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Ionic Thermocurrents in Alkali Halide Crystals Containing Substitutional Beryllium Ions*

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The dielectric relaxations of NaCl and KCl single crystals containing beryllium ions have been studied using the technique of the ionic thermocurrents (ITC) in the range of temperatures between 1.2 and 300°K. The ITC spectra are characterized by three types of relaxations in both host crystals. The analysis of such relaxations and the observed temperature dependence of their relaxation times indicate that: (1) a large fraction of the beryllium ions are associated with cation vacancies that occupy nearest-neighbor (n.n.) positions as well as next-nearest-neighbor (n.n.n.) positions with respect to the impurity; (2) the relaxation rates with which the Be-vacancy dipoles change their orientation under the influence of an electric field are dominated by the frequency of direct interchange between Be and vacancy (ω_2) and by the frequencies of jump between n.n. and n.n.n. positions (ω_3 and ω_4); (3) the activation energy for the diffusion of Be ions is 0.5 eV for NaCl and 0.45 eV for KCl. In discussing the results, the possibility that the Be ions occupy off-center positions has been considered.

1. INTRODUCTION

WHEN divalent metallic impurities substitute for the monovalent ions in alkali halide crystals, the condition of electrical neutrality requires that an equal amount of positive ions vacancies are present in the crystal. The impurities tend to become associated since this minimizes the free energy. The degree of association will therefore depend on the temperature.[1] At room temperature almost all impurities are associated with vacancies. These impurity-vacancy (I–V) complexes have a permanent electric dipole moment which depends upon the relative position of the impurity and the vacancy and their effective charge. The presence of the I–V dipoles has been detected in the past by measuring the dielectric relaxations of alkali halide crystals containing different types of divalent metallic ions, at temperatures at which the thermal energy of such dipoles allows their reorientation under the influence of an electric field.[1–4] Additional information has also been obtained from mechanical relaxation[5] and EPR measurements.[6] The results of these experiments can be summarized as follows:

(1) For the most widely studied impurities, i.e., Ca, Ba, Sr, Mn, Fe, Co, and Cd, the vacancy is either in a nearest-neighbor (n.n.) position (on the positive ions sublattice) or in a next-nearest-neighbor (n.n.n.) position with respect to the impurity and the magnitude of the resulting dipole moment is approximately given by the electronic charge times the geometrical distance between impurity and vacancy.

(2) The orientation of the I–V dipoles in an electric field mainly occurs by motion of the vacancy around the impurity, as shown in Fig. 1 (a), the jump rate of the impurity ion into the adjacent vacancy being a relatively slow process. The rate of change of the number of dipoles of different orientations is described by differential equations in terms of four vacancy jump rates[7]: ω_1 for the motion of the vacancy from a n.n. position to another n.n. position, ω_2 for the direct interchange between vacancy and impurity, ω_3 for the motion of the vacancy from an n.n.n. to an n.n. position, and ω_4 for the motion of the vacancy from an n.n. to an n.n.n. position. In the presence of an electric field, the relaxation process is governed by two relaxation times given by[3]:

$$\tau_1^{-1}=\omega_1+\omega_2+2\omega_3+\omega_4+[(\omega_1+\omega_2-2\omega_3+\omega_4)^2+4\omega_3\omega_4]^{1/2},$$
$$\tau_2^{-1}=\omega_1+\omega_2+2\omega_3+\omega_4-[(\omega_1+\omega_2-2\omega_3+\omega_4)^2+4\omega_3\omega_4]^{1/2}. \quad (1)$$

The dielectric and mechanical relaxation experiments, carried out by Dreyfus[3] and by Dreyfus and Laibowitz,[5] respectively, showed that $\omega_3>\omega_4>\omega_1>\omega_2$. They also concluded that, for the types of impurities investigated, if the radius of the impurity ion decreases, ω_4 and the fraction of vacancies occupying n.n.n. positions both increase.

(3) Annealing at temperatures between room temperature and ~100°C causes the I–V dipoles to condense into microprecipitates whose structure has, up to the present time, only been estimated from the order of the kinetics of the precipitation process.[8,9] The rate of migration of the I–V dipoles through the

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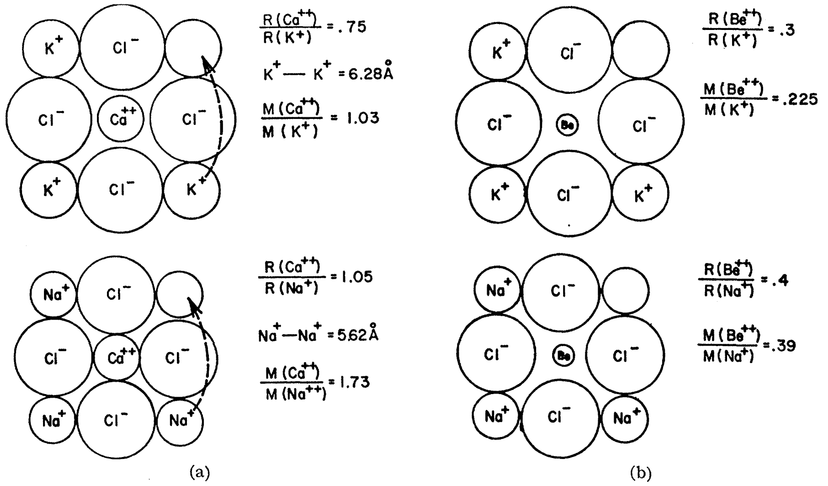

FIG. 1. Two-dimensional picture for (a) calcium impurity ions in NaCl and KCl (the arrows indicate the motion of the vacancy around the impurity from an n.n. to another n.n. position) and for (b) beryllium impurity ions in the same crystals. The distortion of the neighboring ions is not shown.

lattice, for the most widely studied divalent impurities, is essentially determined and limited by the frequency of direct interchange between vacancy and impurity (ω_2), since the motion of the impurity around the vacancy alone does not lead to a spatial displacement of the dipole.

The purpose of the experiment described in this paper is to obtain information concerning the properties of the I–V dipoles when the size and the mass of the impurity are considerably smaller than the size and the mass of the substituted metal ion. The systems that we have examined are potassium chloride and sodium chloride crystals in which divalent beryllium ions have been introduced in small amounts to replace, respectively, potassium and sodium ions, as shown in Fig. 1 (b). The ratios of the ionic radia are $R(\text{Be})/R(\text{K})=0.3$ and $R(\text{Be})/R(\text{Na})=0.4$ while the masses ratios are $M(\text{Be})/M(\text{K})=0.22$ and $M(\text{Be})/M(\text{Na})=0.39$. In analogy with the thermodynamical behavior of previously studied impurities, we assume that, in the absence of microprecipitates, the beryllium ions are mostly associated to cation vacancies and a small fraction of them are isolated. According to these different types of environments, a number of qualitative predictions can be made in advance.

Isolated beryllium ions. The situation of the beryllium ions surrounded by six chlorine ions in KCl or NaCl lattices is very similar to the corresponding situation of Li impurities, which has been investigated in detail both theoretically[10] and experimentally.[11] The presence of an excess positive charge on the beryllium might induce a more pronounced collapse of the neighboring chlorine ions and a longer range distortion of the lattice. Because of the smallness of the beryllium ions, elementary electrostatic considerations predict that, for a rigid undistorted lattice, the impurity ion will be situated in one of eight equivalent off-center positions in the ⟨111⟩ direction. If one considers the displacements of the chlorine ions such that the electrostatic attraction of the beryllium ions is counterbalanced by the overlap repulsion of the chlorines, the volume available to the beryllium ions would be only six times its volume, as determined from the ionic radius. Under this condition, it is questionable whether the beryllium can assume an off-center position. The real situation corresponds to neither one of these two extreme cases. The motion of the impurity ion might be accompanied by a readjustment of the neighboring chlorine ions and the potential, in a one-dimensional picture, would be a double-well type in which the occupied well has lower energy than the other. The height of the barrier between these wells determines the behavior of the beryllium ions. Energy level structures have been theoretically estimated for the limiting cases of low barrier and high barrier[12] but no experimental data are available to indicate which is the right model for the beryllium.

Beryllium-vacancy complex. At those temperatures at which the complexes are stable, the vacancy may occupy preferentially a nearest-neighbor position n.n. with respect to the beryllium, since the electrostatic energy of the complex would be minimum in such a configuration. If, in addition, the beryllium occupies off-center positions, its potential energy in the position closest to the vacancy will be lower than in the other wells. The complete localization of the beryllium in such a well yields a further decrease of the energy of the complex. It is therefore to be expected that the beryllium-vacancy complexes have a smaller electric dipole moment than that of I–V dipoles involving larger impurities which occupy a centered position.

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[12] S. P. Bowen, M. Gomez, J. A. Krumhansl, and J. A. D. Matthew, Phys. Rev. Letters **16**, 1105 (1966).

Furthermore, in the case of a small ion as beryllium which allows considerable motion of the neighbors under the influence of the various electrostatic forces, it is apparent that the potential barrier between the impurity and the vacancy becomes reduced. If this potential barrier is small enough it is possible that the reorientation of the beryllium-vacancy dipoles in an electric field can occur by direct interchange. It was hoped that experiments on the temperature dependence of the relaxation time of the beryllium-vacancy dipoles would allow us to discriminate between the various processes.

We have therefore decided to investigate the dielectric relaxations of KCl and NaCl crystals containing small amounts of beryllium ions, using the ionic thermocurrents technique in temperature range between 1.2°K and 300°K. This technique has been chosen instead of the dielectric loss method or the dc polarization method because of its much higher sensitivity and because the same polarization processes can be detected at lower temperatures. The last feature is quite important when precipitation of the impurities is likely to occur.

The ionic thermocurrent (ITC) spectra, as described below, are expected to yield information concerning: (a) the existence of the beryllium-vacancy dipoles, (b) the mechanism of orientation of such dipoles in an electric field, and (c) the parameters characterizing the temperature dependence of their relaxation time, namely, the activation energy E and the frequency factor τ_0.

2. IONIC THERMOCURRENTS

When the relaxation processes obey the classical rate theory, the temperature dependence of the relaxation time is given by

$$\tau=\tau_0\exp\{E/kT\}\,, \tag{2}$$

where T is the temperature, E the activation energy, and k the Boltzman constant. For this case, the shape of the ITC curves—depolarization current versus temperature—has been previously calculated under the assumption that the orientation of the electric dipoles can be described by a monomolecular kinetic. Several experimental results of ITC measurements have been published in clear agreement with the calculations.[4] The depolarization current detected during the warming process of the crystal will be given by[4]

$$i(T)=N_d\frac{p^2\alpha\mathcal{E}_p}{kT_p}[\tau_0\exp\{E/kT\}]^{-1}\times\exp\left(-\int_{T_0}^{T}[b\tau_0\exp\{E/kT'\}]^{-1}dT'\right). \tag{3}$$

where N_d is the number of dipoles in the crystal; μ is their dipole moment; T_p is the temperature at which an external electric field $\mathcal{E}_p$ is applied to the crystal for a length of time much greater than the relaxation time of the dipoles; T_0 is the temperature—*much lower* than T_p—at which the electric field is reduced to zero; b is the warming rate from T_0; and α is a geometrical factor depending on the orientations of the dipoles.

The activation energy E and the frequency factor τ_0 for the relaxation time for a single process can be obtained directly and with good accuracy from a single measurement by plotting, as a function of temperature, the right-hand side of the following equation:

$$\tau_0\exp\{E/kT^*\}=\int_{T^*}^{\infty}i(T)dT\bigg/i(T^*)\,, \tag{4}$$

in which the numerator is the area under the ITC curve from $T=T^*$ to $T=\infty$ and the denominator is the value of the current at $T=T^*$. We notice that the determination of E and τ_0 is independent of the warming rate b. Useful information can also be obtained from the ITC curves if the relaxation process of ionic dipoles does not follow the classical rate theory. Thus, for the tunneling processes of ions the temperature dependence of the relaxation time will be of the type[13]

$$\tau(T)=AT^{-\alpha}\,, \tag{5}$$

where A is a constant factor determined by the features of the potential energy, by the mass of the ion, and by the vibrational properties of the host crystal. When α is zero, A^{-1} is the temperature-independent tunneling frequency corresponding to the case of two equivalent potential wells. When α is equal to one, we are dealing with one-phonon-induced tunneling between nonequivalent potential wells. The integration of the rate equation for the oriented dipoles $dN/dt=-(1/\tau)N$, for linearly increasing temperature, is straightforward in this case and yields the following temperature dependence of the depolarization current:

$$i(T)=\frac{N_db}{A}T^{\alpha}\exp\left\{-\frac{T^{(\alpha+1)}}{b(\alpha+1)A}\right\}. \tag{6}$$

The shape of such an ITC band is clearly different from the classical case; from the slope of the curve at T less than the temperature of the band maximum T_M, the factor α is readily determined and from the value T_M the constant A can be calculated from the equation

$$T_M=(\alpha bA)^{1/(\alpha+1)}. \tag{7}$$

It must be emphasized, however, that the possibility of detecting such processes with the ITC method is limited to the relaxation times that, at the lowest attainable temperature, are of the order of several minutes. For shorter relaxation times, obviously, the

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[13] J. A. Sussmann, Physik Kondensierten Materie **2**, 146 (1964).

induced polarization will decay rapidly after the electric field has been removed and it is then impossible to warm the crystal before depolarization has occurred.

3. EXPERIMENTAL DETAILS

The beryllium-doped sodium chloride and potassium chloride crystals were obtained by adding 0.1% of beryllium chloride to the melt. NaCl and KCl powders were chemically purified according to the procedure indicated by Buttler and co-workers.[14] Subsequently, the material was melted while dry chlorine gas was bubbling through it. The beryllium chloride purchased by the K & K laboratories was only 98% pure and no better material was available commercially. Ca and $BeSO_4$ were among the major impurities. Several crystals were grown in our laboratories (samples L) in helium atmosphere and the concentration of beryllium was determined by chemical analysis to be 45 ppm. The calcium concentration as a result of $BeCl_2$ contamination was 50 ppm. The small amount of beryllium found in the samples compared with the amount introduced in the melt may have its origin in the fact that the solubility of beryllium ions in the solid solution of NaCl and KCl is two orders of magnitude smaller than the solubility of the calcium ions.

Other crystals were grown in the laboratories of the Material Science Department of Cornell University in a dry chlorine atmosphere (samples C), after having similarly chlorinated the host materials. In these crystals the relative concentration of beryllium and calcium ions was also found to be approximately the same, ranging between 10 and 100 ppm. Because of the dangerous properties of the $BeCl_2$, any further purification of this material was not contemplated. The above described samples L and C were nevertheless judged to be acceptable for the purposes of the experiment. The technique of the ITC is sensitive enough to detect the small amount of impurities present in such samples. Furthermore, the total amount of divalent impurities was small enough so that interactions between them could be assumed to be negligible in our measurements. The apparatus used for the ITC measurements between 5 and 300°K has been described in detail elsewhere.[15] Measurements in the temperature range between 1.2 and 70°K have been carried out by using a different sample container consisting of a metallic cell which could be put in contact with the liquid-helium bath through a He-gas heat exchanger. After the cell was thermally insulated from the liquid-He bath, the temperature of the cell was increased by means of a wire heater. The sample was located inside the cell and firmly held between two electrodes. In order to attain the best electrical insulation, the electrodes are made of magnetized Alnico V disks one of which was attached to the cell by means of Teflon spacers while the second electrode was attracted toward it, without requiring, therefore, any insulator to keep it in place. The Alnico V alloy was chosen because it does not exhibit changes of magnetization at low temperatures. The temperature sensors, a cobalt-activated-gold versus gold-activated-silver thermocouple and a $\frac{1}{10}$-W carbon resistor, were also located inside the cell, in which a pressure of $\frac{1}{2}$ mm Hg of He gas was maintained in order to obtain a uniform temperature.

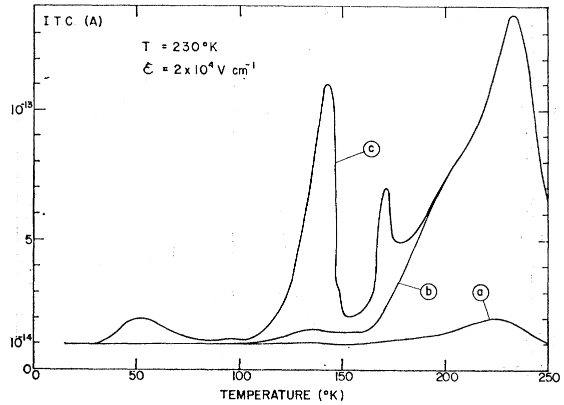

FIG. 2. ITC spectra of NaCl (Be^{++} and Ca^{++}) (a) as grown, (b) after annealing at 500°C and quenching to room temperature, and (c) after annealing at 500°C and quenching to LNT. In all cases $\mathcal{E}_p=2\times10^4$ V cm^{-1}; $T_p=230$°K and $b=0.05$°K sec^{-1}.

4. RESULTS AND DISCUSSION

All the samples that were kept at room temperature for several weeks showed no ITC bands over the whole range of temperature. After annealing at 500°C and subsequent quenching to room temperature, both $KCl:BeCl_2$ and $NaCl:BeCl_2$ exhibited several ITC bands in the temperature range between 150 and 250°K. These bands were similar to the ITC spectra of $NaCl:CaCl_2$[4] and can be attributed to the orientation of calcium-vacancy dipoles.[16] If, however, the annealing is followed by a quenching to liquid-nitrogen temperature (LNT), the subsequent ITC measurements show, in both types of crystals, three bands at temperatures below 170°K, in addition to the calcium bands at higher temperatures (Fig. 2).

The analysis of these bands revealed the following results: (a) The intensity of the beryllium bands is proportional to the applied electric field, (up to 5×10^4 V cm^{-1}, the largest field employed) and is not affected by changes in the surface to volume ratio of the sample, indicating that we are dealing with volume polarization from noninteracting dipoles; (b) precipitation processes of the beryllium ions proceed at a very high rate because

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[14] C. Buttler, J. Russell, R. Quincy, and D. La Valle, in Oak Ridge National Laboratory Report (unpublished).

[15] C. Bucci, Phys. Rev. **152**, 833 (1966).

[16] The ITC spectra of Ca-doped crystal described in Ref. 4 contain, in addition to the relaxation modes of the Ca-vacancy dipoles, several other weak bands whose nature is still unknown. For the purposes of our experiment, however, we simply notice the similarity of the two groups of bands.

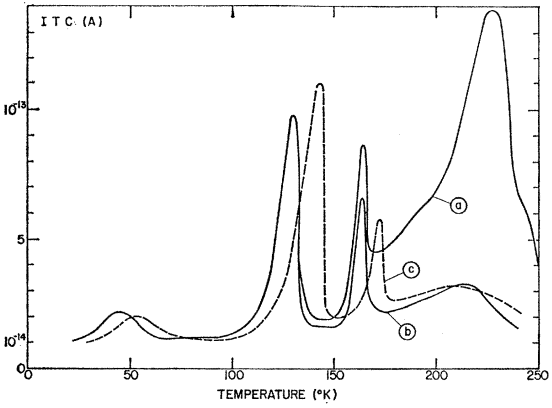

FIG. 3. ITC spectra of KCl: (Be^{++} and Ca^{++}). (a) $T_p=250$°K, (b) $T_p=170$°K, and (c) ITC of NaCl: (Be^{++} and Ca^{++}), obtained with $T_p=170$°K.

the beryllium bands disappear after the samples are kept at room temperature for more than 30 min; (c) the total area under the beryllium bands, i.e., the total induced polarization, is considerably smaller than that under the calcium bands, even though the concentration of beryllium and calcium is approximately the same.

In Fig. 3, ITC spectra are shown for two polarization temperatures $T_p=170$°K and $T_p=250$°K for KCl:$BeCl_2$; we notice that the effect of the calcium bands on the ITC spectrum can be greatly reduced by polarizing at the lower temperature. Similar results were found for the NaCl:$BeCl_2$.

In all these experiments, the only noticeable difference between L samples and C samples was in the ratio of the intensities of the calcium and beryllium bands, which could be correlated with the variation of the impurity contents of the samples.

The beryllium bands in NaCl and in KCl can be described as follows: a band (band A) occurs at ~ 50°K in NaCl and ~ 40°K in KCl, which is so weak in both cases that the analysis of its shape was rather inexact; another band occurs at 142 and 133°K in NaCl and KCl, respectively, (band B) is approximately 100 times more intense than band A, while a third band (band C) at 170°K in NaCl and 161°K in KCl is by a factor three less intense than band B.

As far as the intensity of these bands is concerned, the experiments showed that the B bands are the most intense and that all bands, A, B, and C, maintain their relative intensity for samples containing different amounts of beryllium ions, as well as for the same sample at different stages of the precipitation process. Both bands B and C exhibit the shape expected for a relaxation process which obeys the classical rate theory. The temperature dependence of their relaxation time, both in NaCl and KCl, has been determined by using relation (4). The values obtained for the activation energies E and the frequency factors τ_0 are listed in Table I. As far as the A band is concerned, it does not seem to have the shape described by Eq. (3) and any attempt to fit it with a curve of the type given by Eq. (6) was not successful.

TABLE I. Properties of the ITC peaks assigned to beryllium impurities.

Host crystal	T_M (°K)	E (eV)	τ_0 (sec)	μ (Be)/μ(Ca)
	(A) 40	?	?	
KCl	(B) 133	0.24	10^{-8}	0.3
	(C) 161	0.45	5×10^{-13}	
	(A) 50	?	?	
NaCl	(B) 142	0.26	5×10^{-9}	0.4
	(C) 170	0.50	1.5×10^{-13}	

It can be seen that the B bands are characterized by considerably smaller activation energies and frequency factors than the C bands; a comparison of these values with the corresponding parameters for the motion of a free vacancy or for the motion of a vacancy around the divalent impurity enables us to rule out the possibility that the B bands correspond to relaxation processes in which the jump rates of the cation vacancy around the beryllium ion dominate. On the other hand, E and τ_0 for the C bands agree closely with the expected values for a vacancy moving between lattice sites that are in the neighborhood of a divalent impurity [Fig. 1 (a)].

We give the following interpretation of the results obtained in this experiment: the B bands in both NaCl and KCl can be attributed to the reorientation of the Be-vacancy dipoles via direct interchange of the two. This means that ω_2 is much larger than the other vacancy jump rates ($\omega_2\gg\omega_3\gg\omega_4\gg\omega_1$) and the two relaxation times, which are the solutions of the rate Eqs. (1), can be approximated as follows:

$$\tau_1^{-1}\approx 2\omega_2+\omega_4\approx 2\omega_2,$$
$$\tau_2^{-1}\approx 4\omega_3+\omega_4\approx 4\omega_3.$$

Using the activation energy E and the pre-exponential factor τ_0 measured for the B bands, we obtain $\tau_1=5\times10^{-9}\exp\{0.26/kT\}$ for NaCl and $\tau_1=10^{-8}\exp0.24/KT$ for KCl. As mentioned in the introduction, a very low activation energy for this process can be expected if the Be can occupy a distinct off-center position in a preferable orientation determined by the vacancy (Fig. 4). The frequency factors are very low compared to the optical phonon frequencies of these crystals. However, since the interchange of the beryllium and the vacancy involves a very large number of neighboring ions, the frequency factor for the interchange process may be determined by acoustical phonons of much lower frequencies.

The C bands can be attributed to the relaxation process governed by the vacancy jump rates ω_3 and ω_4 involving the motion of the vacancy from the n.n.n. to the n.n. position and vice versa. We therefore have $\tau_2\approx(4\omega_3+\omega_4)^{-1}=1.5\times10^{-13}\exp0.5/KT$ for NaCl and

$\tau_2=5\times10^{-13}\exp0.45/KT$ for KCl. The vacancy jump rate ω_1 does not contribute to the relaxation process because the rate of direct interchange ω_2 is much higher and the motion of the vacancy from a n.n. to another n.n. position proceeds more easily via an n.n.n. position. Direct experimental evidence in favor of this indirect process for larger impurities in NaCl was found by means of mechanical relaxation measurements.[5]

As a consequence of this interpretation we expect to find, for the dipole moment of the off-center beryllium-vacancy, a smaller value than for the I–V dipoles involving a centered impurity[17] (e.g., Ca^{++}). The unavoidable presence of calcium impurities in our samples can be exploited in order to obtain a relative value of the dipole moment of the beryllium-vacancy complexes (μ_{Be}) with respect to the calcium-vacancy complexes (μ_{Ca}). The only assumption that must be made is that, at temperatures below room temperature, almost all the beryllium and calcium impurities are associated with vacancies in the n.n. position so that we can approximate the number of I–V dipoles with the number of impurities determined by chemical analysis (n_{Be} and n_{Ca}). We thus have

$$\mu_{Be}/\mu_{Ca}=P_{Be}/P_{Ca}\times n_{Ca}/n_{Be}, \qquad (5)$$

where P_{Be} and P_{Ca} are the polarizations due to the beryllium-vacancy dipoles and calcium-vacancy dipoles, respectively, which are equal to the areas under the ITC bands. We find, for the ratio of the dipole moments, the value 0.4 for NaCl and 0.3 for KCl; because of the approximations that were made, this result provides only a qualitative support for our model.

The diffusion of Be impurities involves direct interchange between Be and vacancy and the motion of the vacancy around the impurity; since the latter is the slower process, the diffusion rate of the Be will be governed by it and would be characterized, according to our measurements, by an activation energy of ~0.5 eV (much smaller than the values for larger impurities).[18] The same process governs of course the precipitation rate of the Be-vacancy dipoles; therefore, the observed rate of change of the Be bands upon annealing at room temperature is consistent with our interpretation of our ITC bands.

As far as the motion of the Be ions between possible off-center positions is concerned, it can be assumed that the height of the potential barrier separating such positions is smaller than the activation energy for the various jumps. The differential equations describing the relaxation process should include, now, at least one additional jump rate ω_5, accounting for the motion of the Be from one off-center position to another. As a consequence, we will have additional solutions, corresponding to additional relaxational modes; detailed calculation along these lines could be carried out only if the displaced positions of the Be ions were known. If ω_5 is considerably different than the other vacancy jump rates, the solutions τ_1 and τ_2 would not be significantly affected.

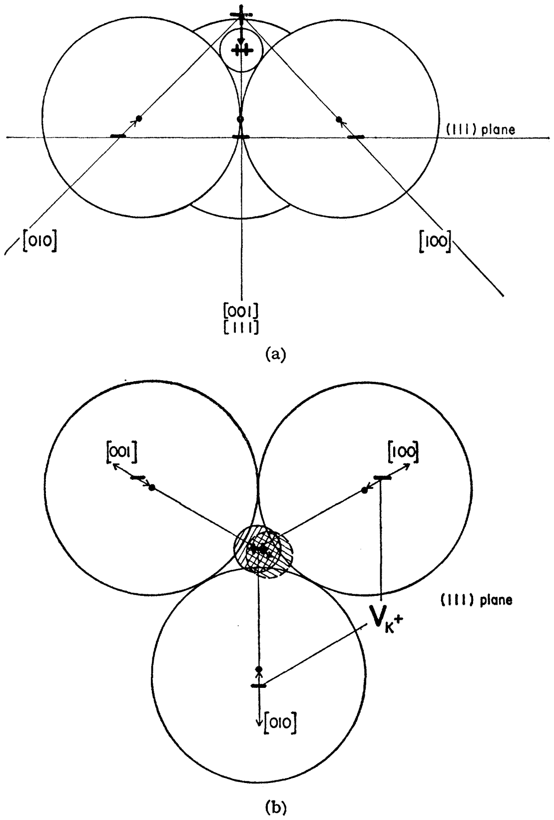

FIG. 4. KCl lattice is shown with the chlorine ions (large circles) displaced toward the beryllium impurity. The beryllium ion (small circle) is shown in an off-center position in the [111] direction (a). The presence of a potassium vacancy V_k+, in the n.n. position with respect to the Be^{++} might induce the displacement of the impurity ion in a direction closer to the [110] direction (b).

It is possible that the *A* bands at 50°K in NaCl and 40°K in KCl are related to an additional relaxation mode of the Be-vacancy dipoles characterized by the impurity jump rate. On the other hand it is also possible to attribute them to the translational alignment of Be ions, that are not associated with vacancies, in a potential characterized by equivalent wells in the [111] direction. In all these cases, the barrier between the wells must be quite high (probably $\frac{1}{10}$ eV.) in order to allow such a low-frequency motion. The only available data, however, are the intensity of the A bands and their shape, which apparently does not indicate the existence of a process following the classical rate theory. This is obviously not enough to draw a final conclusion, mainly because there are many other possibilities open to several speculations.

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[17] It seems reasonable to assume that all divalent impurities, when associated with vacancies, occupy an off-center position; for large impurities, however, the displacement from the lattice site is very small and can be neglected.

[18] A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XX, p. 288.

Optical absorption, Raman scattering, and double nuclear magnetic resonance measurements have been attempted on the same samples. The concentration of impurities was too small for the sensitivity of such methods. Further experiments using samples with higher content of beryllium impurities should yield additional useful information. This necessitates the availability of beryllium halides of great purity.

As a final remark, it must be noticed that the detection and the study of the dielectric relaxations induced by the beryllium ions in alkali halides could not have been carried out by means of the conventional technique of the dielectric losses. Such measurements must be performed at temperature near 300°K and under these conditions the precipitation processes of the impurities are already too fast compared with the time necessary for the measurements. Also isothermal dc polarization measurements would not have been useful because of their limitations in discriminating between partially overlapping relaxation processes. The experiment described here is, therefore, another example in which the investigation of dielectric relaxations can be carried out only by means of ionic thermocurrent measurements.

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Determination of the Gradient Elastic Tensor in Sodium Iodide by Means of Nuclear Magnetic Resonance*

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Uniaxial stress has been applied to single crystals of NaI, producing resolved satellites, or, in some crystals, only line broadening of the ^{127}I nuclear magnetic resonance due to an electric quadrupole interaction. The position of the satellite lines has been measured as a function of applied stress, and from such measurements the components of the gradient elastic tensor, $C_{11}=(3.5\pm0.5)\times10^4$ statvolts/dyne, $C_{44}=(28.0\pm0.5)\times10^4$ statvolts/dyne, have seen determined. The changes in intensity of the ^{23}Na and ^{127}I NMR lines have been examined in the elastic and inelastic region of strain, providing information concerning dislocations in these crystals. The existence of the intensity anomaly in the ^{127}I NMR line, which appears with $\mathbf{H}_0$ parallel to [100], is explained in terms of oriented dislocations and the values of the components of the gradient elastic tensor. A value 4.5 ± 1.5 for the ratio of the Sternheimer antishielding factor for the iodine ion to that for the sodium ion has been determined. It has also been possible to estimate a value of the Sternheimer antishielding factor for the iodine ion ($\lambda\approx58$).

INTRODUCTION

If a nucleus of spin I possesses a nonzero quadrupole moment, its nuclear-magnetic-resonance (NMR) line is split into $2I$ components whenever an electric field gradient is present at the site of the nucleus. At crystalline sites possessing perfect cubic symmetry, such as lattice sites in perfect alkali halide crystals, the electric field gradient is zero. In such cases the splitting of the NMR line is also zero. It is possible to reduce the symmetry of a cubic crystal by application of an axial stress, thereby inducing an electric field gradient. Experiments of this type were first undertaken with alkali halides by Watkins.[1] Watkins and Pound[2] reported that the observed intensities of the ^{79}Br, ^{81}Br, and ^{127}I resonances corresponded very nearly to the intensities of the $m=\frac{1}{2}\leftrightarrow m=-\frac{1}{2}$ transitions alone. This diminution of intensity was attributed to the smearing out of the satellite lines by the presence of crystalline imperfections. Hon and Bray[3] reported the existence of an anomalous maximum in the angular dependence of the intensity of the NMR of ^{127}I in NaI single crystals whenever the externally applied magnetic field $\mathbf{H}_0$ is parallel to a $\langle100\rangle$-type direction. This phenomenon was attributed by them to the effect of oriented dislocations. Subsequently, axial compression experiments were performed by Hooper and Bray,[4] demonstrating the elastic character of the strain for a fairly wide range of stresses.

The present work was undertaken to determine the nonzero elements of the gradient elastic tensor for NaI,

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