.

EXPERIMENTAL

The ITC and optical-absorption measurements were carried out in a Dewar, specially designed for high-impedance measurements, whose tail piece was provided with two pairs of windows set on mutually perpendicular axes. The electrode and specimen arrangement is shown schematically in Fig. 1. One set of windows was fitted with Corning No. 7943 (nondarkening) fused silica to permit measurement of optical-absorption spectra in the range 190–800 nm. These windows were shuttered to prevent optical bleaching of color

centers by room light subsequent to irradiation. The shutters could be opened by a lever after the Dewar was situated in the Cary 14R spectrophotometer. The second set of windows was fitted with 0.25-mm-thick aluminum to admit the 1.5-MeV-electron beam from the Van de Graaff accelerator. The tail piece was rotatable through 90° so that the broad face of the KCl specimen could be exposed to either set of windows. Transparent platinum electrodes were sputtered onto the broad faces of the specimen to facilitate both optical and ITC measurements *in situ*. A heater coil in the specimen chamber was used to control the specimen temperature over the range 10–500 °K. Linear-heating rates were imposed with the aid of a Trend-Trac programmer and the displacement currents were measured with a Cary model 31 vibrating-reed electrometer. A copper-constantan thermocouple was employed to measure specimen temperature. The I_d-vs-T curves were plotted directly by means of a Hewlett–Packard X-Y recorder.

The irradiations were performed using a 2-MeV High Voltage Engineering Corp. Van de Graaff accelerator. The electron energy was nominally 1.5 MeV. Beam currents were kept low to avoid heating the specimens. A typical beam intensity was 2 $\mu A/cm^2$.

The KCl crystals used in these studies were cleaved from an ingot of high-purity KCl provided by Butler of the Oak Ridge National Laboratory. The important impurities as determined by chemical analysis of crystal ingots grown by this same method have been reported elsewhere.[9]

EXPERIMENTAL RESULTS

It is important in ITC measurements to ensure that the motion of free charges ("charge-release peaks") does not obscure the peaks associated with the motion of bound charges ("dipole peaks"). Charge release can yield large currents which are not usually reproducible. In unirradiated crystals charge release is due to ionic motion and one is constrained to work on dipolar systems whose reorientation is clearly separable from the migration of intrinsic defects, e.g., cation vacancies. Such a separation holds for most alkali halides below 250 K. This is fortunate since M^{2+}-cation-vacancy dipoles in NaCl and KCl relax below 230 K. In making ITC measurements on irradiated crystals it is necessary to eliminate electronic currents which arise from the release of electrons and holes from traps during warming. In those cases where the irradiation temperature is below the maximum temperature of interest in the ITC run (~ 200 K), interfering carriers can be eliminated by warming the crystal 50 K above the maximum temperature of the ITC run prior to polariza-
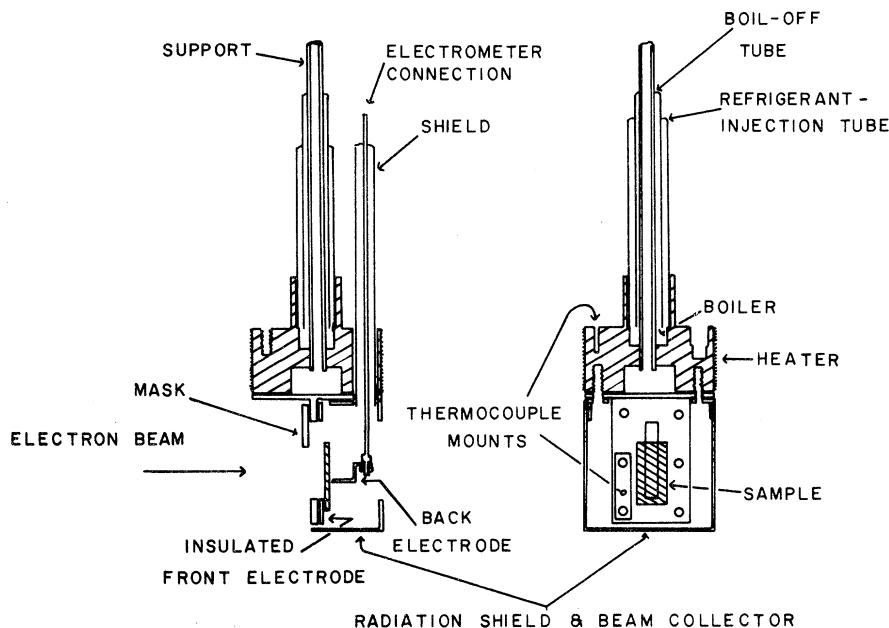
FIG. 1. Schematic description of the electrode and specimen arrangement in the ITC high-impedence cell.

tion. In a typical run after polarization by application of 500 V at 220 K, the crystal was cooled to 80 K with the field applied to freeze in the dipole alignment. Upon removal of the field and warming at a rate of 12 K min^{-1}, only the dipole peaks should be observed.

To test the efficacy of this means of eliminating electronic current, several successive ITC runs were made upon a specimen after a single irradiation at 250 K and it was found that the I-vs-T curves were reproducible within experimental error. Since a single run will exhaust the concentration of carriers in traps which empty in the temperature range of the run, this reproducibility is reasonable assurance that electronic currents are not present. How they may contribute is readily seen in the following experiment. After irradiation at 250 K, the crystal was cooled to 80 K, a field was applied, and the charge distribution of the specimen was deliberately altered by exciting with F-band light. Subsequent warming gives the I-vs-T curve represented by the dashed line in Fig. 2, which is compared to the curve obtained without F-band excitation (open circles). Clearly F-band excitation induces a profound change. The peak at 125 K appears to be almost entirely due to the escape of electrons from a shallow trap. There is evidence of another trap which discharges above 190 K and which may well be due to thermal bleaching of F$^-$ centers.[3] Moreover, the 160-K ITC peak seems to be almost completely suppressed, which is not surprising since polarization at 80 K is not expected to introduce dipole alignment in this peak because the activation en-

ergy is too high.

From Fig. 2 (open circles) three ITC peaks at 193, 160, and 125 K are evident. In addition, there is a peak at 145 K which is not resolved but which appears as a prominent shoulder on the 160-K peak. From other experiments, small peaks have been observed at temperatures above 193 K. However, since this and the 125-K peak are somewhat variable in position and prominence, we shall confine our attention mainly to the 145-, 160-, and 193-K peaks. Each of these appear to be much broader than the simple Debye-type relaxation peaks owing to noninteracting dipoles with a discrete reorientation energy. The temperature of irradiation T_I was found to have an important bearing upon both the number and position of the peaks. Figure 3, in which I_d is plotted against temperature for various irradiation temperatures, shows how the peak spectrum shifts and develops with increasing T_I. For each run the same irradiation dose and polarization temperature T_p were used. Irradiation at 150 K produces at least four peaks, but with the exception of a peak at ~200 K the yield is small and the peaks are poorly defined compared to those produced by irradiation at a higher temperature. The highest yields are obtained for T_I in the range 260 K, whereas for $T_I \gtrsim 300$ K there is a distinct reduction in the overall magnitude of I_d.

To demonstrate that the effect is intrinsic rather than sensitive to accidental trace impurity, measurements were made upon three different high-purity ingots which were grown as much as 18 months apart. Figure 4, which was obtained with
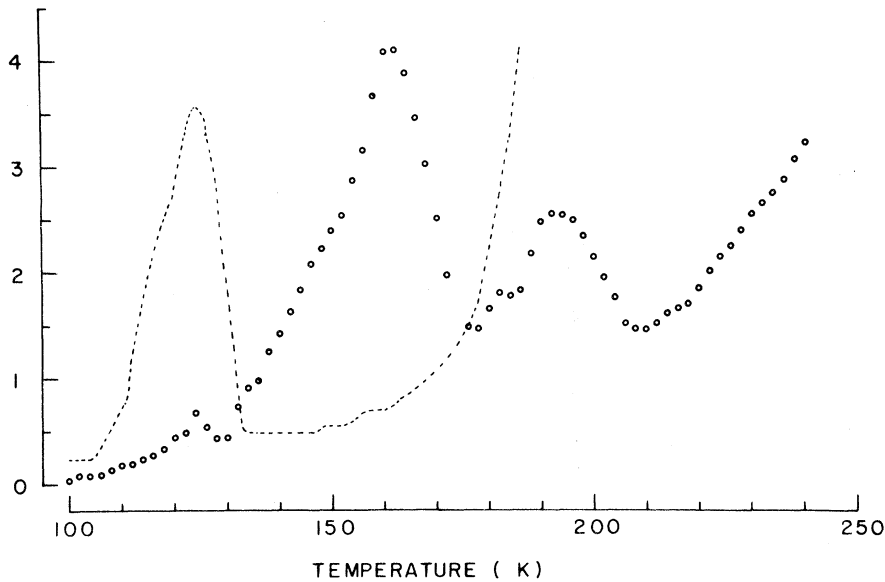
ITC SPECTRUM OF IRRADIATED PURE KCl

FIG. 2. Thermal depolari-
zation of a KCl crystal after
1.5-MeV-electron irradiation
at 250 K and polarization at
220 K. Open circles repre-
sent the normal ITC curve.
Dashed curve was obtained
after polarization and subse-
quent F-band excitation at 80
K.

$T_I = 250$ K and a dose of 1.2×10^{16} electrons/cm^2,
shows that with the possible exception of the
peak(s) near 200 K the behavior is almost identical
for each. Therefore, it is safe to conclude that
the peaks centered at 160, 145, and 120 K are quite
likely intrinsic in nature.

In order to gain an insight into the nature of the
production mechanism, the yield of dipoles re-
sponsible for each peak as a function of irradia-
tion was explored. Successive runs on the same
specimen after the indicated exposures at $T_I = 250$
K are shown in Fig. 5. The peaks at 125, 145,
~160, and 193 K all grow with irradiation. Other,
less well-resolved structure is also present. How-
ever, the dominant effect of increasing exposure is
the development of the peak at ~160 K and its

shoulder at 145 K. These increase at a greater
than linear rate with dose

$$I_d \propto \Phi^{1.4} ,$$

where Φ is the electron fluence. In contrast, the
193-K peak grows linearly with exposure. The
160-K peak shifts to higher temperatures with in-
creasing exposure as indicated.

A final set of experiments focused upon the an-
nealing behavior of the induced polarization. The
effect of annealing at 350 and 375 K is shown in
Fig. 6. The main peak structure is diminished,
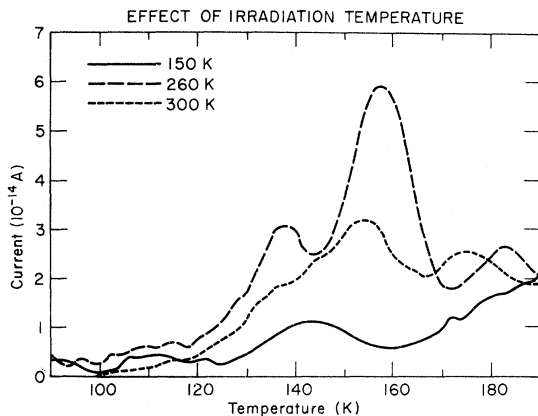whereas the polarization processes evident below

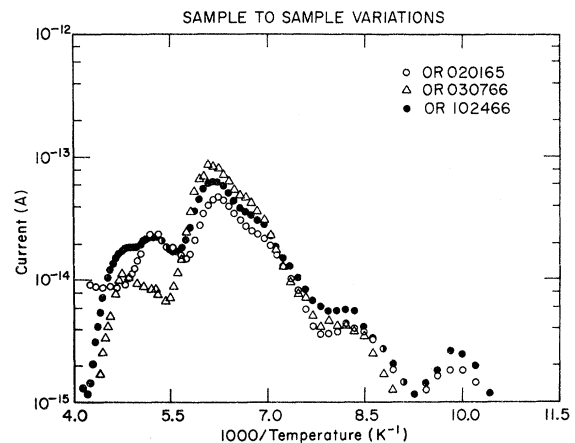FIG. 3. ITC curves for different irradiation temperatures.

FIG. 4. ITC curves for KCl specimens from three
different ingots grown as much as 18 months apart. Ex-
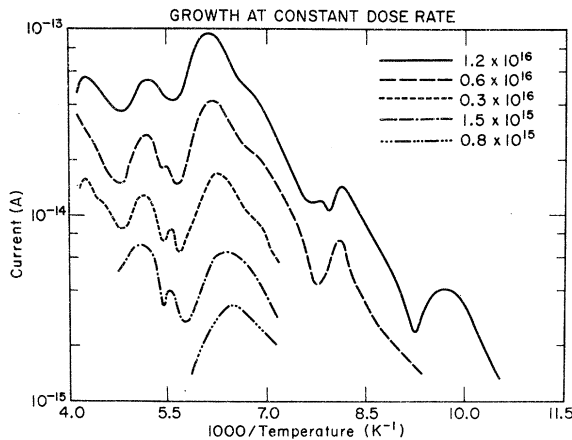posure, 1.2×10^{16} 1.5-MeV-electrons/cm^2.

GROWTH AT CONSTANT DOSE RATE

FIG. 5. ITC curves obtained after successive irradiations at 250 K.

FIG. 7. Yield of unit dipoles as a function of exposure to 1.5-MeV electrons. Plotted for comparison is the concentration of F centers produced by the irradiation measured on the same specimen.

120 K are first enhanced and then diminish. Annealing at 400 K almost completely removes the radiation-induced polarization.

DISCUSSION

Before attempting to propose structures to account for the ITC spectrum, it is necessary to make a reasonable estimate of the number of dipolar defects relative to a defect whose production rate has been thoroughly studied, namely, the F center. To make this comparison, the total polarization resulting from each exposure of Fig. 5 was obtained by integrating under the I_d-vs-T curve and multiplying this total area by the reciprocal of the heating rate to convert the area to coulombs. For a system of discrete dipoles, the total polarization charge is related to the dipole concentrations by the expression
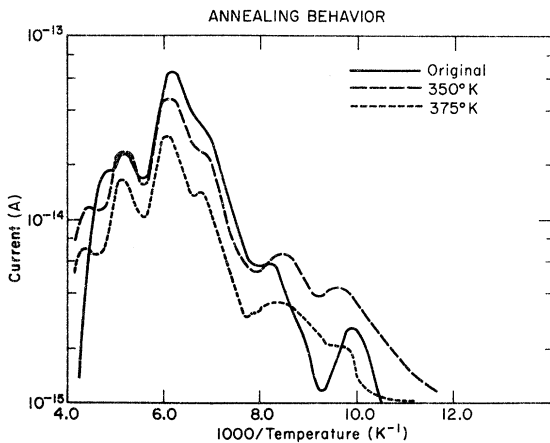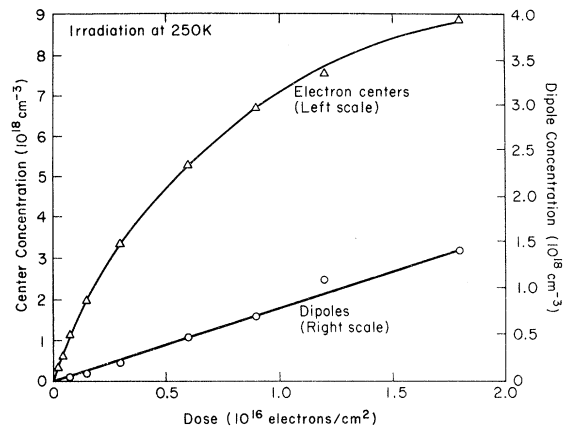
ANNEALING BEHAVIOR

FIG. 6. Effect of annealing above room temperature on the ITC spectrum of a KCl crystal irradiated at 250 K.

$$P = (E_p/3k)\sum_i \mu_i^2 N_i T_{pi}^{-1}, \tag{1}$$

where E_p is the polarizing field and N_i is the concentration of dipoles whose dipole moment is μ_i. To determine the upper limit on dipole density, we assume that the unit dipole moment μ^*, which is the product of the interionic distance and the electronic charge, is the smallest moment that radiation-induced dipoles can possess. This seems to be a reasonable assumption for a pure crystal since the length of a reorientable dipole composed of point defects in some arrangement can hardly be much less than the shortest lattice length, and the highly ionic nature of KCl makes fractional charges unlikely. Hence, the sum in Eq. (1) can be replaced by $\mu^* N_T$, where N_T is the upper limit of $\sum_i N_i$. The value of N_T for the range of observation (80–220 K) is plotted against electron fluence in Fig. 7. It is interesting to note that, although the 160-, 145-K peak system grows at a greater than linear rate, N_T grows linearly with radiation dose over the entire exposure range. The F-center concentration obtained on the same crystal is plotted for comparison and it shows a marked tendency toward saturation. The ratio of initial slopes for the two curves shows that the F-center creation rate is ~ 18 times greater than the rate of N_T production. After 1.8×10^{16} electrons/cm^2, the F-center density is only six times as great because of saturation of the F-center growth.

The important question is how valid is this estimate of dipole density. If all of the dielectric relaxation of dipoles is encompassed by the temperature range employed, the value plotted in Fig. 7 would be an overestimate because simple dipoles and dipolar clusters constructed from point defects would have a μ equal to or larger than the unit

moment. However, there is no assurance that there are no relaxation peaks below 80 or above 220 K which escape detection under the experimental conditions we employ. Thus without accurate models for the defects responsible for I_d we cannot definitely say what their concentrations are, but it seems unlikely that any of these effects would alter the values by more than a factor of 2. Since the uncertainties are to some extent compensatory, the actual error is probably rather less.

It is difficult to account for such a wide variety of relaxation processes with defects on the anion sublattice alone. In pure crystals it is difficult to conceive of any dipolar structures involving an interstitial halogen which would be stable in the temperature range employed in these experiments. On the other hand, a variety of structures involving the components of Frenkel pairs on both sublattices can be expected to be stable; e.g., K^+Cl^- interstitial molecules, cation-anion vacancy pairs, H centers trapped in the vicinity of cation vacancies, etc. In addition small clusters of interstitial ions would be expected to change their configuration in an applied electric field with a resultant displacement current. We therefore are led to the conclusion that the dipoles responsible for the complex ITC spectrum are composed of various combinations of cation and anion Frenkel defects.

The temperature dependence of their yields suggests that separation and migration of Frenkel-pair components are necessary for optimum production of dipoles. The low yield for irradiations near room temperature, on the other hand, suggests that growth of large interstitial or vacancy clusters may be occurring which exhausts the concentration of dipolar couples and small aggregates which are able to undergo relaxation. It would seem reasonable to assign the 160-K peak to the most prevalent of the defects which would be expected to have a low activation energy for reorientation. Since vacancy pairs would probably relax near the same temperature for divalent-cation-cation-vacancy reorientation,[6] i.e., > 200 K, we tentatively assign this peak to reorientation of interstitial K^+Cl^- pairs. The reason for the superlinear dependence of the 160-K peak amplitude upon radiation dose is not known.

The anamolously large width of the various ITC peaks needs explanation since the relaxation of a single well-defined dipolar species in low concentration is found to give a peak which closely resembles an ideal theoretical peak. Experiments using partial polarization to elucidate the peak structure indicated that they were envelopes of numerous unresolvable overlapping peaks. This is significant since, with suitable care, the ITC technique is capable of resolving very closely

spaced peaks (~ 0.01 eV intervals for comparable concentrations). Therefore, it seems that irradiation creates special species of dipoles, each with a distinct average reorientation energy, but that the energies of the individual dipoles are distributed about this average value. This suggests that either the dipoles are sufficiently closely spaced so that interactions of various degrees exist between them, or, alternatively, they could be randomly distributed in the strain fields of dislocations.

Next to be considered are plausible mechanisms for cation Frenkel-defect creation. The excitonic mechanism[8] of radiolytic-defect creation in the alkali halides accounts quite adequately for defect creation in the anion sublattice through the energy released upon exciton recombination. However, it does not seem very likely that such a process would lead to defects on the cation sublattice. One possibility is creation of defects during 1.5-MeV-electron bombardment by a direct displacement process. Indeed, Farge[10] has detected what appears to be Li^+ interstitial centers in LiF exposed to either 1.5-MeV electrons or neutrons. The maximum energy transferred in a collision between a relativistic electron and a lattice ion is given by

$$T_M = 2(E_e + M_e c^2) E_e / Mc^2 , \qquad (2)$$

where E_e is the energy of the incident electron, M_e its rest mass, c the velocity of light, and M the mass of the struck atom. In our case $T_M = 206$ eV. Since the energy required for direct atomic displacement T_d in most solids lies in the range 5–50 eV,[11] there is adequate energy in a primary recoil to displace a K^+ ion. The important question of course is whether the displacement probability is large enough to account for the experimentally observed yield of dipoles derived from cationic Frenkel pairs. The displacement cross section σ_d can be obtained from the formulation of Seitz and Koehler.[12] Some of the recoils will have sufficient energy E to generate secondaries and their contribution to the total defect yield may be determined by using the usual Kinchin and Pease model[13] and averaging over all collisions for which $E > 2T_d$. Such a calculation of the total displacement cross section σ_d' was carried out using a computer program developed by Oen.[14] The calculated values of both σ_d and σ_d' for $E_e = 1.5$ MeV and several values of T_d are listed in Table I. The magnitude of T_d for displacements on the cation sublattice are not known. Balarin,[15] using Born–Mayer potentials, estimated that the energy required to initiate a focused-displacement-collision sequence along a close-packed $\langle 110 \rangle$ row in the anion sublattice is 1–2 eV for most alkali halides. However, because of the smaller ion size he pointed out that defocusing would occur for cation

TABLE I. Calculated values[a] of the displacement cross section σ_d and the total displacement cross section σ_d' for 1.5-MeV electrons and a range of displacement energies T_d.

T_d (eV)	σ_d (10^{24} cm^2)	σ_d' (10^{24} cm^2)
15.0	80.4	112.0
12.5	99.8	145.1
10.0	130.8	210.5
7.5	177.8	287.6
5.0	272.8	493.9

[a]Using the McKinley-Feshbach approximation to the Mott series as described in Ref. 12, p. 331. These values were supplied by Oen.

close-packed directions for recoil energies below those required to create a displacement in a focusing event. Therefore, any displacement of cations would probably have to occur without the assistance of focusing and therefore require a somewhat higher displacement energy. A reasonable value for T_d in the cation lattice might be 10 eV, though on the basis of a "computer experiment" and Born-Mayer and Vervey potentials, Torrens and Chadderton[16] place it at twice this value for KCl.

The values in Table I are to be compared to the experimental value of σ_d' from Fig. 7: $\sigma_d' = 5 \times 10^{-21}$ cm^2, a value that is an order of magnitude larger than the calculated value. Actually, the disagreement is even greater than indicated since the values of Table I are for an infinitely thin crystal, i.e., no degradation of the incident-electron energy, whereas the specimens used in these studies had thicknesses comparable to the range of 1.5-MeV electrons in KCl. Since σ_d' decreases with electron energy to zero at the threshold value ~0.1 MeV required for imparting T_d to the struck atom, the calculated values of σ_d' averaged over the electron range in the crystal would be even smaller than the values in Table I. Therefore, it is difficult to reconcile the large experimental value with the small calculated value of σ_d'. The disparity seems to be too large to be remedied by a further reduction of T_d or an increase in μ_d. Indeed, if the larger T_d value preferred by Torrens and Chadderton is correct, this mechanism would be placed completely out of consideration.

Another point of evidence which suggests that direct displacements cannot be the origin of the dipoles is the observation of dielectric relaxation in crystals exposed to x rays.[4,6] Here the possibility of a direct displacement process may be almost completely discounted. Even if T_d were sufficiently small for the 40- to 50-keV photoelectrons to induce displacements, the yield would be entirely too small[2] to account for the observed density of dipoles. The crystallographic voids and

dislocation loops observed[17,18] in crystals damaged on the electron microscope stage by the 50- to 100-keV-electron beam probably owe their origin to the defects we are considering, since in heavily damaged crystals such dipoles would tend to coalesce: Aggregating cation and anion vacancies would form voids or loops and aggregating cation and anion interstitials would form loops or three-dimensional structures. Again the incident-electron energy is too small to create cation Frenkel pairs in high yield. Recently, Hobbs, Hughes, and Pooley[19] reported observations of interstitial loops identified by diffraction contrast. They attempted to account for the loop structures on the basis of interstitial halogen molecules thus eliminating the need for cation defects. Recent analysis,[20] however, has convinced them that both alkali interstitials and halogen interstitials are present in these loop structures. They also observe that the number of cation interstitials necessary to account for the number and size of the loops is comparable to that needed to account for the dipole densities we observe. By this we do not intend to say that the two types of observation arise from the same defect but that in each case a cation-intersitial creation rate much smaller than for anion Frenkel pairs is adequate for the production of both interstitial platelets and dipoles.

The important point is that both experiments strongly suggest that cation-sublattice damage is occurring. These considerations force us to the conclusion that in addition to the production of Frenkel defects on the anion sublattice by an excitonic process, ionizing radiation is capable of creating disorder on the cation sublattice as well. The yield of cation damage is smaller by one to two orders of magnitude. However, since it shows no tendency to saturate after prolonged irradiation, dipolar defects can become an important component of the total disorder after extensive exposures. The mechanism producing cation defects is not known. It may be associated with some low-probability event utilizing exciton-recombination energy, or perhaps some sort of atomic rearrangement needed to stablize the anion defects such as suggested by Hobbs et al. may be responsible.

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Anharmonicity in the Silver and Thallium Halides: Low-Frequency Dielectric Response*

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The isobaric temperature dependence of the low-frequency (1–100 kHz) dielectric response of AgCl, AgBr, TlCl, and TlBr for the range 2–290 K and the isothermal pressure dependence of the dielectric response for pressures up to 11 kbar in the range 77–290 K are reported. These measurements are used to determine the thermal strain and low-frequency anharmonic self-energy for the $q \approx 0$ transverse-optic mode for these materials. The results reveal that the anharmonic self-energy contribution arising through the quartic anharmonicity is dominant for all four materials at low temperatures. At higher temperatures the quartic anharmonicity continues to provide the dominant contributions for the thallium halides, but for the silver halides the cubic anharmonicity has a stronger temperature dependence and provides the dominant anharmonic self-energy contribution. The quartic self-energy contributions for the thallium halides are sufficiently large that they dominate the thermal-strain self-energy contributions at all temperatures, thus causing the dielectric response for these materials to behave like ferroelectrics in their paraelectric state. No marked difference between the low-frequency and far-infrared anharmonic self-energies is found.

INTRODUCTION

The coupling of phonons through an anharmonic potential is well known to create a frequency-dependent complex self-energy for each of the normal-mode energies in a crystal, the real part of which changes the mode energy and the imaginary part of which is the reciprocal of the phonon lifetime. Recent studies have shown the Hermitian self-energies associated with the $q \approx 0$ optic phonons in materials like the alkali halides to be small[1-3] and of the order of a few percent of the harmonic normal-mode energies. Interest is now centering on more strongly anharmonic systems such as displacive ferroelectrics for which it has been proposed that strong anharmonic interactions are responsible for stabilizing the paraelectric state of these materials.[4,5] In this paper we report on the temperature dependence of the low-frequency self-energy contributions associated with the $q \approx 0$ transverse-optic phonons in some silver and thallium halides. Although crystallizing in simple cubic structures, these are considerably more anharmonic materials than the alkali halides, and the thallium halides are especially important since their low-frequency and far-infrared dielectric