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ABSTRACT

A number of experiments carried out by means of ITC technique in the temperature range 80-200 K shows unequivocally that *n. n.* Rare Earth Fluorine Interstitial (RE-FI) dipole reorientation occurs in CdF_2 :Eu, resolving the puzzle of the lack of this kind of relaxation in trivalent ions doped CdF_2 , as reported by previous authors. The activation energy for orientation ($E = 0.40$ eV) and the preexponential factor ($\tau_0 = 10^{-13}$ s) are evaluated for the principal ITC peak ($T_M = 152.5$ K) discussed and compared with the analogous parameters in Eu doped Ca and Sr fluorides. Other ITC peaks at 168 and 186 K are also analyzed.

A parallel study on CdF_2 :Gd shows that electronic effects are not negligible and can mask dipolar relaxations. The difference between Eu and Gd is discussed.

1. Introduction

An increasing interest has been devoted recently to the study of dielectric and ionic transport properties of CdF_2 pure and doped with monovalent and trivalent cations⁽¹⁾⁻⁽⁴⁾. This interest was stimulated since the discovery of the conversion of CdF_2 containing small amounts of trivalent ionic impurities from an insulator to a *n*-type semiconductor when heated in Cd vapor at 500°C ^{(5),(6)}. In alkali doped CdF_2 , between 20-300 K, Kunze and Müller⁽¹⁾ found ionic thermoconductivity (ITC)⁽⁷⁾ peaks due to reorientation of monovalent cation-fluorine vacancy dipoles in the low temperature range, and peaks due to space charge in the high temperature range. Surprisingly, in the rare earth doped samples no signal due to orientation of trivalent cation-fluorine interstitial (RE-FI) dipoles was detected. This feature outlines a striking difference between CaF_2 and CdF_2 since it is well known that rare earth doped CaF_2 shows two well defined ITC peaks^{(8),(9)} due to orientation of RE-FI dipoles. The lower temperature peak (~ 50 K) is assigned by Stott and Crawford to the presence of fluorine interstitial in the next-nearest-neighbour-position (trigonal symmetry). It seems however unlikely that jumps from one *nnn* position can take place⁽¹⁰⁾. The higher temperature peak (~ 140 K), ascribed to the presence of fluorine interstitial in the nearest-neighbour position (tetragonal symmetry), was examined more extensively^{(8),(9),(11)-(13)}. This unexplained difference between RE doped CaF_2 and CdF_2 stimulated us to undertake the study of CdF_2 doped with Eu^{3+} and Gd^{3+} by means of ITC technique.

2. Experimental details.

The samples were obtained from Optovac Inc. (pure CdF_2). Some samples were kindly supplied by Dr. J. B. Feldmann (pure CdF_2 and Gd doped CdF_2) and by Dr. E. Loh (Eu doped CdF_2). Thin slices were obtained by cutting single crystal ingots with a wire saw: the specimen surfaces were then polished by lapping. The thickness of samples ranged from 0.6 to 1 mm, the area from 0.5 to 1.2 cm^2 .

The samples were submitted to different etching procedures: 1) they were washed in

ammonia solution then rinsed in methanol as suggested by Kunze and Müller⁽¹⁾; 2) they were simply rinsed in acetone or ethanol

The ITC measurements were obtained: 1) by putting the bare sample within electrodes; 2) by coating the sample surfaces with colloidal graphite in order to improve the contact with electrodes, 3) by interposing two thin teflon foils between electrodes and sample in order to obtain blocking electrodes

The ITC measurements were performed by the usual procedure⁽⁷⁾. The crystal slab was polarized in a static electric field (ranging from 10^3 to 2×10^4 V/cm) for the polarizing time t_p , at the temperature T_p and then cooled down to the temperature T_f , where the field was switched off. The polarizing time t_p ranged from 1 to 15 min: it is worthwhile noticing that generally t_p was 3 min. During the above steps the dipoles become polarized at saturation and remain orientated in the same configuration obtained at the polarization temperature, because at low temperature the relaxation time is practically infinite. The crystal was then warmed up at nearly constant rate: the dipole relaxation time for orientation gets shorter and shorter and dipoles lose their preferred orientation, giving rise to a depolarization current. This was detected at linearly increasing temperature by a vibrating reed electrometer (Cary 31V) and recorded by Speedomax. The apparatus can measure currents as low as 10^{-16} A. The reproducibility of measurements was within 2%.

Two cryostats with different performances were employed: the former, with vertical identical shaped aluminium electrodes, assured the minimum temperature gradient through the sample: in the latter, with horizontal gold electrodes, the top one can be put in contact with liquid nitrogen in order to get a very fast quenching of the sample.

3. Results

3.1 General features of ITC peaks in $\text{CdF}_2:\text{Eu}$ and $\text{CdF}_2:\text{Gd}$

In our ITC measurements we were concerned with the temperature range between 80 K and 200 K, neglecting on purpose the higher temperature region where the complex space charge or charge displacement peaks occur, as reported by previous authors^{(1) (3)}. Moreover in the above low temperature range ITC peaks due to reorientation of interstitial fluorine-rare earth dipoles are expected to occur for the sake of analogy with CaF_2 rare-earth doped^{(8) (9) (11)-(13)}.

Figure 1 shows the ITC spectrum of an Eu doped CdF_2 slice between teflon blocking electrodes (see section 2).

Curves a) and b) were obtained by polarizing the sample at $T_a = 165$ K and $T_b = 175$ K respectively for 3 min with 500 V. Two peaks can be resolved at 152.5 K and 168 K. It is worthwhile noticing that another peak appears at 186 K, but it will not be considered extensively in this work. This complex structure resembles that found by Wagner and Mascarenhas in $\text{SrF}_2:\text{Eu}$ ⁽¹⁴⁾.

Figure 2 shows the ITC spectrum of Gd doped CdF_2 , with graphite improved contacts, for different polarization temperatures $T_{p,n}$ (indicated by arrows) and $T_{f,n}$ (see section 2). The

polarization temperature range for each ITC run is shown by horizontal lines. The polarization field and polarization time t_p were 160 V/cm and 3 min respectively

It turns out, from figure 2, that the proper choice of T_p and T_f allows to distinguish at least three peaks at 118, 143 and 160 K. By comparison of figures 1 and 2, ITC peaks both in Gd and in Eu doped CdF_2 , appear in the same temperature region where RE-F1 dipoles reorientation peaks occur in CaF_2 and SrF_2 as shown by the vertical arrows at the top of figures

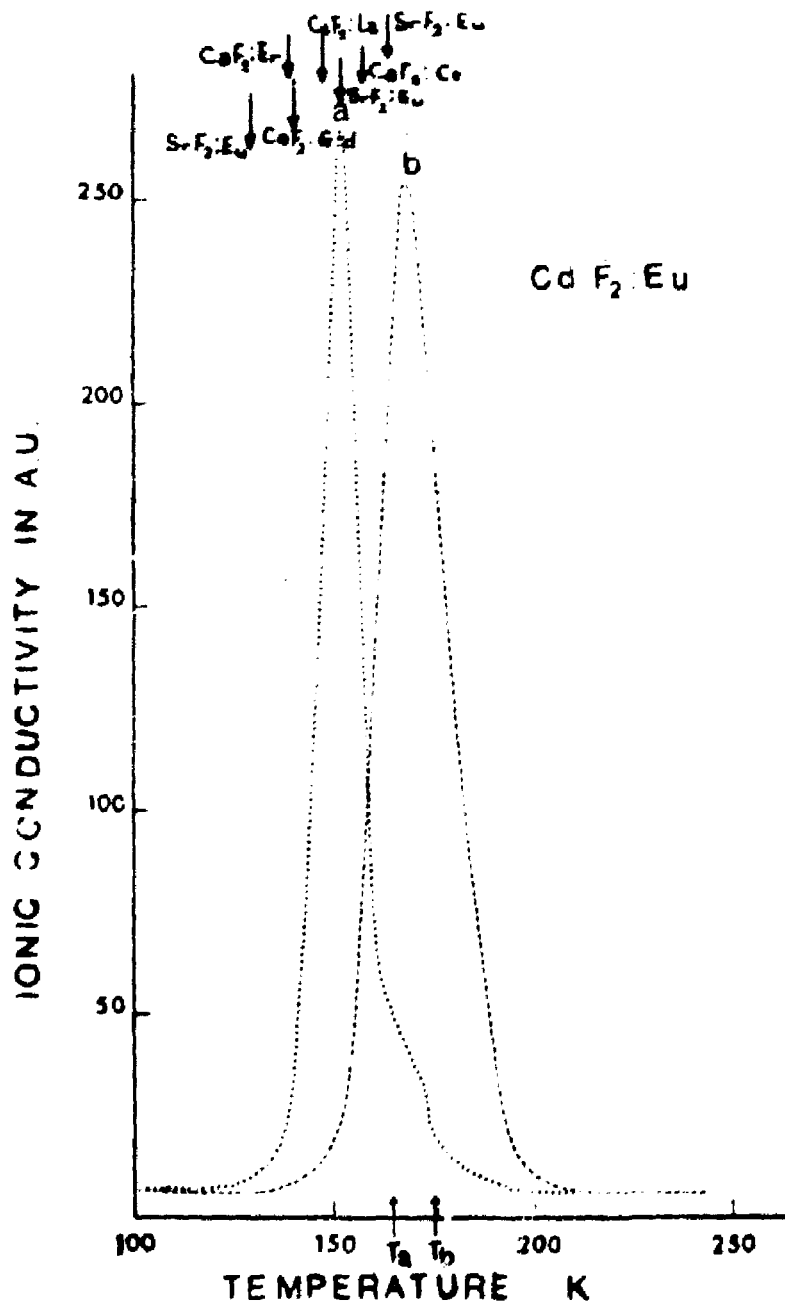


Fig 1

Ionic thermoconductivity in $\text{CdF}_2 : \text{Eu}$ with blocking electrodes.
Polarization temperature was $T_p = 165 \text{ K}$ for curve a; $T_p = 175 \text{ K}$ for curve b.
The arrows on the top show the peak temperatures of ITC band due to RE-F1 dipoles in rare earth doped CaF_2 and SrF_2

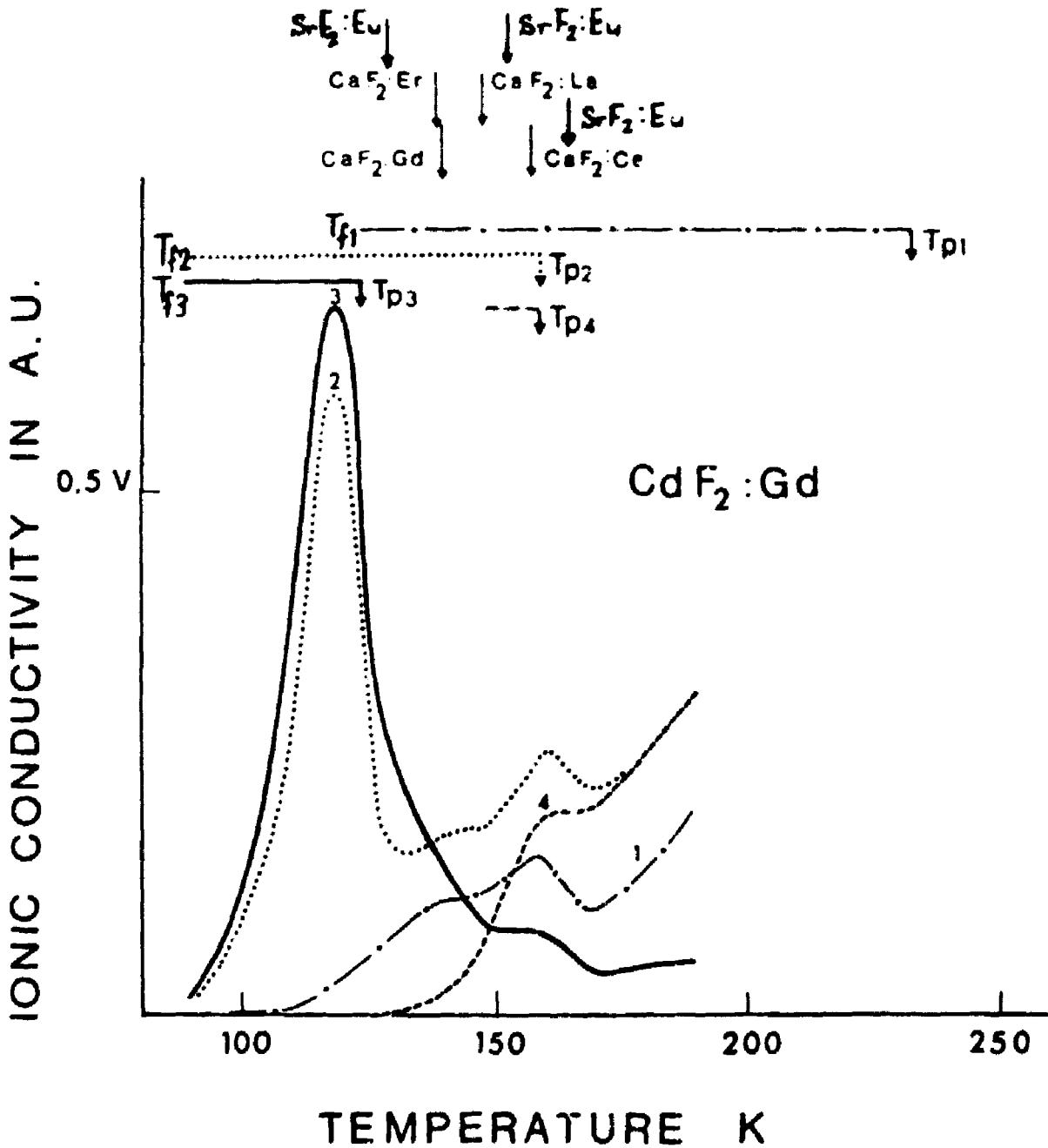


Fig 2

Ionic thermoconductivity in $\text{CdF}_2:\text{Gd}$ with graphite improved contacts.

Polarization temperatures $T_{p,n}$ and temperatures at which the electric field was turned off, $T_{f,n}$ are shown for each curve n . The arrows on the top show the peak temperatures of ITC band due to RE F1 dipoles in rare earth doped CaF_2 and SrF_2 .

3.2 Effect of T_p , t_p and contacts on the position and intensity of ITC peaks in CdF_2 : Eu and in CdF_2 : Gd

We must emphasize that the position, at which various peaks occur in Gd and Eu doped CdF_2 , does not depend on the polarization temperature T_p and polarization time t_p : the slight peak shifts among different curves shown in figure 2 must be obviously ascribed to the mutual overlapping of the neighbour bands, whose intensity changes on the polarization temperature T_p . Moreover the different kinds of contacts described in the previous section do not affect the position of peaks. However the use of blocking electrodes affects the intensity of depolarization peaks due to Eu and Gd in surprisingly different way. In Gd doped CdF_2 the depolarization current signals I and I_0 of samples with and without blocking electrodes respectively are strikingly different and their ratio is quite far from the expected value⁽¹⁵⁾:

$$I = I_0 \frac{\epsilon_1 d_c}{\epsilon_1 d_c + \epsilon_c d_t} \quad (1)$$

where $\epsilon_1 = 2$ and $\epsilon_c = 9$ ⁽¹⁶⁾ are the static dielectric constants of teflon and CdF_2 respectively. d_c and $d_t/2$ are the thicknesses of the sample and of the teflon layer respectively. The expected value of I/I_0 in CdF_2 : Gd was ≈ 0.3 , while the measured one was less than 10^{-2} . This striking difference turns out chiefly for the peak at 118 K, while is less astonishing for the other peaks. On the contrary, in the case of CdF_2 : Eu the expected and measured values of I/I_0 were in a reasonable agreement.

3.3 Comparison with pure CdF_2

It must be noticed that in the same temperature range ITC spectrum of pure CdF_2 does not show any peak which can be identified with those appearing in Gd and Eu doped CdF_2 . Actually a weak ITC band occurs in pure CdF_2 in the temperature range 120-200 K (see Fig. 3) but with striking differences with respect to Eu and Gd doped CdF_2 as explained in the following.

- 1) The band is very small, i. e. nearly 300-400 times weaker than the peak in Gd and Eu doped CdF_2 respectively (in all the cases, bare samples were introduced between electrodes, see section 2).
- 2) The Temperature at which the maximum of ITC peak occurs in pure CdF_2 does depend on the polarization temperature T_p and polarization time t_p . In figure 3 curves 1, 2 and 4 were obtained by polarizing the sample with $E_p = 8330$ V/cm at $T_p = 151$ K for $t_p = 3, 15$ and 1 min respectively, down to $T_f = 123$ K. The observed peak temperature shift cannot be at all ascribed to differences in the heating rate during ITC detection. In fact, the heating rate β , which was 0.125 K/s in the region where ITC band occurs, showed changes within 1.5% through the three runs. Also the band intensity is strongly affected by t_p . Curve 3 is still more meaningful: T_p, t_p, T_f and E_p were the same of curve 2, so the polarization P , which remains frozen in when the field E_p is turned off at T_f , must be the same given by the area under curve 2. The sample was then warmed up, but the heating was stopped at $T = 155$ K (a temperature slightly lower than the peak temperature of curve 2: during this step only a fraction of polarization P is released. The sample was cooled down again to T_f and finally warmed up in order to release the residual

frozen in polarization completely: curve 3 gives the depolarization current versus temperature detected during this step. The peak is still more shifted to higher temperature. The above results suggest that the ITC spectrum in the temperature range 120-200 K in pure CdF_2 is not given by a single peak, but is due to the thermal induced disordering of "dipoles" with different relaxation times, possibly with a continuous relaxation time distribution (or to the thermal induced release of carriers from traps with energy depths distributed continuously)

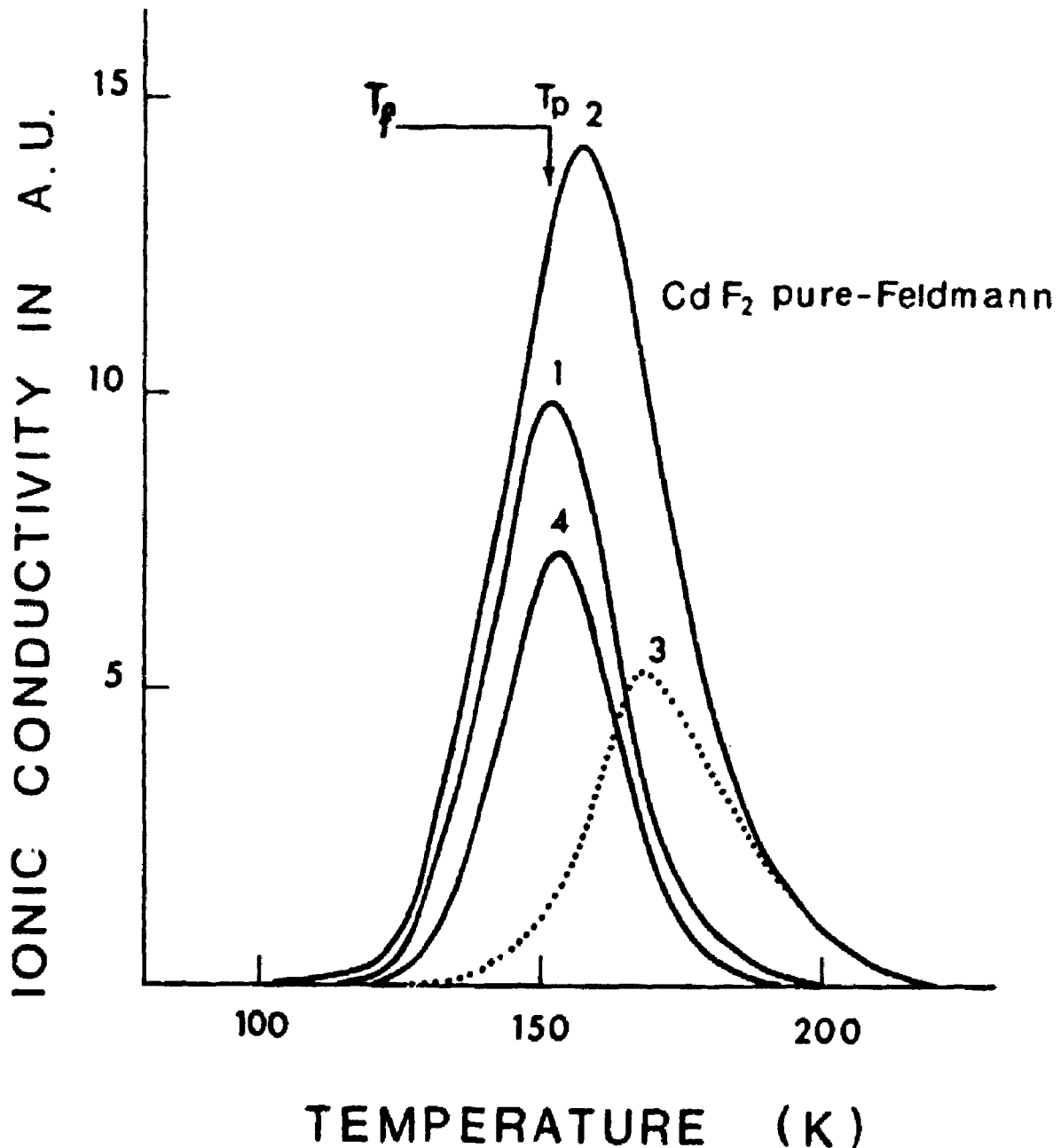


Fig. 3

ionic thermoconductivity in pure CdF_2 . The polarization temperature range (shown on the top) and the polarization field $E_p = 6.330 \text{ V/cm}$ are the same for all curves; polarization time t_p is 3 and 1 min for curves 1 and 4 respectively; 15 min for curves 2 and 3. Curve 3 is obtained after a partial discharge to 150 K.

It must be recalled that Kunze and Müller⁽¹¹⁾ really found an ITC peak in the range 180-220 K in Na doped CdF_2 , that they ascribed to charge carrier displacement (CD band). However the features shown by our band in pure CdF_2 are not consistent with those of the Kunze and Müller band. So we rule out the possibility that our band is due to the presence of sodium traces. Nevertheless we looked for the low temperature band due to the reorientation of Na ion fluorine vacancy dipoles found by the above authors at 103.5 K. We actually found a very weak band peaked at 106 K which we ascribed to residual Na impurities, due to their relatively high solubility in CdF_2 (as NaF)⁽¹⁷⁾. Furthermore the low intensity of the band allowed us to conclude that our samples are quite pure. Incidentally, here we report the activation energy for orientation of sodium anion vacancy dipoles measured by using the methods⁽¹⁷⁾ described in details later. The activation energy was found to be 0.34 ± 0.02 eV in good agreement with Kunze and Müller value of 0.31 eV.

As a concluding remark to this section, we can say that the peaks detected in $\text{CdF}_2:\text{Gd}$ and $\text{CdF}_2:\text{Eu}$ in the temperature 120-200 K are really different from ITC bands detected in the same range in pure and Na doped CdF_2 .

3.4 $\text{CdF}_2:\text{Eu}$: Linearity and Activation Energy Measurements

The intensity of a) and b) peaks was studied versus the intensity of the polarizing voltage V_p for Eu doped CdF_2 : the results are shown in figure 4. Linear relationship between peak intensity and V_p holds for both peaks, at least up to 1500 V, as expected for non interacting dipoles.

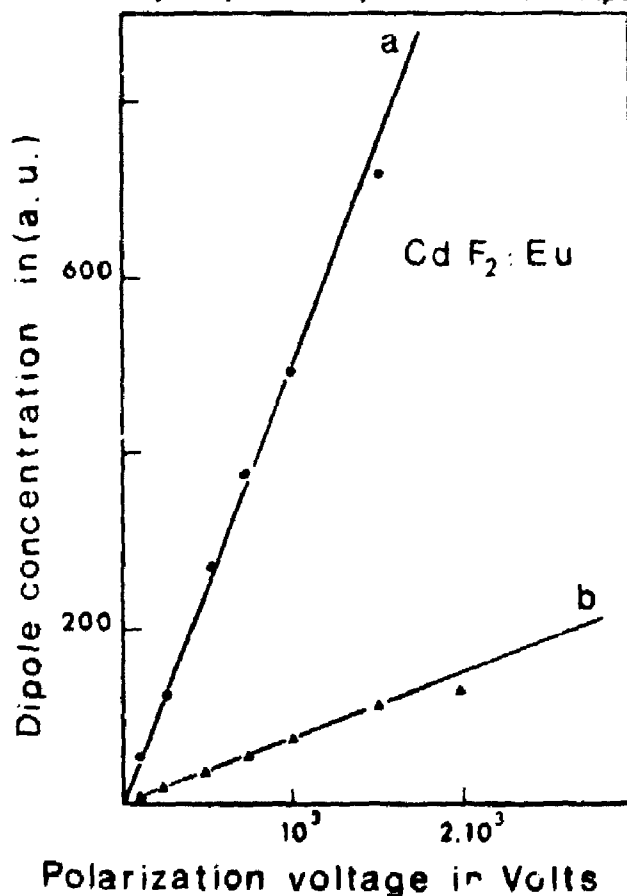


Fig. 4

The dipole concentrations related to ITC peaks a and b of figure 1 are plotted versus polarizing voltage V_p for $\text{CdF}_2:\text{Eu}$ sample with blocking electrodes.

This result stimulated us to investigate if the dipole disorientation kinetics could be obtained from the shape of at least one of the peaks. If the dipole disorientation occurs through a first order monomolecular kinetics, the depolarization current density $j(t)$ is described by⁽⁷⁾:

$$j(T) = \frac{Np^2 E_p \alpha}{\kappa T_p} \left(\tau_0 \exp \frac{\epsilon}{kT} \right)^{-1} \times \exp \left[- \int_0^T (\beta \tau_0 \exp \frac{\epsilon}{kT'})^{-1} dT' \right] \quad (2)$$

where N is the dipole concentration, p the dipole moment, α a geometrical factor, T_p and E_p are the polarization temperature and field, $\tau_0 \exp \epsilon/kT = \tau(T)$ is the dipole relaxation time, τ_0 the pre-exponential factor, ϵ the activation energy for dipole orientation and finally β the heating rate. If the above hypothesis holds, the activation energy ϵ can be obtained in two ways, i. e.:

$$\ln \frac{\int_T^{\infty} j(T') dT'}{j(T)} = \ln \tau_0 + \frac{\epsilon}{kT} \quad (3)$$

and, for $T \ll T_M$

$$\ln j(T) \cong \text{const.} - \frac{\epsilon}{kT} \quad (4)$$

where T_M is the temperature at which the peak maximum occurs. A logarithmic plot of the left hand side expressions in (3) and (4) versus $(T)^{-1}$ gives two specular straight lines, i. e. with the same slope absolute value, but opposite sign. In figure 5 the experimentally determined values of the left hand side of eq. (3) (curve 1) and (4) (curve 2) were plotted versus $1000/T$, for instance for band a). Obviously care was taken to avoid the overlapping of side peaks, by properly choosing T_p and T_f and by using the partial discharge technique⁽⁷⁾. Two straight lines can be really identified in figure 5; from the absolute value of the slope, the orientation activation energy turns out to be 0.40 eV. From eq. (3) the pre-exponential factor too can be calculated as $\tau_0 \cong 10^{-12}$ s. These values are in fine agreement with those found for RE-FI dipoles in CaF_2 (8), (9), (11) (14), as discussed in detail in section 4.

It must be noticed that such an unequivocal behaviour cannot be ascertained for peak *b* due to the unavoidable overlapping of the neighbour peaks. Incidentally it must be reported that the linearity checks carried out for band appearing at 186 K did not give satisfactory results. However the relative activation energy ϵ could be evaluated easily: ϵ was found to be 0.40 eV and $\tau_0 \sim 10^{-11}$ s.

3.5 CdF_2 : Gd

The situation in Gd doped samples is much more complex, because, even if the ITC peaks are, unambiguously, due to Gd however their intensities are not linear function of E_p and activation energy determination becomes difficult due to the important overlapping of the nearest bands. An attempt to evaluate ϵ for band peaked at 118 K gave very low values (about 0.1 eV), which are too far from the value 0.4 eV typical of RE-FI dipoles in CaF_2 and CdF_2 : Eu.

It is worthwhile noticing that preliminary dc measurements (i. e. measurements of the dc current which flows through the sample when electric field E is on) performed at constant temperature ($T_p = 162$ K) showed the same current versus applied field functional dependence that was found for the thermal induced depolarization current (measured at the peak for the ITC

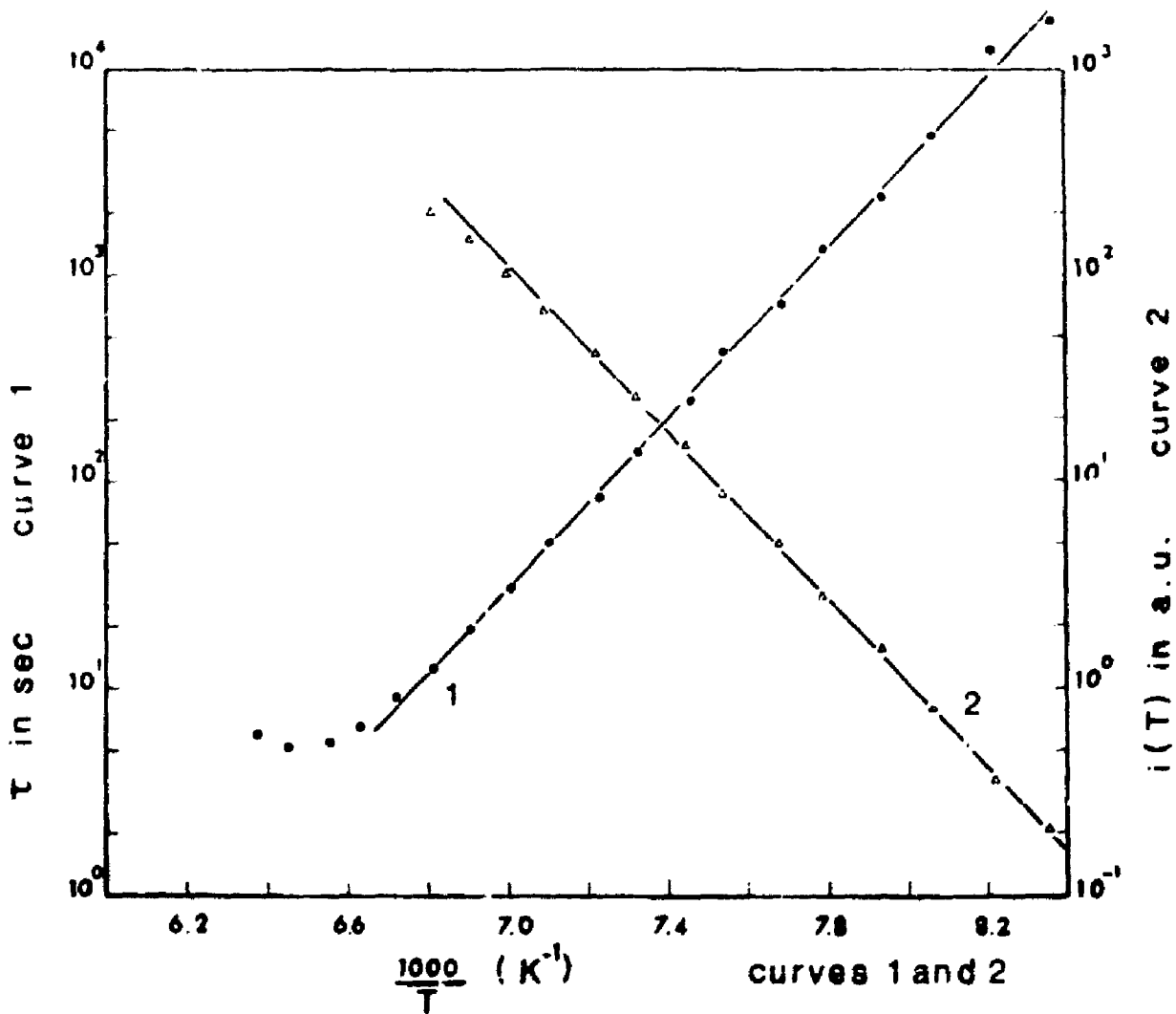


Fig. 5

CdF₂ : Eu with blocking electrodes: determination of orientational activation energy for peak a.

Curve 1: logarithmic plot of relaxation time τ versus $1000/T$ as obtained from experimental data by using formula (3).

Curve 2: logarithmic plot of current density versus $1000/T$ following formula (4).

band at 118 K), when the polarization temperature T_p was still 162 K. The functional field dependence of current I was of the Poole-Frenkel type⁽¹⁸⁾ in both cases, i.e.

$$I \propto \exp\left(\frac{BE^{1/2}}{kT_p}\right) \quad (5)$$

Where B is constant. The formula usually describes the Poole-Frenkel carrier detrapping from a single localized donor level, when Coulombic well is assumed for the donor potential. The same field dependence of thermocurrent and dc current suggests that both can be related to the same mechanism and moreover effects due to the presence of electrons cannot be ruled out.

4. Concluding remarks

From the above results, it turns out that the principal features of band a) in $\text{CdF}_2:\text{Eu}$ can be summarized as follows:

- 1) The peak is really due to the presence of europium.
- 2) The band is not due at all to charges injected from electrodes, because it is developed also with teflon blocking electrodes;
- 3) The peak temperature does not depend both on T_p and t_p ;
- 4) The peak temperature is in the region where the second RE-FI dipole reorientation band occurs in CaF_2 doped with various trivalent cations and in $\text{SrF}_2:\text{Eu}^{(14)}$;
- 5) The polarization induced is a linear function of the polarizing field E_p , as predicted by the Langevin formula for uniform bulk polarization due to non-interacting dipoles, in the approximation $pE_p \ll kT_p$;
- 6) The band shape is nicely described by formula (2), which holds for non-interacting dipoles, whose disorientation occurs through a first order monomolecular kinetics;
- 7) The activation energy for dipole orientation obtained in the above frame is 0.40 eV, in fine agreement with those of the homologous band in CaF_2 .

The discrepancy from the values of activation energy found for Eu peaks in $\text{SrF}_2^{(14)}$ (≈ 0.3 eV) can be understood by taking into account that the Sr^{2+} ionic radius (1.38 Å) is appreciably different from Ca^{2+} and Cd^{2+} ionic radii (1.26 Å) and 1.21 Å, respectively) in fluorides⁽¹⁹⁾. The activation energies, pre-exponential factors and cation radii are summarized in table I for Ca, Cd and Sr fluorides. The frequency factor $1/\tau_0 = 10^{12} \text{ s}^{-1}$, obtained for the peak at 152.5 K, is realistic if compared with the vibrational frequencies in CdF_2 lattice. In fact, by using data on reststrahlen absorption wavenumber and on static and high frequency dielectric constants, reported by Eisenberger and Pershan⁽¹⁸⁾, one can evaluate ω_{LO} (longitudinal optical frequency) $\approx 7.8 \times 10^{12} \text{ s}^{-1}$ and ω_{TO} (transverse optical frequency) $\approx 4 \times 10^{12} \text{ s}^{-1}$, both higher than $1/\tau_0$.

The whole phenomenology of 152.5 K ITC peak in $\text{CdF}_2:\text{Eu}$ fits nicely to the picture of the other europium doped fluorides and more generally of CaF_2 doped with trivalent rare earths. The attribution of ITC peak at 152.5 K to the disorientation of substitutional trivalent europium-fluorine interstitial dipoles in CdF_2 seems quite reasonable, in this way resolving the puzzle of lack⁽¹⁾ of these dipolar defects in a crystalline structure so close to that of CaF_2 .

However from our results in $\text{CdF}_2:\text{Gd}$, the formation of rare earth-fluorine interstitial dipoles does not look as a common feature of RE doped CdF_2 . Even if the strong peaks we

Table I

Motion parameters for ITC peaks in the temperature range 120-190 K
in Ca, Cd and Sr fluorides doped with europium

Matrix	Activation energy (eV)	Pre exponential factor τ_0 (s)	Reference	Divalent cation radius \AA (19)
CaF ₂	0.40	1×10^{-11}	(14)	1.26
CdF ₂	0.40 (peak at 152.5 K)	1×10^{-12}	presente work	1.21
	0.40 (peak at 186 K)	1×10^{-11}		
SrF ₂	0.26	2×10^{-9}	(14)	1.39
	0.28	5×10^{-8}		
	0.33	2.5×10^{-9}		

found in CdF₂:Gd, in the range 100-180 K, must be unequivocally attributed to the presence of Gd, however, their properties are not consistent with those of a uniform bulk polarization of a system of non-interacting dipoles. The practical suppression of depolarization current signal, caused by blocking electrodes, suggests that injection of carriers from electrodes can take place, in absence of blocking electrodes. Moreover the relation (5) which seems to hold at 162 K both for thermal induced depolarization current and for dc current, suggests that electronic effects could be present, possibly due to a weak non-stoichiometricity of the sample, and can overlap or mask the weak reorientation signals due to RE-FI dipoles (we recall here that we obtained small signals with blocking electrodes). It is still puzzling why Eu gives RE-FI dipole reorientation signal and Gd does not. ESR and ENDOR measurements in CdF₂:Gd⁽²⁰⁾ showed that the predominant ESR spectrum arises from substitutional Gd³⁺ in cubic sites and no charge compensating F⁻ ion is present within 7 Å from Gd³⁺, while non-cubic sites, due also to the presence of unwanted paramagnetic impurities, are less than 10%. This supports that Gd³⁺ in tetragonal symmetry (that expected for RE-FI dipoles) represents only a small fraction of Gd³⁺ and in part can account for the difficulty in detecting unambiguous ITC signals. This difficulty seems to hold also for other trivalent ions, for instance La and In, as shown by Kunze and Müller⁽¹⁾ Kessler⁽³⁾ ascribed this fact to the use of blocking electrodes, but our results in CdF₂:Eu showed that the detection of RE-FI dipole reorientation peak when it is really present is not limited at all by the use of blocking electrodes. It is worthwhile noticing that a thermal depolarization current peak was found by Kessler⁽³⁾ in CdF₂:Y at 129 K, which the author attributed to Y³⁺-FI dipole reorientation. However, in our opinion, there is a little shadow of doubt that it can be unambiguously due to dipole relaxation because its presence was not checked by using blocking electrodes and, furthermore, its activation energy was found to be only 0.205 eV which is far from the 0.4 eV value reported for RE-doped CaF₂. In this way overlapping electronic effects can affect the dipole relaxation detection, as in our CdF₂:Gd. At present it looks that only Eu gives undoubtedly RE-FI dipole reorientation ITC peaks in CdF₂; consequently it would be worthwhile to analyze the behaviour of other trivalent

ions in CdF_2 in order to understand why RE FI pairs are not a common feature of all trivalent ions as in CaF_2 .

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RESUMO

Várias experiências realizadas utilizando a técnica de ITC, na região de temperatura entre 80 e 200 K, mostram inequivocamente que ocorre a reorientação dipolar dos dipolos n. n. Terra Rare Fluor Intersticial (RE FI) em CdF_2 Eu, resolvendo o enigma da inexistência desse tipo de relaxação em CdF_2 dopados com íons trivalentes, como relatados por autores precedentes. A energia de ativação para a orientação ($E = 0.40$ eV) e o fator pré-exponencial ($\tau_0 = 10^{-12}$ s) são calculados para o pico principal de ITC ($T_M = 152.5$ K) discutidos e comparados com parâmetros análogos em fluoretos de Sr e Ca dopados com Eu. Outros picos em 168 e 186 K são também analisados. Um estudo paralelo sobre CdF_2 Gd mostra que os efeitos eletrônicos não são desprezíveis e que podem mascarar relaxações dipolares. A diferença entre Eu e Gd é discutida.

RESUME

De nombreuses expériences ITC effectuées entre 80 et 200 K montrant sans équivoque les dipôles en second voisin terre rare-fluor interstitiel dans CdF_2 Eu. L'énergie d'activation d'orientation (0.40 eV) et le facteur pré-exponentiel ($\tau_0 = 10^{-12}$ s) sont évalués pour le pic ITC principal ($T_M = 152.5$ K) et comparés aux paramètres obtenus dans les fluorures de strontium et de calcium dopés à l'europlium. D'autres pics à 168 et 186 K sont aussi analysés.

Une étude parallèle sur CdF_2 Gd montre que des effets électroniques ne sont pas négligeables et peuvent masquer des relaxations dipolaires. La différence entre Eu et Gd est discutée.

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