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Analysis of the ionic-thermal-current peaks with a distribution in the reorientation energy

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A computer program has been written to analyze ionic-thermal-current (ITC) peaks. The reorientation energy is assumed to have a distribution of width σ around a mean value E_0. The relaxation parameters E_0, σ, τ_0 and the number of dipoles N_D are calculated by two different methods. One set is obtained after a least-squares fitting of the experimental data was performed and another set by matching a set of experimental parameters chosen with a certain criterion. The two methods are applied to analyze SrF_2:La ITC spectra in the cases of the monoenergetic model, the Lorentzian, and the Gaussian energy distribution. The Gaussian distribution for the reorientation energy gives the most credible results, provided that the curves are efficiently cleaned. Only in this case do the two methods converge to the same set of relaxation parameters; the value of σ is then an increasing function of the nominal concentration and not of N_D. The origin of the curve broadening is discussed in terms of dipole-dipole interaction, and it is shown that this effect alone is not responsible for the energy distribution. Moreover, evidence of the presence of satellite peaks on each side of the main relaxation peak is presented. These satellite peaks explain the need of analyzing only efficiently cleaned curves for obtaining reliable results.

I. INTRODUCTION

In 1964 Bucci and Fieschi[1] introduced the ionic-thermal-current technique (ITC) which is a powerful tool for studying the electric-dipole relaxation in ionic crystals. The electric dipoles present in a crystal are mainly due to the different types of defects in the lattice. For example, in fluorite crystals doped with trivalent cations R^{3+} (R^{3+} being La, Ce, Pr, Nd, Sm, Gd, Ho, Tm, and Y), it is well known that the compensating defect is an interstitial fluorine ion F_i^-. If these ions are in the vicinity of each other, we will have NN (nearest-neighbor) or NNN (next-nearest-neighbor) dipoles. In these structures several other types of larger defects have been postulated such as dimers,[2] tetramers,[3] and R^{3+} F_{i2}^- complexes.[4]

During an ITC warmup, the values of the current as a function of the temperature are reproducible for similar experimental conditions, such as polarization time, temperature and electric field, and heating rate; the critical features of the ITC curve such as the temperature of the maximum current, and the height and width of the curve, are found to vary by no more than 2% from run to run. From the ITC spectrum, using the Bucci and Fieschi equations, one can obtain the values of the relaxation parameters, E (the activation energy for the reorientation of the dipole responsible for the relaxation under study), τ_0 (the inverse frequency factor), and N_D (the number of dipoles of each species present in the crystal if we assume an undistorted point ion model for calculating the dipolar moment). The main difficulty is to assign to each ITC peak a specific dipolar relaxation, especially if more than one peak is present in the spectrum.

Another difficulty comes from the overlapping of two neighboring peaks. It is then necessary to "clean" the curve either by partially discharging the low-temperature tail of the composite curve and/or choosing carefully the polarization temperature to preclude polarization of the high-temperature species. From these clean peaks the values of E and τ_0 are determined. Our experience on CaF_2 (Ref. 5), SrF_2 (Ref. 5), and BaF_2 (Ref. 6), doped with trivalent cations of the lanthanide series and Y^{3+}, shows a systematic disagreement between the experimental clean ITC peaks and the Bucci and Fieschi theory, a disagreement which is well outside the experimental uncertainty. A typical case is shown in Fig. 1. A similar departure from the theoretical expectation has been reported already in several articles from Den Hartog's laboratory, using doped SrF_2 (Ref. 7) and CaF_2 (Ref. 8). These authors have found that the agreement of the calculated curve with the experimental points may be greatly improved by assuming that the reorientation energy is not single valued, but has a Gaussian distribution with a small width ($\sigma \simeq 3\times10^{-3}$ eV) around a mean value E_0. They perform a four-parameter least-squares fitting (E_0, σ, τ_0, N_D) by using the Marquardt method. The assumed energy distribution has been attributed by them to the electrostatic interaction between dipoles and also to contributions from elastic lattice deformations. The dipole-dipole interaction was first introduced by Shelley and Miller[9] in order to explain the broadening of ITC curves observed in powdered samples of CaF_2:Na^+. They conclude that dipole-dipole interaction is one possible explanation for some of the complexities of the ITC spectra.

The purpose of this paper is to investigate the

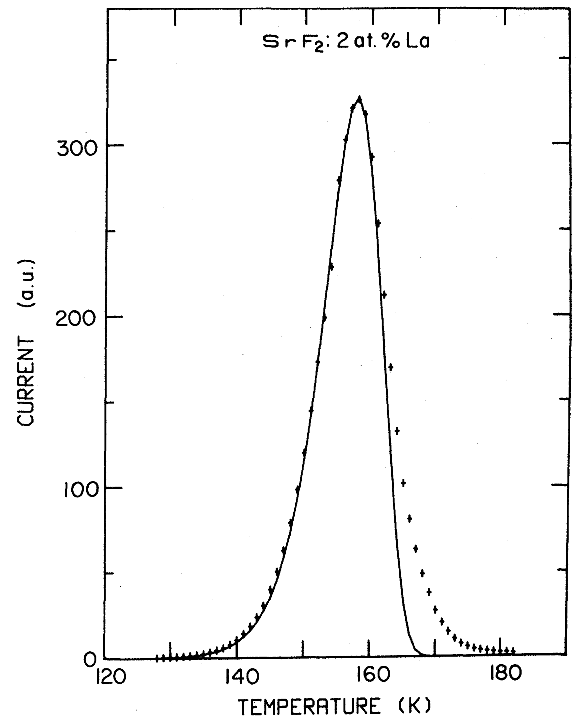

FIG. 1. An ITC experimental peak (++++) and the corresponding calculated curve (solid line) using the Bucci and Fieschi theory. The experimental points have an uncertainty of ±2 arbitrary current units.

role that a particular distribution in the energy has on the agreement between the experimental points and the calculated ITC curve. It will be seen that several sets of values of E_0, σ, and τ_0 can be obtained from the same experimental points, depending on the criteria used in the analysis, and on the method used in cleaning the ITC peak. We find below that the most reliable set of values for E_0, τ_0, and σ is obtained for "very efficiently cleaned" peaks by considering a Gaussian distribution for the reorientation energy.

II. THEORY

The monoenergetic theory for ITC, introduced by Bucci and Fieschi, is based on the existence of N_D noninteracting dipoles per unit volume, each with dipole moment μ. These dipoles reorient with a unique characteristic relaxation time

$$\tau(T)=\tau_0\exp\left(\frac{E}{kT}\right). \qquad (1)$$

If one has a partially oriented state, at a temperature T, where the crystal has a polarization $P(T)$, and is heated with a linear rate b in the absence of an applied electric field, then the depolarization current density is

$$J(T)=\frac{P_0}{\tau_0}\exp\left(\frac{-E}{kT}\right)\exp\left[\frac{-1}{b\tau_0}\int_0^T dT'\exp\left(-\frac{E}{kT'}\right)\right], \qquad (2)$$

where P_0 is the equilibrium polarization for the crystal at the effective polarization temperature T_p. For cubic crystals, P_0 is given by

$$P_0=\frac{N_D\mu^2\epsilon_p}{3kT_p} \quad \text{for } kT_p \gg \mu\epsilon_p, \qquad (3)$$

where ϵ_p is the externally applied polarization field and k is the Boltzmann constant.

As we have stated already, the clean experimental ITC curves given by fluorite crystals are generally wider than the curves calculated with the model outlined above. One way for broadening the theoretical curve is to assume that the reorientation energy is not single valued but has a distribution $D(E)$ around a value E_0, as has been previously done for a Gaussian distribution by Van Weperen *et al.*[7] Let us call $P(E,T)dE$ the polarization at a temperature T of the sample due to those dipoles whose activation energy lies between E and $E+dE$. In the case where $kT_p \gg \mu\epsilon_p$, the polarization $P(E,T)dE$, which is proportional to the number of dipoles whose energy lies between E and $E+dE$, can be written

$$P(E,T)dE=P(T)D(E)dE\,. \qquad (4)$$

The contribution to the total current density of the dipoles in this energy interval for a temperature T is

$$J(T,E)dE=\frac{P(E,0)dE}{\tau_0}\exp\left(-\frac{E}{kT}\right)\times\exp\left[-\frac{1}{b\tau_0}\int_0^T dT'\exp\left(-\frac{E}{kT'}\right)\right]. \qquad (5)$$

The total current density produced by the crystal at temperature T can now be written in the following way:

$$J(T)=\frac{P_0}{\tau_0}\int_{-\infty}^{+\infty} dE\, D(E)\exp\left(-\frac{E}{kT}\right)\times\exp\left[-\frac{1}{b\tau_0}\int_0^T dT'\exp\left(-\frac{E}{kT'}\right)\right], \qquad (6)$$

where

$$P_0=\int_{-\infty}^{+\infty} dE\, P(E,0) \qquad (7)$$

and the value of P_0 is given by expression (3).

In order to evaluate $J(T)$ a computer program was written which allows for the following possibilities: (a) Given a set of parameters E_0, τ_0, N_D, μ and b, and an energy distribution $D(E)$, the program computes the ITC curve for this relaxation; (b) given a set of experimental points $J(T)$, b, the form of $D(E)$ and μ, it computes the best set of values for E_0, τ_0, σ the width of the energy distribution and N_D using a least-squares fitting (LSF); (c) given a set of experimental parameters, chosen with certain criteria, it computes the best set of values for E_0, σ, τ_0, and N_D, that best matches these experimental parameters. (As the LSF method generally gives different set of values corresponding to very closely spaced minima, we have made sure that the values for the relaxation parameters reported here correspond to the absolute minimum.) The set of input parameters is the following: The temperature at which the maximum current occurs T_M, the maximum intensity of the current I_M, the reorientation energy E_e calculated from the low-temperature side of the experimental curve between two temperatures T_i and T_f, the width of the ITC experimental curve at a certain height, typically $0.2I_M$, the linear heating rate b, and the electric dipolar moment μ. This method will be referred to from now on as the EPF method.

The input energetic parameter E_e is obtained from the variation of $\log I$ as a function of $10^3/T$ as is shown in Fig. 2 for SrF_2:La^{3+}. This figure is representative of many ITC peaks. The slope calculated between T_i and T_f gives a value for the energy E_e within 1% or better. T_i and T_f are chosen by a linear regression program so as to maximize the correlation factor between the experimental points. The minimum number of points to be considered is imposed by the user. In this work the minimum number of data points considered was nine points with a density of one point per degree. The obtained value for E_e would not depend on the choice of T_i and T_f if the energy is single valued and $T_f \ll T_m^1$. Actually, E_e depends on the choice of T_i and T_f; if after the fitting, we calculate the slope of the current curve between these two same temperatures, the same value for the energy should be obtained.

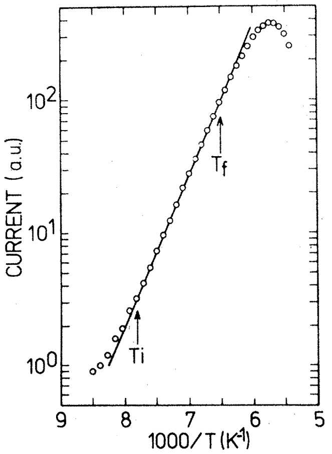

FIG. 2. Variation of $\log I$ versus $10^3/T$ for an ITC peak given by a crystal of SrF_2: La^{3+}. T_i and T_f indicate the temperature range chosen to evaluate E_e. The experimental points (000) have an indetermination of ±2 arbitrary current units.

Besides the relaxation parameters E_0, σ, τ_0, and N_D, the program yields the value of the mean-square displacement Φ which is a measure of the quality of the EPF method. For a given peak the Φ obtained in this way is not necessarily the Φ obtained with a least-squares fitting. The parameter Φ is defined as $\Phi \equiv I_M^{-1}\sum_i[(I^{(i)}_{\rm exp} - I^{(i)}_{\rm calc})^2]/(N^2 - N)^{1/2}$.

III. RESULTS

In our laboratory the kind of analysis described above has been systematically applied to ITC curves in the systems BaF_2:R^{3+} (R^{3+} being La, Ce, Pr, Nd, Sm, Gd, Ho, Tm, and Y),[6] SrF_2:La, and CaF_2:La,[5] all of these systems yield satisfactory results. In the case of BaF_2 crystals, the ITC spectrum presents two relaxation peaks overlapping to some extent. An efficient cleaning of the curve was performed before making any relaxation parameter determination. For as given CaF_2:La crystals, a simpler spectrum with a single peak is obtained. The intensities involved here are very low and prevent any attempt of cleaning the curves efficiently. In SrF_2:La the spectrum is composed of two nonoverlapping curves, the lowest-temperature peak ($T_M = 158$ K) being approximately 20 times more intense than the other ($T_M = 219$ K). This intense peak has been attributed to the relaxation of NN dipoles, whereas the second peak has been assigned to a cluster.[5] Because of this isolated peak, SrF_2:La seemed to be the appropriate system for a thorough analysis and comparison of the different methods used to obtain a set of relaxation parameters from an ITC relaxation peak.

The dipolar peak shown in Fig. 3, before cleaning [curve (a)], does not appear to depart significantly from the shape predicted by the monoenergetic model. Curve (b) in Fig. 3 shows the same peak after an efficient cleaning has been performed.

A. Results using the monoenergetic model

The ITC curve shown in Fig. 3 [curve (a)], was fitted assuming the monoenergetic model, using the two modes of operation of our program. The LSF and EPF modes gave significantly different values for the energies and τ_0. For the two analyses, the parameters obtained for a crystal with a La concentration c, expressed in mole fraction,

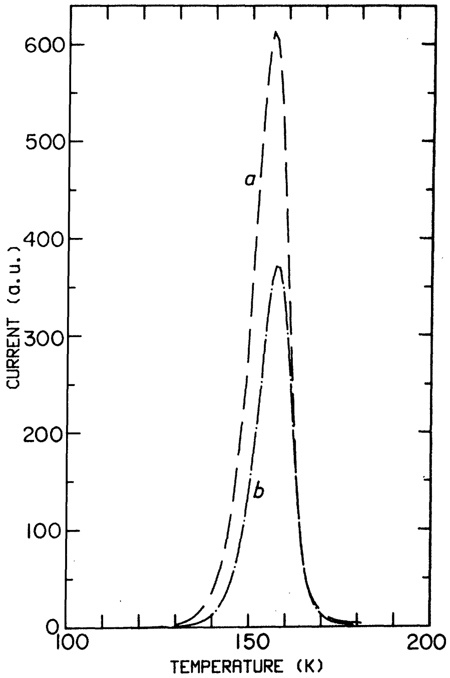

FIG. 3. The low-temperature ITC peak for a SrF$_2$: 5 $\times 10^{-3}$La^{3+} before [curve (a)] and after [curve (b)] an efficient cleaning. Curve (a) corresponds to a polarization temperature higher than T_M while curve (b) corresponds to a polarization temperature of 152 K and was partially discharged up to T_M. The uncertainty of the data is ±2 arbitrary current units ($I_{Ma} = 2.44 \times 10^{-12}$ A).

of 5×10^{-3} are $E = 0.436$ eV, $\tau_0 = 3.8\times10^{-14}$ sec, $\Phi = 2.50\times10^{-3}$ and $E = 0.409$ eV, $\tau_0 = 3.1\times10^{-12}$ sec, and $\Phi = 3.67\times10^{-3}$, respectively. It can be seen that for the case of the LSF mode, the value obtained for Φ shows a better agreement between the data and the model than for the case of the EPF mode. Moreover with the EPF mode, the calculated curve is wider than the experimental one for uncleaned peaks.

A cleaned curve [e.g., curve (b) of Fig. 3] for this same concentration was then fitted. The LSF mode usually gave values of the energy lower than the EPF mode. The results are $E = 0.450$ eV, $\tau_0 = 1.6\times10^{-13}$ sec, and $\Phi = 3.07\times10^{-3}$; and $E = 0.462$ eV, $\tau_0 = 6.4\times10^{-14}$ sec; and $\Phi = 3.24\times10^{-3}$, respectively. In Fig. 4, the values of the energies obtained for concentrations ranging from 10^{-3} to 5×10^{-2} are shown for cleaned and uncleaned peaks and for different modes of operation of our program, assuming that $\sigma = 0$.

B. Results using a Lorentzian energy distribution

The Lorentzian energy distribution $D(E) = \sigma\pi^{-1}/[(E - E_0)^2 + \sigma^2]$, where σ is the half-width at half-height, was used for fitting cleaned and uncleaned ITC peaks. The LSF mode gave, in both cases, the best mean-squares displacement Φ, of all the other fittings performed using different expressions for $D(E)$. The relaxation parameters are shown in Table I for SrF$_2$ doped with 5×10^{-3} La^{3+}. It is worth noting that if one calculates the energy E_c, given by the rise of the calculated curve between the same values of T_i and T_f which were chosen for calculating E_e, the difference $\Delta E = E_c - E_e$, can reach 0.08 eV, which is far beyond the precision of our energy determinations. Also the values obtained for the inverse frequency factor are, in general, much too small (by approximately a factor of 100) to have a physical meaning. Now, if we want the value of E_c to be equal to E_e, the program should be used in the EPF mode. In this case, however, it was found that the program was never able to fit simultaneously both the low-temperature side and the width of the ITC curve.

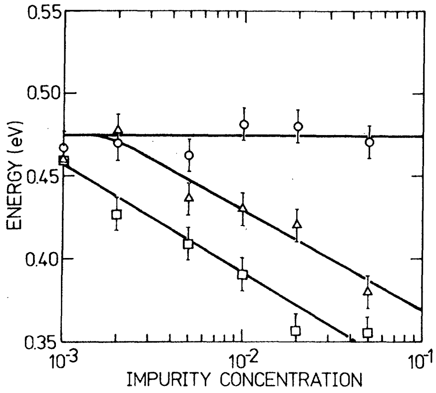

FIG. 4. Variation of the reorientation energy as a function of the nominal impurity concentration in SrF$_2$: La^{3+}, assuming $\sigma = 0$. ○○○: Clean peaks, EPF mode; □□□: unclean peaks, EPF mode; △△△: unclean peaks, LSF mode.

C. Results using a Gaussian energy distribution

A Gaussian energy distribution of the form

$$D(E) = \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right), \qquad (8)$$

was then tried. In the EPF mode this distribution

TABLE I. Relaxation parameters obtained for SrF$_2$:La with a Lorentzian energy distribution. (LSF mode).

E_0 (eV)	σ (10^{-3} eV)	τ_0 (10^{-15} sec)	Φ (10^{-3})
0.505 [a]	3.7	2.1	2.11
0.540 [b]	4.5	0.19	1.39

[a] Unclean curve.

[b] Clean curve.

was used to analyze only clean relaxation peaks, because the width of the unclean peaks was larger than the one calculated for $\sigma=0$. The results obtained for the values of E_0, σ, τ_0, and Φ are shown in Table II as functions of the nominal lanthanum concentration of the SrF_2 crystals. For each concentration, the LSF method was also tried and the relaxation parameters obtained for very efficiently cleaned peaks were equal to the ones obtained with the EPF method within the precision of our technique.

TABLE II. Relaxation parameters obtained for SrF_2:La with a Gaussian energy distribution (EPF mode).

c	E_0 (eV)	σ (10^{-3} eV)	τ_0 (10^{-14} sec)	Φ (10^{-3})
10^{-4}	0.474	0	2.3	3.32
10^{-3}	0.467	0	2.9	3.09
2×10^{-3}	0.470	2.0	3.3	1.76
5×10^{-3}	0.463	2.5	6.3	2.86
10^{-2}	0.485	5.8	1.4	3.17
2×10^{-2}	0.489	9.1	1.0	4.60
5×10^{-2}	0.492	11.0	0.9	4.10

IV. DISCUSSION

The discrepancy in the energy values for $\sigma=0$ in the EPF mode reported in Fig. 4 depends on the cleaning of the curve and the impurity concentration of the crystal; this shows the need of an efficient cleaning before any energy determination, even if the unclean peak does not seem to have any complicated structure, as it is the case for SrF_2:La [see Fig. 3(a)]. In the LSF mode the same kind of discrepancy exists but the difference in the energy values of clean and unclean peaks is smaller, although nevertheless significant. Moreover the uncleaned curves analyzed in the EPF mode (in which the low-temperature side of the curve is heavily weighted) give the smallest values for E; this indicates that some structure must be present in the ITC peak.

As we have seen above, the experimental clean curves can only be consistently described with the nonmonoenergetic model. The existence of a distribution of activation energy has been previously attributed to dipole-dipole interaction.[10] In order to evaluate the magnitude of this interaction we used a Monte Carlo calculation for a system of N point dipoles ($N=10^3$) occupying fixed random positions and orientations, chosen from those allowed in the fluorite structure. This calculation was performed for various impurity concentrations. The resulting energy for a dipole i in the field of the N-1 remaining dipoles can be written

$$E=-\vec{\mu}_i\cdot\frac{\sum_{j=1}^{N}3\hat{r}_{ij}(\vec{\mu}_j\cdot\hat{r}_{ij})-\vec{\mu}_j}{r_{ij}^3}\,, \tag{9}$$

where $\vec{\mu}_i$ is the dipolar moment of the ith dipole, r_{ij} is the distance between the ith and the jth dipole, $\hat{r}_{ij}$ is the unit vector in the direction of $\vec{r}_{ij}$, and the summation is performed over all the j values except $j=i$.

The results for BaF_2 with 10^{-3} impurity concentration and for the case of NNN dipoles are shown as a histogram in Fig. 5. This histogram looks very similar to that obtained by Van Weperen *et al.* in Ref. 10. It can be easily seen that the histogram is well described by a Lorentzian distribution which is drawn as a solid line in the same figure. This motivated the previously described use of a Lorentzian energy distribution to fit the ITC data. The results described in the preceding section show that this distribution provides the lowest values for Φ. However, the low values obtained for τ_0, and the inability for the program to fit simultaneously both the low-temperature side and the width of the ITC curve make the use of this energy distribution unreliable for obtaining a set of relaxation parameters from the ITC peaks.

Concerning the Gaussian distribution, there is still a discrepancy between the results obtained with unclean ITC curves when analyzed by the EPF and LSF methods. The results obtained from either method should converge to the same set of values if the distribution energy is purely Gaussian. This lack of convergence can be best visualized in Fig. 6. In this figure, the variation of $\Delta E=E_c-E_e$, obtained using the LSF method, versus the nominal impurity concentration is repre-

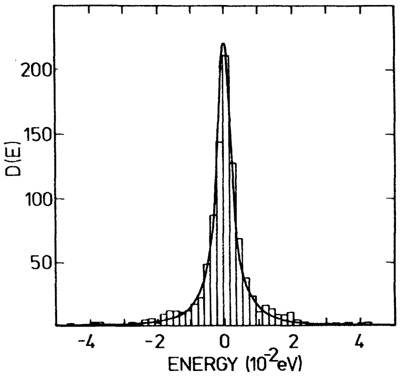

FIG. 5. The histogram is the result of a Monte Carlo calculation of the energy distribution due to the dipole-dipole interaction for 10^3 randomly quenched dipoles in a fluorite structure with a dipole concentration of 10^{-3} (mole fraction). The solid line represents the Lorentzian which has the same width at half-height.

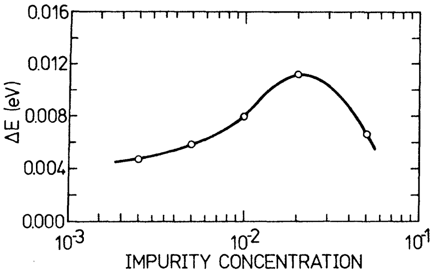

FIG. 6. $\Delta E = E_c - E_e$ versus nominal lanthanum concentration in SrF_2. E_c was obtained with the LSF method.

sented. The value of E_c was obtained by performing an LSF calculation with a fixed value for E_0. This value is the average value of the reorientation energies shown in the second column of Table II. The fact that ΔE has a positive value indicates that the low-temperature tail of the experimental curve presents a higher contribution to the current than what is expected if the energy distribution is purely Gaussian. One possible interpretation is that this effect can be due to the existence of satellite peaks besides the central peak. This central peak is the one which remains after an efficient cleaning of the curves. The satellite peaks are clearly visible in Fig. 3 of Ref. 11, in the case of BaF_2:La^{3+}. In the case of SrF_2:La^{3+}, these satellite peaks were seen after a very careful choice of polarization temperature and time.

Now, the question arises as to whether the inclusion of a distribution of activation energy is necessary to describe the experimental curve, or if the existence of these satellite peaks is sufficient to account for the observed broadening of efficiently cleaned curves. In Fig. 7, we have represented the variation of σ (which is a measure of the broadening of the curve) obtained in the EPF mode and for a Gaussian distribution of activation energy as a function of the nominal impurity concentration in SrF_2:La^{3+}. These σ were obtained after exactly the same cleaning procedure. Now if one supposes that the contribution of the satellite peaks to the total intensity is related to the intensity of the main relaxation peak, then two situations can be thought of. First, if the relative intensity of the satellite peaks to the main peak is conserved as the doping level increases, then the widening of the clean curves should not vary with dopant concentration; σ should be independent of the nominal impurity concentration, which is not the case as can be seen in Fig. 7. Second, if the intensity ratio is proportional to the impurity concentration in dipolar form c_D, then c_D should have a similar behavior to the one shown in Fig. 7. In Fig. 8 we have plotted the variation of c_D versus the nominal concentration of La^{3+}; c_D was calculated from the height of the unclean curves using the method described previously by us.[11] As one can see, c_D is not an increasing function of the nominal concentration and presents a maximum between 10^{-2} and 2×10^{-2} in a region where σ is definitely increasing. The evidence just discussed justifies the necessity to take into account the distribution energy in addition to the existence of satellite peaks. Another fact that points in this direction is the behavior observed in Fig. 6 for the variation of ΔE versus c. The decrease of ΔE as c reaches higher values can be explained by the widening of the main peak. The value of $\Delta E = E_c - E_e$ (between T_i and T_f) for unclean peaks should be zero in the absence of satellite peaks. If we start from low concentration, as σ and c_D are small, most of the intensity is due to the main peak and in the region chosen by the program to calculate E_e, the contribution of the satellite peaks is not significant and ΔE should be small. As the concentration and σ increase, we first expect an increase in ΔE because the contri-

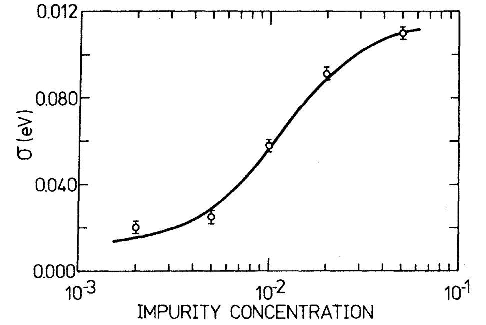

FIG. 7. Variation of σ as a function of the nominal lanthanum concentration in SrF_2 for clean peaks, using a Gaussian energy distribution.

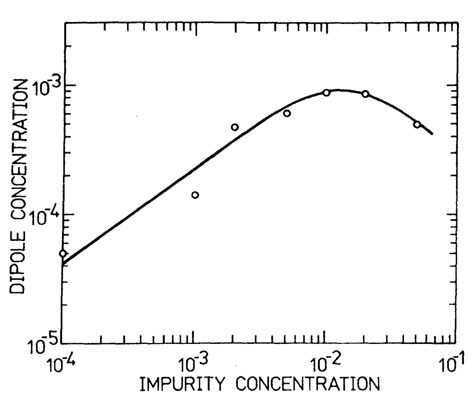

FIG. 8. Variation of the lanthanum concentration under dipolar form versus the nominal lanthanum concentration. (The error bar on the dipole concentration is of the size of the open circles.)

bution of the satellite peaks becomes more important; and second, as σ still increases, the widening produced on the main relaxation peak diminishes the effect of the satellite peaks in the region where ΔE is calculated and the value of ΔE decreases. Therefore ΔE versus c should present a maximum as shown in Fig. 6.

Another consequence of the existence of a distribution energy is the correction resulting from peak broadening that should be made on the values of I_M, the maximum depolarization current, used to calculate the number of dipoles N_D responsible for a given relaxation peak. In the case of SrF_2:La, with $c = 5 \times 10^{-2}$, this correction produces an increase in the value of N_D of 17%. This is due to the fact that the area under the ITC curve produced by a constant number of dipoles N_D is constant. The widening of the curve then produces a decrease in the height of the maximum, which can be evaluated.

V. CONCLUSIONS

In this paper we have shown, by comparing two methods of analysis of the ITC curves (EPF and LSF modes) the necessity of using very efficiently cleaned curves when performing a computer determination of a reliable set of dipole relaxation parameters. Such a cleaning procedure has not been used in the computer fittings done by previous authors. A relaxation peak can be considered efficiently cleaned when analysis with the EPF and the LSF modes produces equivalent sets of relaxation parameters.

We have shown that in the case of SrF_2:La there are contributions to the main relaxation peak from hidden satellite peaks. This main relaxation peak is, in addition, broadened by a distribution in the reorientation energy, whose width σ is an increasing function of the nominal impurity concentration in the crystal, and not of c_D. The dipole-dipole interaction calculated with a model of a quenched random configuration of dipoles does not account for the Gaussian distribution observed in SrF_2:La, as the histogram is described by a Lorentzian distribution. Even if we do not exclude the fact that the Gaussian form of the energy distribution could be produced by a more realistic model of mobile dipoles, we observe that the behavior of the width of the distribution does not follow the variation of the number of free dipoles in the crystal. Therefore the dipole-dipole interaction alone cannot be responsible for the calculated σ values. Another effect that could produce a distribution of energy is the deformation induced in the lattice by all the types of defects present in the matrix, as the variation of σ is strongly correlated to the nominal impurity concentration of the crystal (e.g., strains due to aggregates and higher dislocation densities produced by higher solute concentrations).

Several possibilities can be thought of to account for the existence of the satellite peaks. The interstitial fluorine ions can follow different paths for reorienting, giving rise to different relaxation parameters that should produce closely spaced ITC peaks. Also, the position of the La cation could be off center of the normal fluorine ions cube, as has been determined by Aalbers and den Hartog[12] in SrF_2:Gd. The impurities, being in an off-center position when the crystal is polarized, produce dipoles of slightly different lengths. These dipoles would then yield satellite peaks on each side of the central relaxation peak which will be the most intense peak.

In conclusion, in this work we have shown that, in systems of the type described here, the analysis of the experimental results using the Bucci and Fieschi model can only be a zeroth-order approximation. A more realistic model must allow for an energy distribution of width σ and to the existence of satellite peaks that in some cases can only be evidenced by a thorough analysis as the one described here.

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

[2] C. R. A. Catlow, J. Phys. C 6, L64 (1973).

[3] C. R. A. Catlow, J. Phys. C 9, 1859 (1976).

[4] J. H. Crawford and G. E. Matthews, Semicond. Ins. 2, 213 (1977).

[5] D. R. Figueroa, M. Puma, E. Laredo, and N. Suárez, *Simposio de Física de la Materia Condensada - parte experimental*, 1ras. Jornadas Científicas de la Universidad Simon Bolivar, edited by E. Laredo (Equinoccio, Caracas 1980).

[6] E. Laredo, D. R. Figueroa, and M. Puma, J. Phys. (Paris) 41, C6-451 (1980).

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

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

[9] R. D. Shelley and G. R. Miller, J. Solid State Chem.

1, 218 (1970).

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

[11] E. Laredo, M. Puma, and D. R. Figueroa, Phys. Rev. B **19**, 2224 (1979).

[12] A. B. Aalbers and H. W. den Hartog, Phys. Rev. B **19**, 2163 (1979).