PHYSICAL REVIEW B VOLUME 19, NUMBER 8 15 APRIL 1979

Dipole reorientation of tetragonal charge-compensation centers in $CaF_2:R^{3+}$

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(Received 31 October 1978)

The effect of the ionic radius of trivalent impurities on the reorientation parameters of tetragonal charge-compensation centers in CaF_2 is studied. As it has been found in an earlier paper that electrical dipole-dipole interaction between the centers significantly modifies the reorientation behavior of dipoles, we have included this perturbation in our analysis of the results of the ionic-thermocurrents experiments. From the results we conclude that in $CaF_2:R^{3+}$ there is an appreciable tendency of the impurities to coagulate to clusters; in contrast to results given in the literature the characteristic relaxation time τ_0 associated with the jumping dipoles does not depend on the size of the trivalent impurity. The activation energy E_0 however increases with increasing R^{3+} radius and the trend found for tetragonal centers in CaF_2 is the same as for SrF_2 observed by van Weperen and den Hartog. It is suggested that the variations are due to changes in the screening of the effective positive charge of the trivalent impurity.

I. INTRODUCTION

During the last decade many results of ionic-thermocurrents (ITC) experiments on local-charge-compensation centers in CaF_2 have been published.[1-3] Reviewing the existing literature we have found that large discrepancies between the dipole reorientation parameters E and τ_0 occur. It was suggested by Lenting, Numan, Bijvank, and den Hartog[4] that the activation energy is not uniquely defined if one is dealing with large concentrations of dipoles. van Weperen, Lenting, Bijvank, and den Hartog[5] later showed that dipole-dipole interaction in moderately doped SrF_2 samples leads to appreciable changes of the ITC curve. In addition, it was observed that if the ITC peaks are treated without taking into account this dipole-dipole interaction, large discrepancies in E and τ_0 are found. The errors increased with increasing dipole concentration.

The above observations have led us to the conclusion that at least part of the scatter in reported values for E and τ_0 is due to the dipole-dipole interaction. It was found by Lenting *et al.*[4] and by van Weperen *et al.*[5] that there is an exponential relationship between E and τ_0,

$$\tau_0 = Ae^{BE}, \tag{1}$$

which is usually obeyed. In (1) B is a proportionality factor and E is the activation energy. This immediately follows from the observation that the position of the ITC peak does not depend upon the dipole concentration; therefore

$$T_m^2 = [E/kf'(T_m)]\tau_0 e^{E/kT_m}, \tag{2}$$

where T_m is the temperature at which the ITC band reaches its maximum current; $f'(T_m)$ is the reciprocal heating rate at T_m. In order to show that for the system $CaF_2:R^{3+}$ (R = La, Ce, . . . , Lu) as studied in the literature concentration effects may also play a role, we have plotted the results obtained by Wagner and Mascarenhas[3] in Fig. 1. A similar correlation between E and τ_0 (although not as clear as for the work of Wagner and Mascarenhas[3]) can be obtained from the results published by Kitts and Crawford[1] and Stiefbold and Huggins.[2] Kitts and Crawford have discussed the values of the activation energy associated with the ITC process, and from the review given above it is clear that in order to draw conclusions about the behavior of E as a function of the ionic radius of the R^{3+} ion, one should be careful not to be confused by concentra-

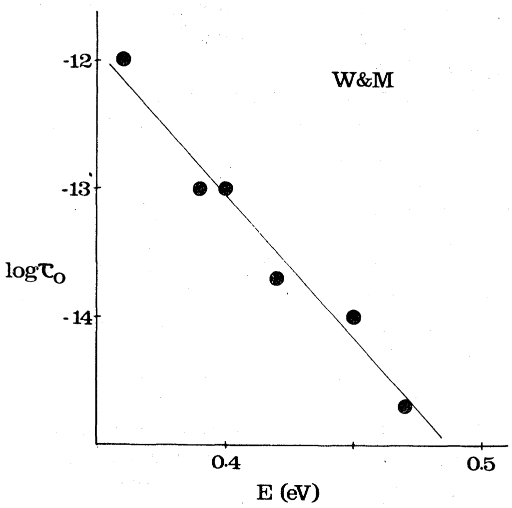

FIG. 1. Exponential plot of the results obtained by Wagner and Mascarenhas (Ref. 3) showing the correlation between the characteristic relaxation time τ_0 and the activation energy associated with the reorienting dipole (E).

tion effects. We therefore carried out a new series of experiments on the system $CaF_2:R^{3+}$, taking into account dipole-dipole interaction.

The results obtained from our experiments suggest that the characteristic relaxation time τ_0 is the same within the experimental accuracy for all R^{3+} impurity ions. The activation energy, however, shows significant variations as a function of the R^{3+} radius.

From a comparison of the behavior of the activation energy E as a function of the R^{3+} radius with that observed in SrF_2 by van Weperen and den Hartog,[6] we found that E shows the same trend with increasing R^{3+} radii in CaF_2 and SrF_2, suggesting that relaxations of the ions neighboring the trivalent impurity cause the variations of the activation energy.

II. EXPERIMENTAL PROCEDURE

The crystals used in this investigation were grown in our crystal-growing facility from Merck Suprapur CaF_2 powder. In order to avoid reaction of the melt with water molecules approximately 1% PbF_2 is added before crystal growth. PbF_2 is known to act as a scavenger:

$$CaO + PbF_2 \rightarrow CaF_2 + PbO\uparrow .$$

Crystal growth takes place under a helium atmosphere. In order to prevent the trivalent impurities from coagulating during the crystal-growth process, the crystals were pulled (by means of a Bridgman setup) through a temperature gradient at a rate of 10–15 mm/h. After growth the crystals (diam ~10 mm) were cooled down to room temperature in a few hours.

The ITC setup and the methods used to interpret the experimental observations have been described elsewhere.[4-6] In some cases the samples were quenched from temperatures of about 1100–1150℃ in order to check whether clustering of defects has taken place, and the results showed that indeed the dipole concentration as measured with ITC increased following quenching, indicating that clustering of dipoles occurs in slowly cooled $CaF_2:R^{3+}$.

III. EXPERIMENTAL RESULTS

Depolarization experiments have been carried out on CaF_2 crystals doped with trivalent rare-earth impurities ($La^{3+}, Ce^{3+}, \ldots, Lu^{3+}$) and U^{3+}. The ionic radii of these impurities are in the range 1.10 Å–1.35 Å (see Shannon and Prewitt[7]); the corresponding Ca^{2+} radius is 1.26 Å. From spectroscopic experiments it has been concluded that the trivalent impurities in CaF_2 are found predominantly at tetragonal positions[8-10]; charge compensation in this host material is of a local nature and the interstitial F^- ions providing this charge compensation are located at nearest neighbor interstitial sites (see Fig. 2). This is in contrast with the results obtained for experiments on $SrF_2:R^{3+}$, where it is has been shown that there are two types of charge compensation: tetragonal and trigonal dipoles. For large trivalent impurities we have predominantly tetragonal centers and for small impurities trigonal dipoles are found.

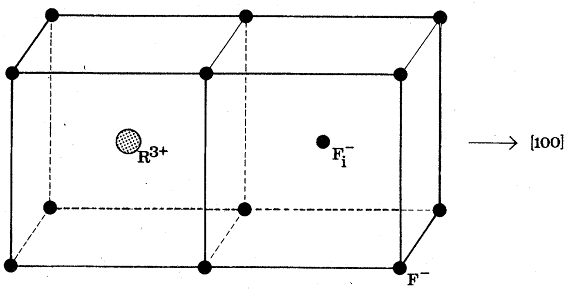

FIG. 2. Three-dimensional schematic representation of a tetragonal dipole consisting of a trivalent impurity and a neighboring interstitial fluoride ion.

The impurity concentration is such that the dipole-dipole interaction causes significant changes in the ITC-reorientation band. Also, the trivalent impurities were found to coagulate during the crystal-growth process; after quenching from temperatures between 1100–1150℃ the ITC band was enhanced by a factor of about 2! These results suggest that it is necessary to correct the ITC results for dipole-dipole interaction effects as proposed by van Weperen *et al.*[5] Coagulation of the impurities reduces these effects and therefore the broadening of the ITC band cannot be used as a measure of the concentration of trivalent impurities. The effect of clustered impurities will be reduced drastically as compared to that of unper-

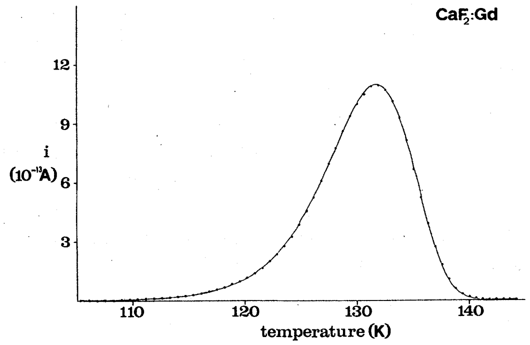

FIG. 3. Example of the results of an ITC experiment on CaF_3:Gd. The points indicated are the experimental points; the drawn curve is the best fit of the theoretical curve providing the parameters τ_0, E_0, the broadening parameter p, and the dipole concentration.

TABLE I. Relaxation parameters of tetragonal dipoles in CaF_2:R^{3+}.

R	E_0 (eV)	τ_0 (10^{-13} sec)	p (10^{-3} eV)	N_d (10^{17} cm^{-3})	T_{max} (K)
U	0.392	1.7	1.1	2.4	134.5
La	0.396	2.9	5.5	3.5	138.5
Ce	0.390	2.8	1.2	6.2	135.5
Pr	0.385	5.0	2.4	3.4	135.5
Nd	0.388	2.4	1.6	6.2	135
Sm	0.378	1.7	4.5	9.2	129
Eu	0.362	8.1	7.8	14.3	129
Gd	0.377	2.8	1.3	10.3	132
Tb	0.363	4.0	0.4	12	128
Dy	0.360	5.8	4.5	11	129.5
Ho	0.360	6.2	1.5	10.2	129
Er	0.363	5.0	3.9	10	128.5
Tm	0.354	3.9	0.1	7	126
Yb	0.381	1.3	7.0	6.5	130
Lu	0.366	1.7	8.3	3.1	126

turbed local charge-compensation centers.

In order to improve the signal-to-noise ratio, which was smaller than for the system $SrF_2:R^{3+}$, we increased the polarization field to about 4000 V/mm. The ITC results were analyzed by means of the method outlined by van Weperen *et al.*[5,6] In this way we obtained for each sample four parameters: E_0, τ_0, p, and the concentration. Here, E_0 is the average activation energy of the jumping dipoles; it is necessary to take the average value of the activation energy, as the dipole-dipole interaction among the local charge-compensation centers will influence the activation energy of each of the reorienting dipoles. τ_0 is the characteristic relaxation time and p is the broadening parameter associated with the Gaussian distribution of activation energies (for a definition we refer to van Weperen *et al.*[5]) The concentration has been obtained from the area under the ITC band. In Fig. 3 we show an example of our experimental reorientation curves together with a theoretical fit using the formula derived by van Weperen *et al.*[5] From Fig. 3 it can be seen that the agreement between theory and experiment is quite satisfactory.

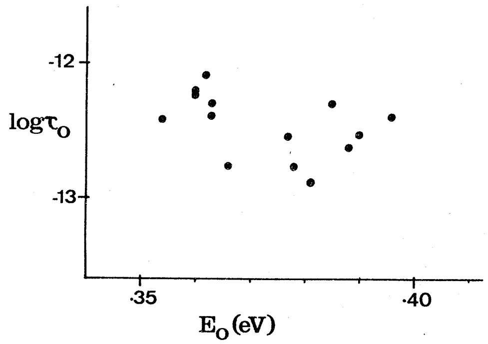

FIG. 4. Exponential plot of the results obtained from our ITC experiments showing that there is no correlation between the parameters τ_0 and E_0. The values of τ_0 are constant within experimental accuracy.

The results obtained for the materials investigated have been compiled in Table I. It can be seen clearly from Table I that the temperature at which the maximum reorientation current is observed decreases gradually but not systematically on going from La to Lu doping. The characteristic relaxation time τ_0 does not show a specific trend when the ionic radius of the trivalent impurities is changed; it only shows irregular fluctuations. This observation is in agreement with the results of ir absorption experiments on R^{3+}-H_i^- complexes in SrF_2 obtained by Timans and den Hartog,[11] which indicate that the eigenfrequencies of the H_i^- ion in tetragonal complexes change less than 6% when the ionic radius of the trivalent ion is changed from 1.17 to 1.32 Å. Because these systems are very similar to the R^{3+}-F_i^- complexes, we suggest that the vibration frequencies of the interstitial F^- ion are the same for different charge-compensation centers studied in this paper. In order to illustrate this we show in Fig. 4 the behavior of the characteristic relaxation time τ_0, which is related to the vibration frequency of the interstitial F^- ion, as a function of the activation energy of the complexes studied. The results shown in Fig. 4 should be compared with those in Fig. 1, and it is obvious that the application of four parameters to fit the ITC results really improve the results; for τ_0 we have found $\tau_0 = 10^{-12.5\pm0.4}$ sec.

It is now of interest to observe the variations of the activation energy E_0 as a function of the ionic radius of the trivalent impurities. The results ob-

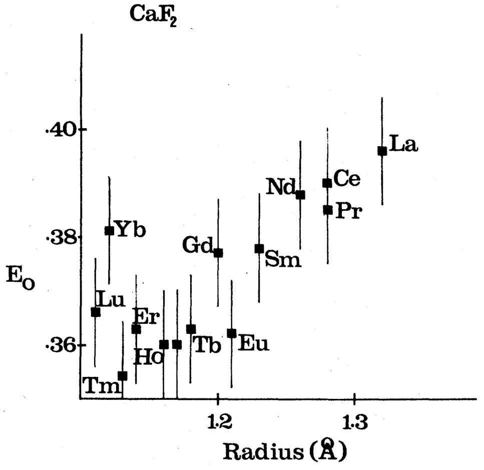

FIG. 5. Plot of the activation energy as a function of the R^{3+} radius for $CaF_2:R^{3+}$. For radii larger than 1.2 Å the activation energy E_0 increases with increasing R^{3+} radius.

tained from the four parameter fits have been plotted in Fig. 5, which shows that the activation energy associated with the reorientational jumps of the tetragonal dipoles in CaF_2 increases gradually with increasing R^{3+} radii, starting at a radius corresponding to that of Dy (1.17 Å). We note that a similar behavior has been observed by van Weperen and den Hartog[6] for tetragonal complexes in SrF_2. The corresponding plot for $SrF_2:R^{3+}$ has been given in Fig. 6. It should be noted that tetragonal dipoles in SrF_2 have only been observed for the rare-earth dopants Dy, Tb, Gd, Nd, Ce, Pr, and La. In SrF_2 samples doped with Lu, Yb, Ho, Tm, and Er the local charge compensation is of trigonal nature.[4]

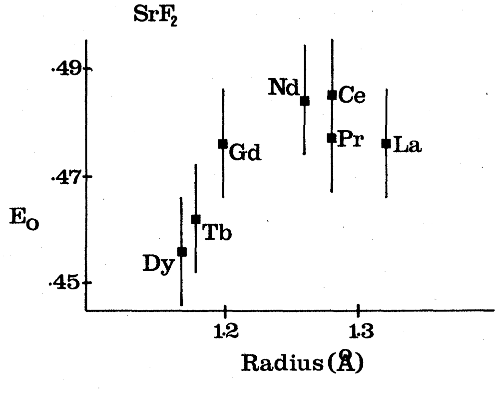

FIG. 6. Plot of the activation energy as a function of the R^{3+} radius for $SrF_2:R^{3+}$.

IV. DISCUSSION

From the experimental results we conclude that the method employed here to interpret the ITC results is a reliable one. The parameters E_0 and τ_0 are independent of the concentration of the trivalent impurities. On the other hand, it can be seen from Table I that the broadening parameter p which accounts for the interaction of the reorienting dipole with other defects does not depend linearly upon the concentration of the trivalent impurities. This is in contrast with the results obtained for $SrF_2:Ce^{3+}$ at moderate Ce^{3+} concentrations.[5] The reason for this deviating behavior is that in CaF_2 there is appreciable clustering of dipolar defects; this is suggested by the results of quenching experiments, showing that after quenching from temperatures between 1100 and 1150°C the dipole concentration could be enhanced quite significantly. Also we have found that the dipole concentration in $CaF_2:R^{3+}$ depends upon the growth conditions such as the growth rate and the cooling rate after growth.

Coagulated defects containing more than one dipole will not contribute to the ITC-reorientation band, but they can contribute to the broadening parameter p. Because we do not have information about the nature and the concentrations of the various possible defect clusters, we are not able to connect p with any specific interaction in the case of $CaF_2:R^{3+}$ samples. On the other hand, however, we note that the broadening parameters as given in Table I are all larger than the one expected on the basis of the interaction between the dipoles only. This indicates that apart from the interaction between the dipoles there are also other kinds of interactions leading to a broadening of the distribution function associated with the activation energy. We know that the dipole-dipole interaction energy can be written

$$U(\vec{r}) = \frac{1}{4\pi\epsilon_0\epsilon}\left(\frac{\vec{\mu}_1\cdot\vec{\mu}_2}{r^3} - 3\,\frac{(\vec{\mu}_1\cdot\vec{r})(\vec{\mu}_2\cdot\vec{r})}{r^5}\right), \qquad (3)$$

where $\vec{\mu}_1$ is the central dipole and $\vec{\mu}_2$ is another dipole located at a position given by $\vec{r}$ with respect to the central dipole. van Weperen *et al.*[5] have calculated that for SrF_2 containing tetragonal dipoles the broadening parameter p connected with the dipole-dipole interaction can be given by

$$p = mN_d; \qquad (4)$$

here N_d is the concentration of dipoles and m is a proportionality factor, which is for $SrF_2:Ce^{3+}$ equal to approximately 7×10^{-22} eV cm^3. In order to estimate from this result the value of m for $CaF_2:R^{3+}$ we should take into account that (i) the dielectric constants of CaF_2 and SrF_2 are different, and (ii) the dipole strength of the tetragonal com-

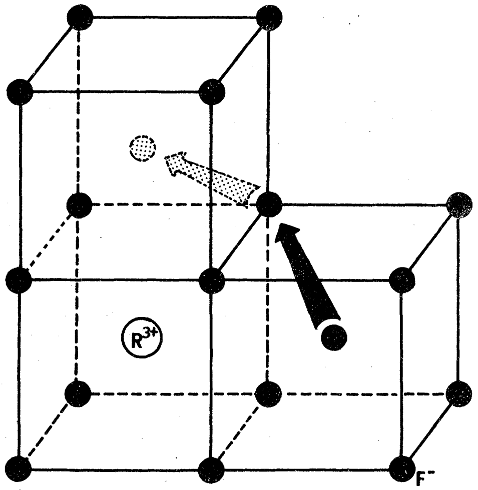

FIG. 7. Schematic three-dimensional representation of a reorienting tetragonal dipole. The interstitial F^- ion moves towards a lattice fluoride ion neighboring the R^{3+} impurity; the lattice fluoride ion is removed from its position and pushed into an interstitial position. The F^- ion that originally occupied an interstitial position is located at the abandoned lattice site.

plexes in CaF_2 is smaller than for SrF_2. As a result we find that

$$m_{CaF_2}/m_{SrF_2} = 1.176 \,, \qquad (5)$$

and for m_{CaF_2} we find approximately 8×10^{-22} eVcm^3. Using this result to calculate the broadening factor associated with dipole-dipole interaction, the maximum broadening factor obtained from the results compiled in Table I is about 10^{-3} eV (!), which should be compared with the maximum value $p\approx 8\times10^{-3}$ eV.

A striking feature of Figs. 5 and 6 is that, apart from the difference in the absolute value of the dipole reorientation energy E_0 for CaF_2 and SrF_2, and trend of E_0 as a function of the ionic radius is the same. This can be understood as follows. During the reorientation process the interstitial ion will remove one of the lattice fluoride ions from its position. The latter ion then jumps in another interstitial positon; this process has been illustrated schematically in Fig. 7. We expect that as a result of the excess positive charge of the trivalent impurity, the eight neighboring fluoride ions move towards the impurity. For large impurities the magnitude of this type of relaxation is small and with decreasing R^{3+} radius the inward displacements will increase, but there is a limitation due to the repulsive interactions between the fluoride ions under consideration.

As a result of the inward motion of the fluoride ions the excess positive charge will be screened to some extent; this effect will be most obvious for the smaller R^{3+} ions. For the larger trivalent impurities the screening is not as effective and the Coulomb attraction between the excess positive and negative charge will be strong. Accordingly, the activation energy increases with increasing R^{3+} radius as observed experimentally. Another parameter of interest is the binding energy of the trivalent impurity and the first-shell lattice fluoride ions. It is assumed that the electrostatic binding energy increases for decreasing R^{3+} radii, but terms with the opposite sign come from the repulsive interaction mentioned above. In conclusion we can say that the increase of the activation energy associated with the jumping dipoles as a function of the R^{3+} radius can be understood qualitatively. In addition we conclude from the similarity of the changes of the activation energy for tetragonal dipoles in CaF_2 and SrF_2 that these changes are due to local effects giving rise to the same energy variations for the two host materials. The treatment given above supports this conclusion.

ACKNOWLEDGMENTS

The authors wish to thank P. Wesseling for growing the crystals used in this investigation. This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie" and has been made possible by financial support from the "Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek."

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