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Ionic Thermocurrent Study of the Dipole–Dipole Interaction in CaF_2 Doped with NaF†

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An investigation of the relaxation of electric dipoles produced by doping polycrystal CaF_2 with NaF was carried out by means of ionic thermocurrents (I.T.C.). I.T.C. measurements were conducted in the temperature range of 77°K to room temperature. Results show four separate peaks. Three relatively small peaks were observed along with a large, main peak, which significantly broadens as the Na^+ concentration increases. The first and fourth peaks are directly dependent on concentration while the second and third seem to vary inversely with concentration. A lattice calculation of the dipole–dipole interaction was made, giving results which predict the main peak and its broadening as a function of concentration and possibly the lowest small peak. It is observed that the dipole–dipole interaction energy can be as great as 0.14 eV and manifests itself as a large effect in samples with doping concentrations on the order of 1 mole% NaF. By analyzing the I.T.C. curves, an activation energy of 0.52 eV and a τ_0 of 6.0×10^{-15} sec is obtained for the reorientation of the uninfluenced Na^+–V_F^- dipole. These values agree with previous measurements obtained by dielectric loss and internal friction.

Introduction

Calcium Fluoride has been extensively studied for several years regarding the defect structures produced upon doping with various cations. In most cases, the cation has been one of the rare earths. In this study we report data and calculations on CaF_2 doped with the monovalent ion Na^+ with special emphasis on the electric dipole–dipole interaction.

Tressler (*1*) has determined the solubility of NaF in CaF_2 and reports a maximum solubility of approximately 2 mole% NaF at 820°C. The monatomic Na^+ ion is incorporated (*2, 3*) in the CaF_2 lattice by substitutionally replacing one of the Ca^{++} divalent ions. Electrical neutrality of the crystal is maintained by creating an equal number of fluorine ion vacancies. It seems that the energetics are favorable for most of the Na^+ ions in the lattice to be associated with the V_F^- at least at room temperature. Johnson et al. (*4*) have observed electrical and mechanical relaxation in CaF_2 doped with NaF and have reported a diffusional motion energy of 0.53 eV for the fluorine vacancy. Of importance to this work is their observation that the dielectric and anelastic loss peaks broaden with dipolar concentration, especially in the case of dielectric relaxation studies.

In attempting to explain the broadening of the dielectric and anelastic loss peaks, these investigators have attributed this behavior to an interaction between the Na^+–V_F^- complexes. Johnson et al. (*4*) have shown that the broadening of the dielectric loss curves obtained from samples of CaF_2:NaF was a direct function of the sample's sodium content and postulate that the effect is due to the dipole–dipole interaction. Lidiard, on the other hand, has considered the effect of vacancies occupying next nearest neighbor sites. Lidiard's (*5*) solution for an ac applied field shows the theoretical dielectric loss peak to be broader than a Debye peak. Southgate's (*6*) experimental work on CaF_2:YF_3 and also Bucci (*7*) work with Be doped NaCl + KCl give examples of systems where Lidiard's hypothesis could very well be operative.

The purpose of this research is to investigate the role of dipole–dipole interactions on the relaxation process in CaF_2 doped with NaF. The I.T.C.

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(Ionic Thermocurrents) technique was chosen as the method of investigating this interaction energy, principally because of the large signal to noise ratio (thus allowing low concentration samples to be studied), the relative ease of extracting the desired data, and the marked effect the apparent dipole–dipole interaction has on the I.T.C. curves. This method is derived from the ionic thermocurrents produced by the relaxation of previously oriented dipoles. The I.T.C. method was first used in ionic crystals by Bucci and Feischi (*8*, *9*) in their work on the alkali halides and is analogous to thermoluminescence glow curves and "temper" annealing experiments (*10*). However, little has been said concerning the complex nature of the spectra obtained. In this study we propose a model for at least some of the complexities.

Experimental Procedure

1. Sample Preparation

The CaF_2:NaF polycrystal samples were prepared by dry mixing the desired ratio of J. T. Baker reagent grade CaF_2 and NaF powder. The resulting mixtures were pressed to 20,000 psi without binder into disk-shaped specimens and fired at 850°C for 25 h. After firing, approximately 0.5 mm of the edges and faces were removed; then the faces were gold plated in an evaporator. This first gold coating was rubbed off to remove any loose particles caused by the grinding. This proved to be an easy and convenient way to "clean" the sample. A second gold coating was evaporated on the sample at pressures less than 10^{-5} mm Hg to form electrodes. This second application of gold electrodes is not easily rubbed off. The samples were then painted with silver paint from G. C. Electronic Company to provide additional mechanical protection.

2. Experimental Method and Apparatus

Consider (for the present) an ideal dielectric containing only one type of noninteracting dipole of moment p and relaxation time τ. In the absence of a field the dipoles are randomly oriented along positions allowed by the lattice. If an electric field, E_p, is applied across the sample for a time longer than τ a portion of these dipoles will align themselves with the field. The dielectric is then cooled to a temperature such that τ is on the order of hours. At this temperature the external field can be removed and the induced polarization will remain "frozen in"; that is, the dipoles will remain in their aligned position and cannot reorient. As the dielectric is warmed up at a constant rate $b = dT/dt$; τ becomes shorter as more thermal energy becomes available and a depolarization current is observed as the dipoles lose their preferred orientations. During this randomization process the depolarization current will first increase exponentially, reach a maximum then drop to zero. The activation energy to reorient the dipole, the fundamental jump frequency (or attempt frequency), and the number of dipoles participating in the relaxation process can all be obtained from examining this depolarization current.

Starting with a first order rate equation $dn/dt = n/\tau$ where dn/dt is the rate at which the dipoles are randomizing. One can develop an equation which will describe the depolarization current

$$I(T) = \frac{N_0(1\text{-}\exp^{t}/\tau_p)p_0^2 E_p}{3kAT_p\,\tau_0}\exp(-\epsilon/kT) \times \exp\left(\frac{1}{b\tau_0}\int_0^T \epsilon^{-\epsilon/kT}\,dT\right), \quad (1)$$

where N_0 is the number of dipoles per volume in the sample, t is the time of polarization, T_p is the temperature of polarization, p_0 is the dipole moment of the dipole, E_p is the field of polarization, τ_p is the relaxation time at the temperature of polarization, A is the cross-sectional area of the sample, k is Boltzmann's constant, b is the linear heating rate and τ_0 is the fundamental relaxation time.

Features of the curve are as follows:

(1) At the depolarization current maximum, the following relationship holds:

$$\epsilon = \frac{kT_m^2}{b\tau_m} = \frac{kT_m^2}{b\tau_0}\,\epsilon^{-\epsilon/kT_m}. \quad (2)$$

(2) The activation energy is given by the initial slope of the curve:

$$I(T) = \text{const}\, e^{-\epsilon/kT}. \quad (3)$$

(3) The area under the curve is proportional to the total number of dipoles in the sample:

$$N_T = \frac{3kT_p V}{p_0^2 E_p bA}\int I dT, \quad (4)$$

where V is the volume of the sample.

(4) The activation energy and the frequency factor, τ_0, 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 side

of the following equation:

$$\tau = \tau_0 \exp(\epsilon/kT) = \frac{1}{b}\int_T^\infty I(r)\,dT/I(T^*), \qquad (5)$$

in which the numerator is the area under the curve from $T = T^*$ to $T = \infty$ and the denominator is the value of current at $T = T^*$.

Apparatus. The equipment consists of a Cary 401 vibrating reed electrometer which is capable of measuring currents as low as 10^{-17} A. A linear heating rate was obtained by matching the output of a thermocouple (which is in close proximity to the sample) to a reference voltage. This reference voltage was developed across a potentiometer which is driven by a cam. The cam was cut such that when rotated at a constant velocity the output across the potentiometer corresponds to a linear increase in temperature. If the sample temperature does not correspond to the reference, the error between the thermocouple voltage and reference voltage is fed after amplification and proper biasing, onto the grids of large power triodes which control the heater currents. The sample temperature is adjusted by passing He gas through the heater then allowing it to flow onto the sample. In this way the linearity of the sample temperature may be kept to within 0.1° over a range of 77–355°K.

The sample chamber is shown Fig. 1. It consists of a Teflon cylinder approximately 2 in. in diameter and 6 in. long in which is imbedded a copper sleeve. This copper shield (approximately 1½ in. diam by 2 in. long) serves as an electrostatic shield as well as a "heat drag." Inside the copper shield is the heater mounted in a very thin brass cylindrical shell which is insulated by nylon supports from the copper shield. The He gas, after being heated to the proper temperature, exists from this heater and flows directly onto the sample. The sample is mechanically supported and also supplied with electrical contact by two very thin circular disks in which large holes have been cut to allow better thermal exchange between the sample and atmosphere. These disks are gold coated and a thermocouple is imbedded in the lower disk a few thousands of an inch below the surface to measure the sample temperature. This lower sample support is held in place by thin

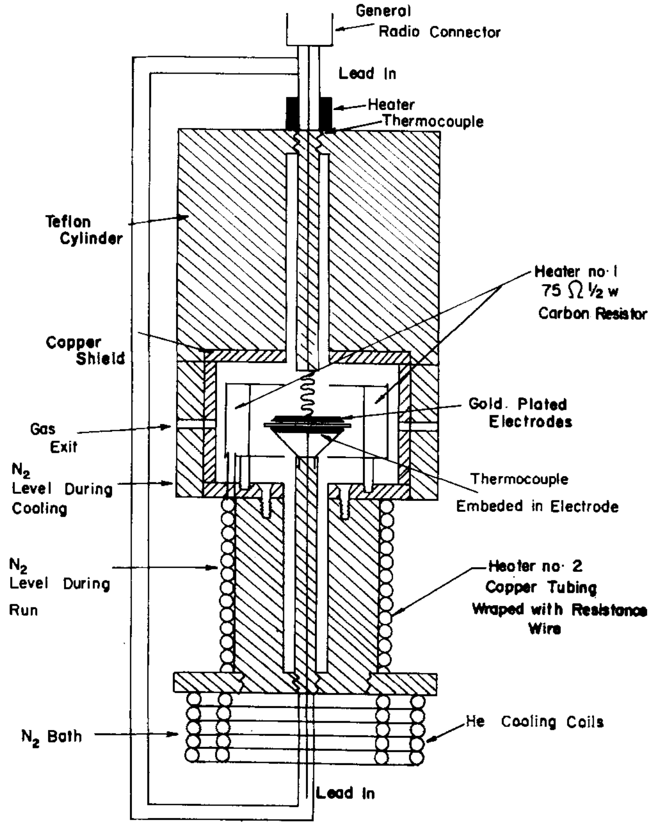

FIG. 1. Sample chamber geometry.

stainless steel wires which are supported by a Teflon rod that extends to the lower extremity of the sample chamber. The upper sample contact is held in place by a weak spring which provides sample contact and some degree of stability to the sample support system. Electrical contact is made by 5 mil Cu wires which pass through the axis of the Teflon rods and out the extreme ends of the chamber. The regions where they pass from the chamber are maintained at fixed temperatures to minimize any spurious Teflon I.T.C. signals. The He gas is cooled to liquid N_2 Temperature before entering the sample chamber and heater assembly by passing it through coiled Cu tubing attached to the bottom of the sample chamber. The sample chamber is immersed in a liquid N_2 bath at the level of the bottom of the Cu shield during the cooling cycle of the experiment and dropped slightly below this during the subsequent warmup. Electrostatic shielding is accomplished by (1) the brass foil surrounding the gas heating chamber, (2) the Cu sleeve, (3) the stainless steel Dewar, and (4) a large aluminum shield placed around the Dewar sample chamber and electrometer preamplifier. All of the electrostatic shields are connected to the same earth ground. With this experimental setup the following background effects have been observed: (1) an electrical insulation of greater than 10^{15} Ω has been maintained between the electrodes and ground, (2) spurious polarization effects due to thermal cycling of the Teflon have been illuminated, and (3) background currents at least as low as 10^{-16} A have been obtained.

Results—Experimental

The dipole relaxation in CaF_2 doped with NaF was studied as a function of concentration and the results are shown in Fig. 2. Note that the first and fourth peaks vary directly with Na Concentration while the second peak and possibly also the third peak vary inversely with the sodium content. Peaks 1, 2, and 3 can be analyzed with the methods discussed earlier and activation energies of 0.32 ± 0.02, 0.33 ± 0.03, and 0.38 ± 0.03 eV and values of τ_0 equal to 2.5×10^{-15}, 2.6×10^{-14}, and 2.3×10^{-14} sec are obtained. The main peak (peak #4) is compared with a theoretical peak for two samples with prepared sodium concentrations of 0.018 and 1.2 wt%. This comparison is shown in Fig. 3. Note

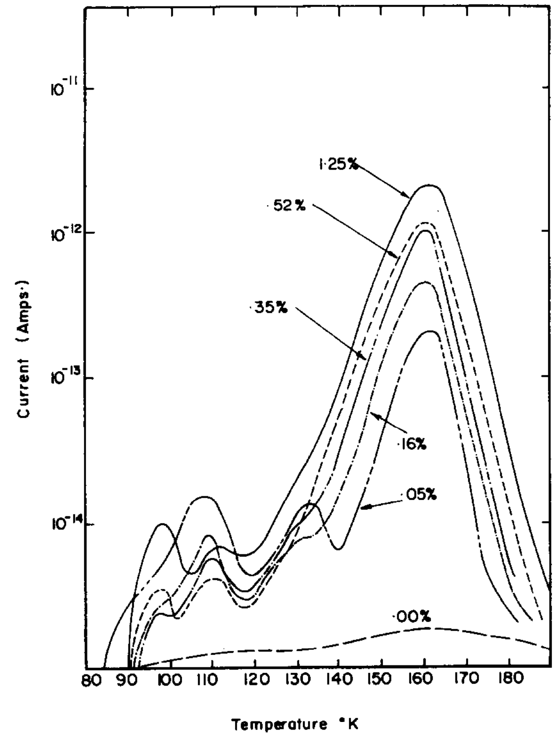

FIG. 2. I.T.C. results for several NaF concentrations in CaF_2. Note that peaks 1 and 4 are directly dependent on the sodium concentration while peak 2 varies inversely with sodium content. All samples were polarized with a field of 4000 V/cm.

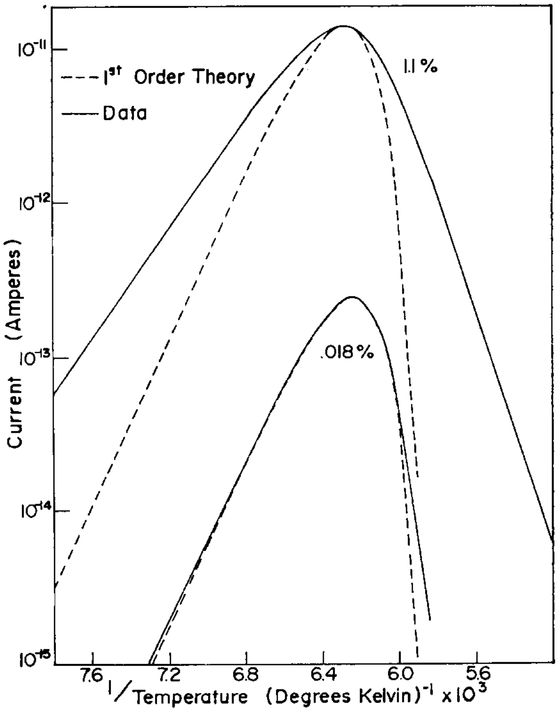

FIG. 3. I.T.C. Curves of 1.1 and 0.018% NaF samples compared with calculations assuming first-order reaction rate.

that for the low concentration sample (0.018% NaF), the experimental curve closely matches that of the ideal curve based on a single uninfluenced dipole relaxing. At higher concentrations the curve is much broader than a theoretical one.

The amount of broadening is a direct function of concentration. This is shown in Fig. 4 where the fourth peak is depicted for samples of varying Na^+ content. A way of looking at the extent of the broadening is to examine the slope of the initial portion of the I.T.C. curves. These slopes would correspond to true activation energies if the process which generated them involved isolated dipoles relaxing in only one mode. Notice at very low concentrations one obtains a value of 0.52 eV which compares favorably with a value of 0.53 ± 0.03 eV obtained from dielectric and anelastic loss for the reorientation of the Na^+–V_F^- dipole. At higher Na^+ concentrations the slopes give lower activation energies, indicating that additional effects or complications begin to perturb the model of a single, uninfluenced, relaxing dipole as the sodium concentration is increased.

Now consider a process that involves a distribution of relaxation energies which are not greatly separated in value. If an I.T.C. run is performed on a sample containing such a process, the temperature can be increased to a point short of discharging the entire polarization and then dropped to its original value. If we assume that τ_0 is approximately the same for all energies in the distribution, then the dipoles corresponding to lower values of motional energy have been eliminated or greatly reduced while those with higher energy values remain essentially intact. Subsequent heating of the sample will now give a curve produced only by randomization of dipoles with the higher motional energy values of the distribution. The 1.2 wt% sample was examined in the light of such a postulate and the results are shown in Fig. 5. The "cut" temperature is the maximum temperature obtained during the first temperature increase. Notice that runs were made where the cut temperature occurred just before the peak and at the three temperatures above the peak maximum. Not only does the activation energy increase with a higher cut temperature but also the temperature of the peak maximum is increased slightly. The shifting of the temperature maximum and the increase in the activation energies obtained from the initial slope of each curve indicate that this fourth peak of the high Na concentration samples is produced not by a process involving single relaxation energies but by a process containing a narrow distribution of relaxation energies.

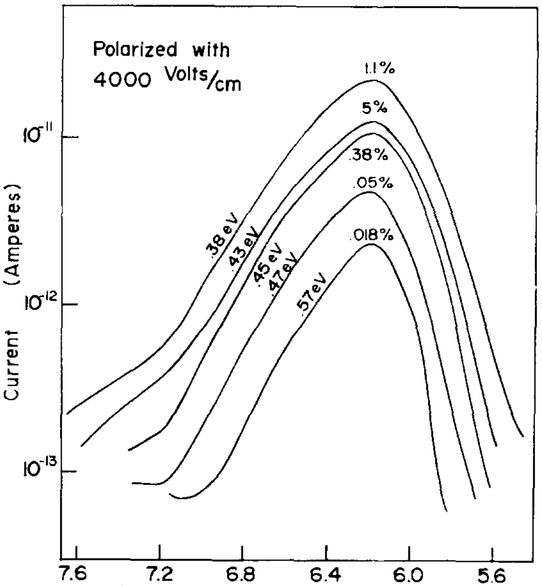

FIG. 4. The fourth (main) peak as a function of NaF concentration showing the apparent change in activation energy.

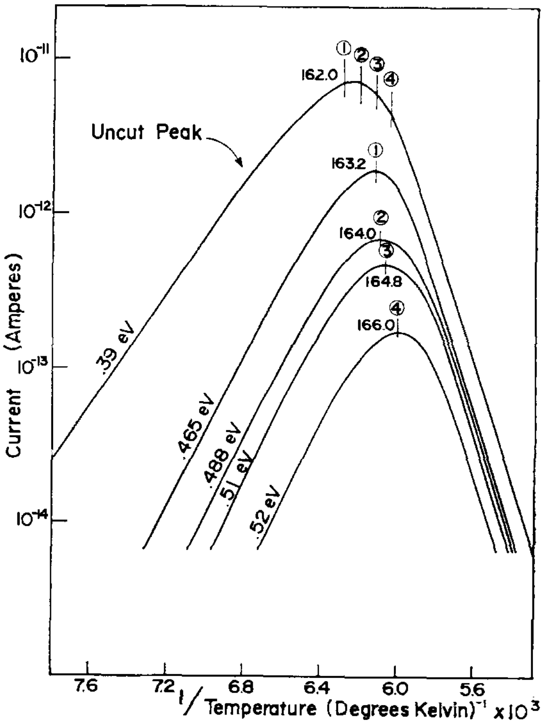

FIG. 5. The effect of "cut" runs on the fourth peak. Note that the apparent activation energy and the temperature of the peak maximum increase with increasing temperature of the "cut."

The experimental evidence, therefore, shows that at very low concentrations the fourth peak of the I.T.C. curves corresponds very closely to a curve that would be expected for dipole relaxing uninfluenced by its neighbors and can be analyzed to obtain only a single activation energy. As the concentration increases, additional effects appear and the I.T.C. curve of the main peak (#4) is not due to a single relaxation process, but to a series of processes with a narrow distribution of relaxation energies. It appears that these processes are closely related to each other and since the distribution of activation energies is strongly dependent on concentration, it is possible that dipole–dipole interactions are causing this "smearing" of relaxation energies, and hence, broadening of the peak.

Lattice Calculation of the Dipole–Dipole Interaction

In order to obtain some insight as to the magnitude of the dipole–dipole interaction and the effect this interaction might have on the I.T.C. curves, it was felt necessary to look at this problem in a semi-quantitative way. One can obtain a first approximation to the interaction energy between two dipoles in a crystal lattice by assuming (1) the stress interaction energy may be neglected, and (2) only the electrostatic interaction between a dipole and a neighboring dipole must be considered. If the dipole relaxes while in the presence of another dipole, we need to know: (1) if the dipole interaction will help or hinder the reorientation, and (2) the probability of a dipole making a reorientation transition while in the presence of one or more dipoles.

Basic Assumptions for the Lattice Calculation

1. Na^+ ions are in an equilibrium configuration at 500°C and are fixed in these positions at room temperature (fast cooling of sample).
2. The macroscopic dielectric constant is used to describe the local dielectric medium.
3. Na^+–V_F^- dipole is to be treated as a point dipole regardless of the distance from the dipole.
4. τ_0, the fundamental relaxation time, remains a constant uninfluenced by any dipole–dipole interaction.
5. Any interaction between more than two dipoles is not considered.
6. The dipole reorients by a $\langle 100 \rangle$ vacancy jump.

The electrostatic interaction energy between two dipoles is given by the classical equation,

$$U = \frac{1}{4\pi\epsilon}\left[\frac{\mathbf{P}_1\mathbf{P}_2}{r^3} - \frac{3}{r^5}(\mathbf{P}_1\mathbf{r})(\mathbf{P}_2\mathbf{r})\right], \qquad (6)$$

where $\mathbf{P}_1$ and $\mathbf{P}_2$ are the electric moments of the dipoles, $\mathbf{r}$ is the vector connecting them and ϵ is the dielectric constant of the medium in which they are imbedded. If we consider one particular dipole, all the surrounding Ca^{++} sites are possible locations for other dipoles. We can organize the calculation such that all the nearest neighbor sites are in the first shell and so forth. Thus, interaction energies can be calculated between the center dipole and a dipole which is in a specific orientation in any shell. Consider the center dipole to be aligned with the field and allow the second dipole to reorient. It is the difference of the interaction energies before and after the reorientation that will either help or hinder the second dipole in relaxing. For example, consider a dipole which is in the first coordination shell of the center dipole. There are twelve sites in this shell. A dipole in any site can be in eight different orientations, thus giving 96 possible configurations. However, from energy considerations, it can be shown that essentially all of the dipoles located in any site of this shell would be found in the lowest energy orientation or configuration. (This is not the case for all shells. For example, in the third shell, almost all dipoles are found in the lowest *two* energy configurations and in the sixth shell, dipoles would be found in all configurations.) Dipoles reorient by a $\langle 100 \rangle$ vacancy jump (*4*) hence, there would in the first shell be three (not necessarily distinct) values of this interaction energy difference, which could be realized for a dipole relaxing in a polycrystal sample. Table I shows the calculated transition interaction energy differences which are possible for dipoles located in the various shells. All calculated transitional interaction energies have been rounded off to the nearest 0.01 eV. It is now necessary to calculate the probability that a dipole will make the reorientation corresponding to these interaction energy differences.

The probability of making a specific transition, P, is

$$P = P_s P_L P_p P_C, \qquad (7)$$

where P_s is the normalized probability of finding the dipole in the shell being considered, P_L is the normalized probability of finding the dipole in a certain, configuration in that shell, P_p is the polarization factor, and P_C is a factor which describes the tendency for association of the dipoles due to their

TABLE I

ELECTRIC DIPOLE INTERACTION ENERGY AND RELATIVE PROBABILITY OF OCCURRENCE AS A FUNCTION OF SHELL NUMBER FOR VARIOUS DIPOLAR ORIENTATIONS

Shell number	Transitional interaction energy	Effective reorientation activation energy	Relative probability		Temperature of the maximum of the I.T.C. curve
			1.2%	0.5%	
1	−0.14 eV	0.38 eV	4.3×10^{-20}	1.5×10^{-20}	118
	−0.27	0.25	5.2×10^{-24}	2.2×10^{-24}	80
2	−0.05	0.47	5.2×10^{-19}	2.7×10^{-19}	147
	−0.09	0.43	1.1×10^{-20}	4.0×10^{-21}	132
3	−0.05	0.47	6.5×10^{-19}	3.4×10^{-19}	147
	−0.02	0.50	9.9×10^{-18}	4.2×10^{-18}	156
	+0.02	0.54	1.4×10^{-20}	7.7×10^{-18}	168
	−0.07	0.45	1.9×10^{-17}	6.6×10^{-21}	141
4	−0.02	0.50	2.8×10^{-18}	1.2×10^{-18}	156
	−0.03	0.49	1.5×10^{-18}	6.3×10^{-19}	153
	+0.02	0.54	6.0×10^{-18}	2.8×10^{-19}	168
	+0.03	0.55	6.5×10^{-18}	3.0×10^{-18}	171
5	−0.02	0.50	5.0×10^{-19}	2.1×10^{-19}	156
	0.00	0.52	4.2×10^{-18}	1.8×10^{-18}	162
	0.00	0.52	1.4×10^{-17}	5.8×10^{-18}	162
	−0.04	0.48	2.3×10^{-19}	1.0×10^{-19}	150
	−0.01	0.51	1.2×10^{-18}	5.2×10^{-19}	159
	+0.01	0.53	8.9×10^{-18}	4.1×10^{-18}	165
	−0.03	0.49	2.9×10^{-19}	1.2×10^{-19}	153
6	−0.02	0.50	1.9×10^{-18}	8.2×10^{-19}	156
	+0.02	0.54	2.2×10^{-18}	1.0×10^{-18}	168
7	0.00	0.52		1.1×10^{-17}	162
	−0.01	0.51		2.5×10^{-18}	159
	−0.02	0.50		1.3×10^{-19}	156
8	0.00	0.52		1.4×10^{-18}	162
9	0.00	0.52		8.4×10^{-18}	162
10	0.00	0.52		5.6×10^{-18}	162

interaction. The inclusion of the factor P_s is necessary because the number of dipoles polarized during the polarization process is, through the Boltzmann factor, dependent on the interaction energy of the two dipoles. That is because of the proximity of a second dipole it may require more or less energy to align itself with the field.

Therefore,

$$P_s = \frac{\text{number of sites in the shell}}{\text{Total number of sites which on the average contains two dipoles}}$$

$$P_L = \exp -\left(\frac{E_I}{kT_p}\right),$$

where T_p is the temperature of polarization;

$$P_p = \exp - \left(\frac{E_2}{kT_p}\right),$$

where E_I is the interaction energy between two dipoles in a specific configuration; E_2 is the difference in interaction energy of the two dipoles before and after polarization;

$$P_C = \exp - \left(\frac{E_I}{kT_q}\right),$$

where T_q is the effective quench temperature and a value of 500°C was used.

If one assumes that the energy required for a dipole to reorient while in the field of another is equal to the activation energy for an uninfluenced dipole plus the interaction energy difference, then it is possible to plot (Fig. 6) the distribution of activation energies which one would obtain from effects of the dipole–dipole interaction versus the relative probability that these activation energies will occur. It is then possible to construct the I.T.C. spectrum for relaxing dipoles including the effects of interaction. This is accomplished by placing an ideal, single relaxation I.T.C. curve at the temperatures which correspond to each of the calculated reorientation activation energies and adjusting the height of each peak to be proportional to the calculated probability for that transition.

In Fig. 7, the I.T.C. data for the 1.2 wt % sample is compared with the theoretical spectrum which is obtained when the dipole–dipole interactions are included. Because the theoretical peak is not normalized (P_p and P_C in the calculation are not normalized probabilities), this spectrum has been shifted along the ordinate until the fourth peak height corresponds to that of the data which is consistent with this zero-order calculation. The calculated spectrum predicts the main peak, which is broadened compared to an uninfluenced I.T.C. peak, and also a small peak at a lower temperature. This main peak is located at the same temperature as peak #4 and describes the broadening with considerable success as the sodium content increases. The calculated peak occurring at low temperature could very well correspond to peak #1 (some discussion of this will appear later). The calculated spectrum does not predict peaks #2 or #3 although, as mentioned before, they do not vary directly with concentration as do peaks #1 and #4. In Fig. 7 a first-order single relaxation peak is superimposed on the fourth peak in order that one may note the much better fit of the dipole–dipole interaction calculation curve than that of a curve based on a single relaxation process.

Discussion

The experimental data clearly show that a single relaxation time cannot describe the I.T.C. curves of CaF_2 doped with NaF unless the concentration of the NaF is quite low (<0.02 %). In order to explain the I.T.C. curves of higher NaF concentration one must

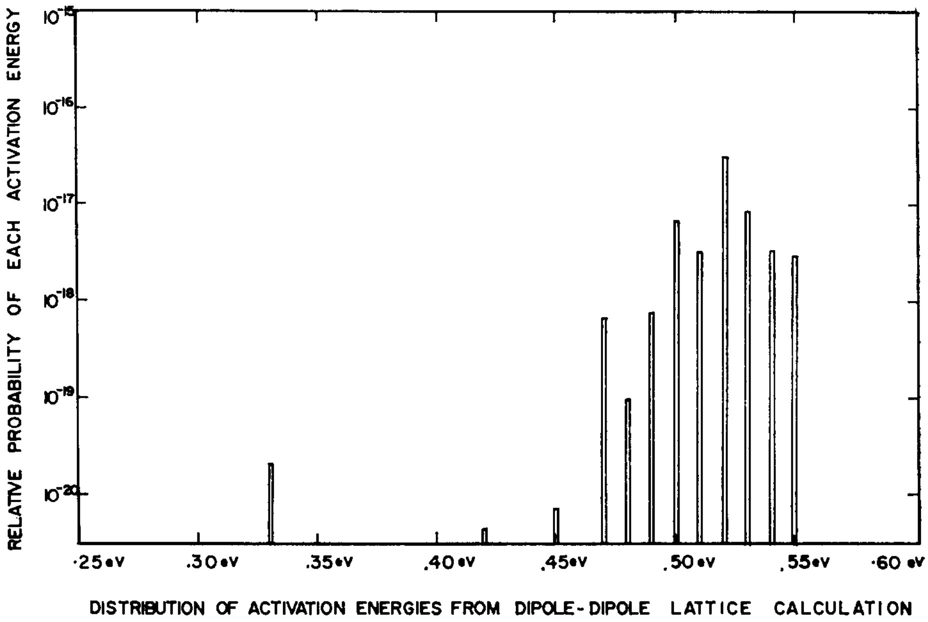

FIG. 6. The distribution of activation energies obtained from the electric dipole–dipole lattice calculation.

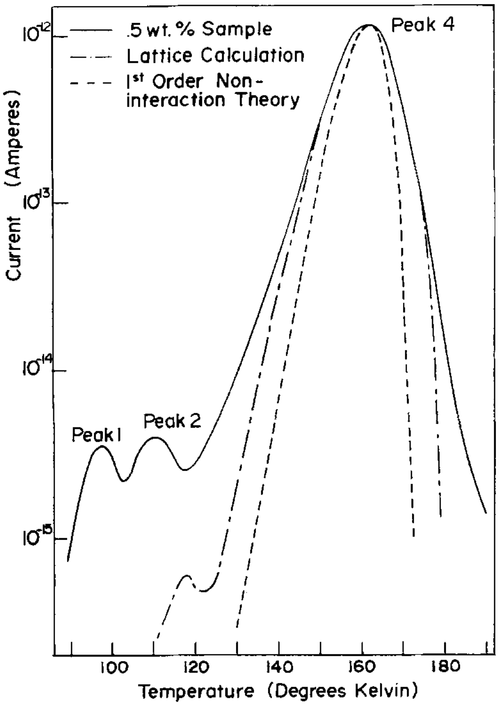

FIG. 7. Lattice calculation compared with 0.5 wt% data and single relaxation first-order theory.

take into account the dipole–dipole interactions. The I.T.C. spectrum derived from the dipole–dipole lattice calculation in most aspects compares favorably with the data. It is now interesting in the light of these results, to reexamine the basic assumptions used in the dipole–dipole interaction calculation. The assumptions of macroscopic τ and point dipoles admittedly might be very poor but should have small effects on the peak *heights* of the I.T.C. curves. However, errors due to these assumptions should manifest themselves as large effects on the *locations* of the peaks. Assumption 4 involving constant τ_0, could have large effects on both the location and magnitude of the peaks. The effects would have their most serious consequences on the I.T.C. peaks corresponding to dipoles located at nearest neighbor sites.

Two other factors could have important effects on the magnitude of the peaks. The probability factor P_s assumes that the energy barrier that the dipoles must surmount during polarization is equal to the activation energy for reorientation of an uninfluenced dipole plus the transitional interaction energy difference. In reality, the barrier is probably somewhat lower than this and hence P_s could be considerably higher. Again this effect would be most noticeable for the first I.T.C. peaks corresponding to dipoles located at nearest neighbor distances. Also when calculating P_C there is some difficulty in determining an effective quench temperature T_q. This also would markedly affect the magnitude of the first peak.

With these uncertainties in the basic assumptions, it is not surprising that the height of the first theoretical peak is not as great as observed in the experiment or that the peak position doesn't coincide exactly with the data. However, the calculation does make plausible the explanation of the I.T.C. spectrum via dipole–dipole interactions. If this hypothesis is indeed correct, one can directly monitor the electric dipole–dipole interaction with this simple technique. In this paper, we only propose the dipole–dipole interaction as one possible explanation for some of the complexities of I.T.C. spectra.

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