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Impurity-concentration effects on the dielectric relaxation of alkali halides

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The effect of the impurity concentration on the reorientation parameters of impurity-vacancy complexes (I-V) in alkali halides has been studied. The systems considered have been LiF:Ni, LiF:Co, NaCl:Pb, KCl:Ca, and KBr:Sr, with concentrations up to 10^3 ppm. A systematic decrease of the reorientation energy with increasing dipolar concentration has been detected. These effects are clear above 100 ppm of free dipoles. The experimental results have been analyzed in terms of the monoenergetic ionic-thermocurrent equations as well as with the modified theory including dipole-dipole interaction. The incidence of such correction of the experimental conditions is also discussed.

I. INTRODUCTION

Since 1964 when the ionic thermocurrents (ITC) technique was introduced by Bucci and Fieschi,[1] dipolar impurity-vacancy complexes in alkali halides and other isulators have been widely studied by using this method.

These studies have paid special attention to the reorientation of free dipoles in the low-concentration limit assuming that each dipole can rotate without interacting with the other dipoles which are present in the crystal. Under these conditions the time dependence of the polarization $P(t)$ can be described with first-order monoenergetic equations:

$$\frac{dP(t)}{dt}=-\frac{P(t)}{\tau_0}e^{-E/kT}, \tag{1}$$

where τ_0 represents the reciprocal frequency factor and E the activation energy for reorientation. The ITC curve is completely described by the activation parameter E, τ_0, and the number of dipoles N. Nevertheless, ionic thermocurrent peaks deviating from the shape predicted by Eq. (1) have been reported in some recent works in rare-earth—doped alkaline-earth halides.[2–5]

These deviations consist mainly in a broadening of the ITC peak, and the parameters E and τ_0, evaluated from Eq. (1), show a systematic dependence with the impurity concentration. Some authors have attributed these effects to dipole-dipole interaction and they have found that the agreement between the experimental and calculated curves can be improved by assuming an activation energy distribution. A Gaussian distribution gives a reasonable approach,[3,4] although Lorentzian form has also been considered.[5]

The ITC curve is now described with a four-parameter formula:

$$\begin{aligned} &I^*(T)=I(T)F(E_0,\tau_0,p,T)\,,\\ &F=\frac{1}{p\sqrt{\pi}}\int_0^\infty dE\,\exp\left[-\frac{(E-E_0)}{kT}-\frac{(E-E_0)^2}{p^2}-\int_0^T\frac{1}{b\tau_0}\left(e^{-E/kT'}-e^{-E_0/kT'}\right)dT'\right]\,, \end{aligned} \tag{2}$$

where $I(T)$ gives the classical expression for the intensity and F represents the new factor where the dipole-dipole interaction effects are included. E_0 and p are the center and the width of the energy distribution,

$$N(E)=(N/p\sqrt{\pi})e^{-(E-E_0)^2/p^2}\,. \tag{3}$$

The p parameter is a measure of the dipole-dipole interaction strength and it is concentration dependent. Pure electrostatic interaction gives a linear dependence with the number of dipoles although other interactions can break this linearity.[4] With respect to E_0 it should be concentration independent and it should correspond to the activation energy for low dipolar concentration (unperturbed energy).

The above-mentioned deviations of ITC peaks from the classical theory have not been reported for impurity-vacancy dipoles in alkali halides. It is clear that the dipolar complexes are different in alkali halides (substitutional divalent impurity and cation vacancy) than in alkaline-earth halides (substitutional trivalent impurity and interstitial anion), but the ITC behavior is determined by the dipolar nature of the defect and so both systems are expected to behave in a similar way.

Therefore, the fact that dipole-dipole interaction effects have not been reported in alkali halides could be due to the absence of systematic work about concentration effects in these materials. In the present work a systematic study considering several dopants and host materials has been made in order to have a survey in alkali halides. The systems considered have been LiF:Ni, LiF:Co, NaCl:Pb, KCl:Ca, and KBr:Sr, with concentrations up to 10^3 ppm.

Concentration effects on the activation parameters have been found above 100 ppm but the analysis of the ITC peaks with the modified equations, as proposed by den Hartog *et al.*, do not improve the fitting obtained with the classical theory. These differences between alkali and alkaline-earth halides are discussed by analyzing the sensitivity of the corrective factor F to the experimental conditions.

II. EXPERIMENTAL PROCEDURE

Crystals of LiF:Ni, LiF:Co, NaCl:Pb, KCl:Ca, and KBr:Sr were grown from suprapure material in the crystal growth laboratory of the Department of Optica y Estructura de la Materia. The growth, by the Czochralski method, was performed in an argon atmosphere.

Slabs of $10\times10\times0.5$ mm^3 were cut from the ingots and gold electrodes evaporated on both large faces of the crystal. ITC measurements have been made after quenching the samples from 350 °C. Annealing treatments have been performed in some cases at 150 °C to accelerate the dipolar aggregation. The impurity concentration in crystals is given in Table I. The ITC setup, described elsewhere,[6] operates in the range liquid-nitrogen to room temperature (LNT—RT). The depolarization currents are measured with a 401 Cary electrometer with time constant lower than 1 s. The noise level in dynamic conditions is $\leq 5\times10^{-16}$ A.

The analysis of the data was performed in the computer center Universidad Autónoma de Madrid IBM with an APL/370 IBM system. When the classical theory is used, the parameters E and τ_0 are obtained from least-squares fitting of $\ln[A_t^\infty/I(t)]$ vs T^{-1} (area method). When the modified theory [Eq. (2)] is considered the parameters E_0, τ_0, and p are obtained by minimizing the difference between the experimental and theoretical normalized curves,

$$\epsilon=\sum(I_{\text{expt}}-I_{\text{calc}})^2/N\ .$$

In both cases the theoretical curve for the best fitting is calculated.

TABLE I. Impurity concentration in the crystals.

Impurity	Concentration (ppm)
LiF:Ni	1100
LiF:Co	190
NaCl:Pb1	30
NaCl:Pb2	240
KCl:Ca	170
KBr:Sr	360

III. RESULTS AND DISCUSSION

The spontaneous aggregation of *I-V* dipoles in alkali halides has been used to obtain a wide set of concentrations. Figures 1 and 2 show the aggregation of LiF:Ni, LiF:Co, NaCl:Pb, KCl:Ca, and KBr:Sr. The free dipole concentration can be varied by a factor of 5 as shown in Fig. 1. The temperature dependence of the aggregation rate has been used to accelerate the process in those cases where RT aggregation was too slow. It can be seen in Fig. 2 that the ITC peaks do not apparently show any other change than the area diminu-

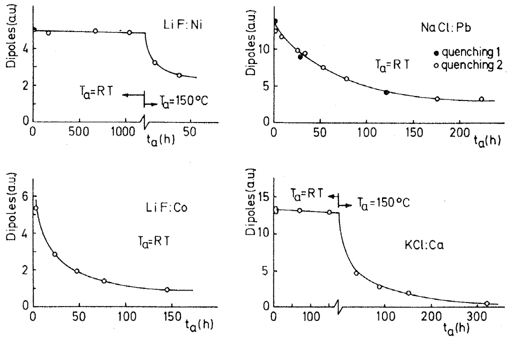

FIG. 1. Dipolar aggregation in doped alkali halides at different annealing temperatures T_a. The samples have been previously quenched at RT from 350 °C.

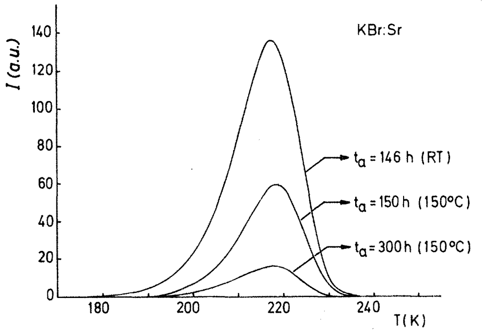

FIG. 2. Impurity-vacancy ITC peak in KBr:Sr at different aggregation stages.

tion. So we consider that aggregation is a suitable way to achieve a great number of concentrations with a limited number of samples.

A. Monoenergetic model

All the ITC peaks respond very satisfactorily to the first-order equations with a single energy. In fact, a plot of $\ln(P/I)$ vs T^{-1} shows a good linearity as given in Fig. 3, and the experimental peaks are nicely fitted with the parameters obtained from these analyses (Fig. 4). In spite of the goodness of the fits the activation parameters show a systematic dependence with the number of dipoles in the materials with the highest impurity concentration, i.e., LiF:Ni, KBr:Sr, and KCl:Ca, as can be seen in Fig. 5.

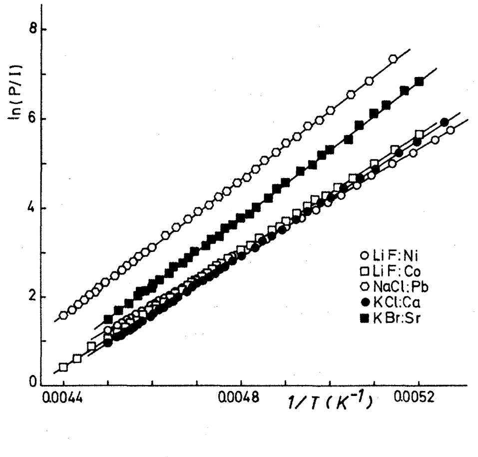

FIG. 3. Analysis of the ITC peaks with the monoenergetic model.

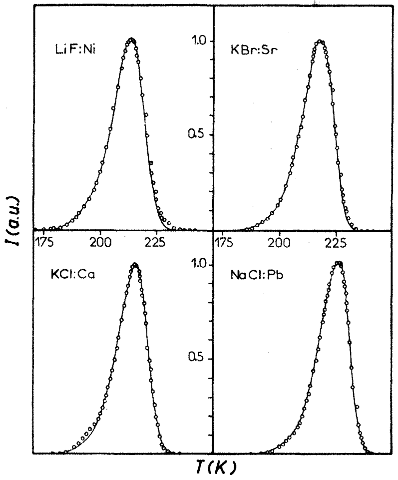

FIG. 4. Experimental (○) and theoretical (—) ITC peaks calculated with the monoenergetic model.

The parameters E and $\nu_0=\tau_0^{-1}$ obtained for different concentrations obey (Fig. 6) the equation

$$T_m \ln\nu_0 = T_m \ln(bE/KT_m^2) + E/K \approx \text{const} + E/K \,, \qquad (4)$$

which holds for first-order relaxation.[7–9]

Nevertheless, the classical ITC theory cannot explain the dependence of the activation energy with the concentration. Therefore we shall consider next the ITC theory modified with dipole-dipole interaction effects to ascertain if this theory can explain the experimental results.

B. Gaussian energy distribution

As it was indicated above an extended ITC theory including dipole-dipole interaction effects has been recently developed.[3–4] It is considered a Gaussian energy distribution with center E_0 and width p, which modifies the classical intensity $I(T)$ by a factor F given in Eq. (2).

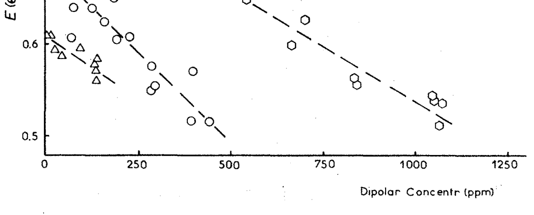

FIG. 5. Activation energy dependence with the dipolar concentration.

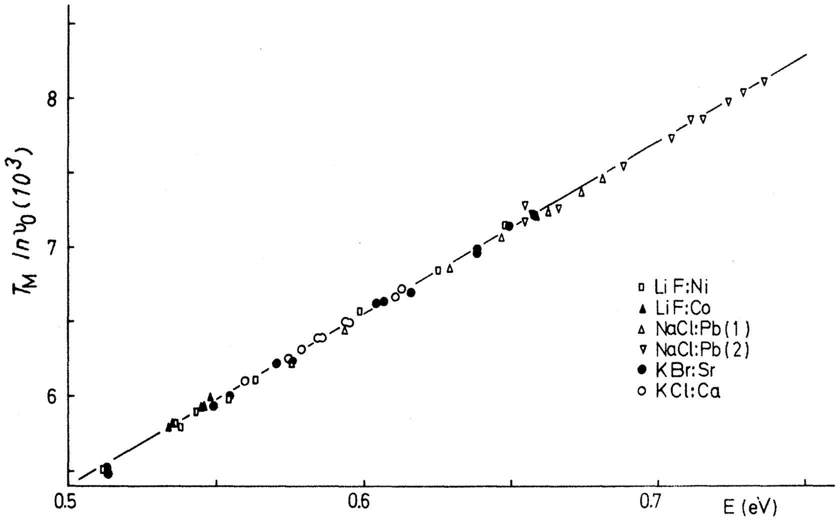

FIG. 6. Activation parameters E and $\nu_0 = \tau_0^{-1}$ are related as expected for first-order relaxation processes.

With this new theoretical approach the following points are expected[3,4,7]:

(i) Better agreement between experimental peaks and theoretical fits.

(ii) Constant values for the average activation energy E_0 and frequency factor ν_0 independent of the impurity concentration.

(iii) A certain correlation (linear for pure electrostatic interactions) between the energy distribution width p and the dipolar concentration N.

The experimental data obtained in the present work have been reanalyzed with the modified theory [Eq.(2)] and the parameters E_0, τ_0, and p have been obtained after minimizing the difference between experimental and theoretical peaks. Figure 7 shows the experimental ITC peaks altogether with the theoretical calculations by using Eq. (2).

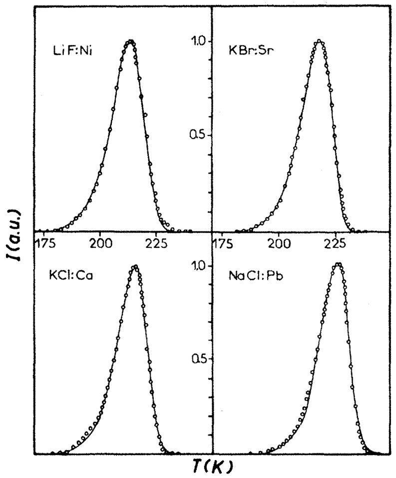

FIG. 7. Fitting of the ITC peaks assuming a Gaussian activation energy distribution. (○) experimental, (—) theory.

The revised theory does not improve the fits even in LiF:Ni where a very small deviation at high temperature appeared. Actually, some fits are slightly worse with the new theory than with the monoenergetic model, as can be seen after comparing the values of

$$\epsilon = \sum (I_{\text{expt}} - I_{\text{calc}})^2 / N ,$$

which gives a quantitative measurement of the error for both models (Table II).

In relation to point (ii) it can be seen that E_0 changes with the impurity concentration (Fig. 8) in the same way that the activation energy E changes for the classical theory, and with respect to the width of the energy distribution [point (iii)], it does not show any correlation with the dipolar concentration.

We conclude, hence, that the activation energy dependence experimentally observed in this work cannot be satisfactorily explained with the modified ITC theory. Let us note that whereas in alkaline-earth halides[3,4] the corrective factor F affects the high-temperature tail of the peak, in alkali halides this factor is only important at temperature above the ITC peak (Fig. 9). In order to understand this disparity the effect of the F factor has been examined in detail. This factor depends

TABLE II. Comparison between the fittings obtained with the classical [Eq. (1)] and modified [Eq. (2)] ITC theories.

	LiF:Ni			KCl:Ca	
N (ppm)	ϵ (10^{-3}) Eq. (1)	ϵ (10^{-3}) Eq. (2)	N (ppm)	ϵ (10^{-3}) Eq. (1)	ϵ (10^{-3}) Eq. (2)
1078	0.28	0.20	142	0.35	0.38
1070	0.16	0.11	140	0.37	0.21
1050	0.24	0.08	139	0.37	0.54
1048	0.14	0.10	138	0.45	0.38
845	0.13	0.62	97	1.12	0.74
841	0.13	0.36	49	0.50	0.31
705	0.39	0.24	30	0.30	0.28
666	0.25	0.15	19	0.84	0.80
550	0.55	0.09	8.3	0.55	0.55

		KBr:Sr			
N (ppm)	ϵ (10^{-3}) Eq. (1)	ϵ (10^{-3}) Eq. (2)	N (ppm)	ϵ (10^{-3}) Eq. (1)	ϵ (10^{-3}) Eq. (2)
445	0.19	0.19	191	0.63	0.51
399	0.35	0.19	189	0.43	0.15
398	0.27	1.18	161	0.92	1.27
297	0.28	0.23	152	2.08	0.93
290	0.29	0.06	132	0.76	1.75
289	0.30	0.13	78	0.69	0.10
228	0.29	0.21	73	1.35	1.02

on the relaxation parameters (E_0,τ_0,p) and on the experimental conditions (heating rate b) and so the difference between alkali and alkaline-earth halides could be due to differences in these experimental or intrinsic conditions.

In the present work the heating rates are close to 0.08 K/s twice the rate given in Refs. 3 and 4, and there are also important discrepancies in the activation energy values between alkali ($0.5 \leq E \leq 0.7$ eV) and alkaline-earth halides ($E \sim 0.4$ eV). The F factor changes notably with b, but simultaneously the depolarization maxima are displaced and the F factor influences always the same portion of the peak. The variations observed by changing the activation energy (Fig. 10) are clearer. The F factor is bigger for low activation energy affecting even the low-temperature side of the depolarization current but for high energies it is almost constant

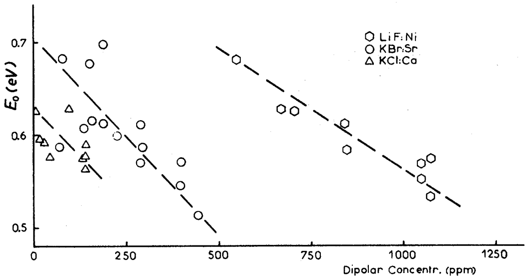

FIG. 8. Mean activation energy (E_0) dependence with the dipolar concentration.

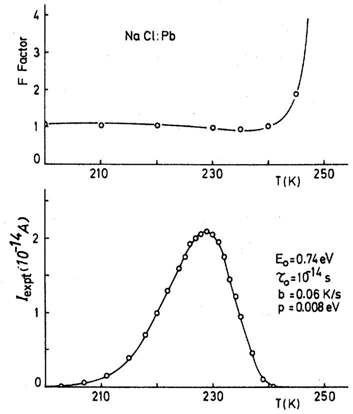

FIG. 9. Corrective F factor introduced by considering dipole-dipole interactions is only important at temperatures above the ITC peak in alkali halides (NaCl:Pb in the figure).

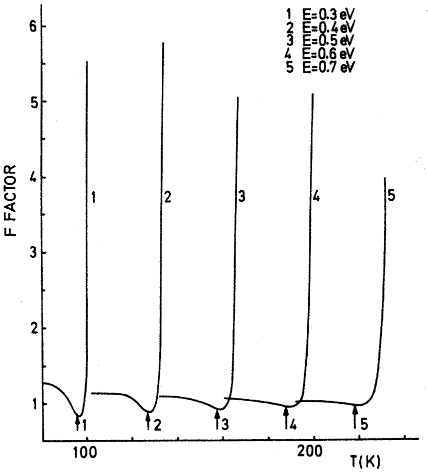

FIG. 10. F-factor sensibility with the activation energy. The arrows indicate the peak maxima. High activation energy peaks are not disturbed.

and equal to one in the peak region. These effects can explain the different influences of the F factor in alkali and alkaline-earth halides.

An alternative way of facing the problem of concentration-dependent activation energies is considering that the proximity of defects reduces the energy for its motion. In fact, the dipolar reorientation energy ($0.5 \leq E \leq 0.7$ eV) is lower than the vacancy migration energy ($0.65 \leq E \leq 0.85$ eV), i.e., the presence of the impurity reduces the activation energy. Along this line, den Hartog *et al.*[4] have found that for dipolar complexes in SrF_2:R^{3+} where the interstitial fluorine ion F^- can be in the nearest-neighbor (NN) ($r = 2.9$ Å) or next-nearest-neighbor (NNN) position ($r = 5.0$ Å) the activation energy decreases from 0.94 eV for isolated F^- migration to 0.64 and 0.47 eV for NNN and NN dipoles, respectively. They also found that the activation energy perturbation due to the proximity of other defects can be expressed as $\Delta E = -\alpha r^{-n}$, where r is the distance between defects and α and n are constants, equal to $\alpha = 1.3$ eV Å and $n = 1$ in SrF_2:R^{3+}.

Assuming that the same law ($n = 1$) remains for alkali halides and that the dipoles are randomly distributed, the reorientation energy should depend on the impurity concentration as

$$E = E_0 - \alpha N^{1/3} , \qquad (5)$$

which could account for the energy variation results (Fig. 11). Nevertheless the concentrations range is not enough to warrant the validity of Eq. (5). The confirmation of this law would require a wider concentration range.

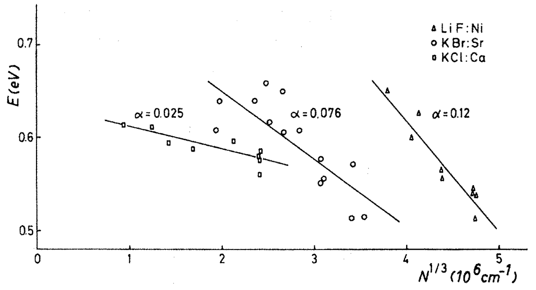

FIG. 11. Fitting of the activation energy dependence with the dipolar concentration assuming a random distribution of dipoles and a change in energy $\Delta E = -\alpha/r$; r is the mean distance between dipoles.

IV. CONCLUSIONS

The most relevant conclusions of this work are the following:

(i) A systematic decrease of the reorientation energy with increasing dipolar concentration has been detected in doped alkali halides. These effects are clear above 100 ppm of free dipoles.

(ii) The ITC theory modifed with dipole-dipole interaction effects, Eq. (2), appears unable to explain these variations in alkali halides. This theory predicts significant changes only for low reorientation energies.

(iii) An activation energy diminution due to the proximity of defects can explain the sign of the changes ΔE observed. The experimental results are compatible with a law $\Delta E = -\alpha/r$ where r is the distance between defects.

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[1] C. Bucci and R. Fieschi, Phys. Rev. Lett. 12 16 (1964).

[2] B. P. M. Lenting, J. A. J. Numan, E. J. Bijvank, and H. W. den Hartog, Phys. Rev. B 14, 1811 (1976).

[3] W. van Weperen, B. P. M. Lenting, E. J. Bijvank, and H. W. den Hartog, Phys. Rev. B 16, 2953 (1977).

[4] W. van Weperen and H. W. den Hartog, Phys. Rev. B 18, 2857 (1978).

[5] E. Laredo, M. Puma, N. Suarez, and D. R. Figueroa, Phys. Rev. B 23, 3009 (1981).

[6] F. Cussó, J. L. Pascual, and F. Jaque, J. Electrostatics 3, 125 (1977).

[7] Z. C. Nauta-Leeffers and H. W. den Hartog, Phys. Rev. B 19, 4162 (1979)

[8] F. Cussó and F. Jaque, Solid State Commun. 35, 965 (1980).

[9] J. Hernández A., H. Murrieta S., F. Jaque, and J. Rubio O., Solid State Commun. 39, 1061 (1981).