[1] N. Kristianpoller and M. Israeli, Phys. Rev. B 2, 2175 (1970); M. Israeli and N. Kristianpoller, Phys. Status Solidi 45, k29 (1971).

[2] N. Kristianpoller and M. Israeli, Phys. Status Solidi 47, 487 (1971).

[3] H. N. Hersh, Phys. Rev. 148, 928 (1966); D. Pooley, Proc. Phys. Soc. (London) 87, 245 (1966); 87, 257 (1966).

[4] M. Israeli and N. Kristianpoller, in Proceedings of the International Conference on Color Centers in Ionic Crystals, Reading, 1971, H165 (unpublished).

[5] See, e.g., F. T. Goldstein, Phys. Status Solidi 20, 379 (1967); Y. Farge, J. Phys. Chem. Solids 30, 1375 (1969).

[6] T. Miyata and T. Tomiki, J. Phys. Soc. Japan 21, 395 (1966).

[7] N. Kristianpoller, M. Israeli, and R. Chen (unpublished).

[8] See, e.g., A. Halperin and R. Chen, Phys. Rev. 148, 839 (1966); M. Israeli and N. Kristianpoller, Solid State Commun. 7, 1131 (1969); E. T. Rodine and P. L. Land, Phys. Rev. B 4, 2701 (1971).

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Ionic-Thermocurrent Study of Rare-Earth-Doped CaF_2 and SrF_2[†]

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The reorientational properties of CaF_2 doped with the rare earths (RE) cerium, praesodymium, samarium, europium, and terbium were studied using the technique of ionic thermocurrents (ITC). The reorientational energies of the RE-F^--interstitial complex formed were found to increase with increasing ionic radius of the impurity rare-earth ion, increasing more rapidly for the larger ions. All energies were much less than the free F^--interstitial activation energy. The preexponential factors were larger than the normal vibrational frequencies in the CaF_2 lattice and perhaps reflect the tight-binding nature of the complex. A natural Brazilian fluoride sample known to contain aluminum fit nicely with the other data. Oscillator strengths for the $4f \rightarrow 5d$ optical transition for the RE ion in tetragonal symmetry in the CaF_2 lattice were determined for Ce, Pr, and Tb using ITC and optical-absorption data. ITC runs on SrF_2: Eu were also made. The peak structure observed was more complicated. Three peaks were separated and their activation energies and frequency factors determined.

I. INTRODUCTION

The measurement of reorientational properties of electric dipolar complexes in insulators has become simpler and more direct with the introduction of the ionic-thermocurrent (ITC) technique by Bucci, Fiechi, and Guidi in 1966. Before the introduction of this method, dielectric loss, NMR, tracer studies, and ionic conductivity were the main techniques for investigating ionic motion in ionic solids. Since its introduction, ITC has been used to determine reorientational properties and monitor other phenomena of various impurity complexes in a good number of alkali halides.[1-4] In almost all cases, these results have been in good agreement with the results obtained using other methods.[5]

Motional effects in the fluorite lattice have not proved as straightforward. A common type of electric dipole complex found in CaF_2 involves a trivalent positive ion such as a rare earth (RE) which enters the lattice substitutionally for the calcium and the charge-compensating fluorine interstitial ion. (The interstitial position in the fluorite lattice is the vacant body center of the cube of F^- that is adjacent to a cube of F^- with the cation at its center.) Owing to the Coulomb attraction of the two ions one would expect them to be bound at sufficiently low temperatures; therefore, the complex will possess a permanent electric dipole moment. A common symmetry of this type of complex is tetragonal, with the F_i^- occupying the nearest-neighbor interstitial position to the 3+ cation. Many other types of dipolar complexes may be thought of and formed in this lattice through the proper introduction of certain impurities, but in this paper we will only be interested in complexes involving trivalent positive ions and fluorine interstitials.

Until recently, measured values of reorientational parameters and just simple diffusion parameters in rare-earth- or trivalent-positive-ion-doped CaF_2 have diverged by 50–100%,[6-8] in great contrast to the results in alkali halides. Lately, things have been improving. There have been recent ionic-conductivity measurements that give reasonable values for the diffusion parameters of fluorine interstitials and fluorine vacancies in CaF_2 and SrF_2.[9] Also recently, using ITC, the reorientational parameters of some RE-F_i^- tetragonal complexes in CaF_2 have been determined with more consistency.[10-12]

In this paper, we report the results of ITC measurements above liquid-nitrogen temperature for five different rare earths in CaF_2. Oscillator strengths of those RE's whose lowest $4f \rightarrow 5d$ optical transition is accessible are also determined. We also report the observation of an ITC peak in a natural Brazilian fluorite which is known to contain aluminum. These results combine with the previous ones to give consistent values for reorientation of this complex. ITC studies of SrF_2: Eu are also reported.

II. EXPERIMENTAL

CaF_2 crystals doped with Ce (0.01 mol%), Pr (0.1 mol%), Sm (0.1 mol%), Eu (0.01 mol%), or Tb (0.1 mol%) as well as SrF_2: Eu (0.1 mol%) and a natural fluorite were used in the experiments. The synthetic crystals were all obtained from the Harshaw Chemical Company as random cuttings. Although some of the samples were from reasonably near the boule edge (mainly some cerium samples), the optical absorption as measured on a Beckman DK2 spectrophotometer showed the typical spectrum of the respective rare earths. Therefore, it was believed that the crystals were of good quality. The fluorite was natural fluorite of green type (verde) obtained from the Brazilian state of Santa Catarina. Mass-spectroscopic analysis showed the predominant impurities to be aluminum and magnesium. We were interested in this crystal due to the aluminum, which should enter the lattice in the same manner as the much larger rare-earth ions (substitutionally as a trivalent cation). Further work is planned on these crystals owing to their possible value as a thermoluminescence radiation dosimeter.

The ITC apparatus has been previously described.[13] The synthetic samples used were single crystals > 0.5 cm^2 in cross-sectional area and 0.4–1.0 mm in thickness. They were not annealed or thermally treated in any way. The natural-fluorite samples were about the same size as the synthetic ones; however, they were polycrystalline, possessing many visible flaws. They proved to be very difficult to anneal without their destruction. Therefore, these samples were prepared only by cleaving and polishing them to the proper dimensions. For electrodes, silver was painted on or aerodag was sprayed on. Both gave good results. To obtain the ITC spectrum, the samples were polarized for 9 min at a temperature near the peak temperature (normally near 140 °K) with an applied voltage of 350–400 V. The temperature was then lowered to less than 90 °K, at which point the applied voltage was removed. The heating rate was about 0.15 °K/sec. Nitrogen was present in the Dewar during the runs. A Keithley 610C electrometer was used to detect the current peak, and this as well as the iron-constantan-thermocouple potential was recorded on a Sargent model DSRG dual-pen recorder. Background current was about 2×10^{-14} A with noise fluctuations < 0.5 $\times10^{-14}$ A. The ITC peak heights were always at least 30×10^{-14} A. For any crystal, the results from one run to the next were very reproducible.

It has been reported,[14] and we have also observed, degradation in the measured activation energy when the concentration of impurities is > 0.05 mol%. The peak, which at low concentrations appears clean and simple, at higher concentrations appears broader and perhaps shifted in temperature. The cause may be electric and/or elastic dipole-dipole interactions between nearby dipoles, or it may be that the peak is composed of at least two types of dipoles of very similar characteristics. Obviously, the best solution to this problem is to use low-concentration samples. An alternative solution is to use "cleaning techniques": After polarizing and cooling the crystal, heat it only part way through the peak, cool, and reheat, looking for changes in the cleaned peak with respect to the original peak. This procedure will steadily clean a complex peak, and therefore the value of the activation energy in the cleaned peak will approach the value in a peak from a low-impurity-concentration sample. Although we have observed these effects using cleaning techniques in some of the CaF_2: Ce samples used by Royce and Mascarenhas, no measurable changes were observed using these techniques on our higher-concentration samples (Sm, Pr, Tb).

The activation energies associated with the observed peaks in the various samples were obtained by plotting on semilog paper the mean jump time τ as a function of the inverse of the absolute temperature $1/T$. The mean jump time at any temperature T is found by taking the ratio of the area under the current peak from T to ∞ to the current at T.[1] The slopes from the Arrhenius plots then give the reorientation energies. The frequency factor $1/\tau_0$ may then be determined. We estimate our errors on the measured activation energies to be less than 0.02 eV except where otherwise noted. The frequencies are then correspondingly within a factor of 2.

A. Results of ITC in CaF_2

Table I shows the results of the present experiment as well as some of the other recent values

TABLE I. Reorientational properties of tetragonal RE^{2+}-F^- dipolar complex in CaF_2.

Impurity	Radius (Å)	Energy (eV)	$1/\tau_0$ (sec^{-1})	Ref.	Technique
Ce	1.28	0.46	2×10^{14}	10	ITC
Ce		0.45	1×10^{14}	a	ITC
Pr	1.28	0.47	5×10^{14}	a	ITC
Sm	1.23	0.42	5×10^{13}	a	ITC
Eu	1.21	0.40	1×10^{13}	a	ITC
Gd	1.20	0.40	2×10^{13}	7	EPR
		0.38	$\sim 2\times 10^{13}$	7	Dielectric loss
		0.395	1.2×10^{13}	12	ITC
Tb	1.18	0.39	1×10^{13}	a	ITC
Er	1.14	0.386	2×10^{13}	11	ITC
Al	~0.80	0.36	10^{12}	a	ITC

[a] Present work.

for the reorientation parameters in rare-earth-doped CaF_2, and for Al in CaF_2. This last impurity is denoted with a question mark and is the result of the ITC measurements on the natural-fluorite samples. The results here fit well with the other values, and aluminum is known to be a dominant impurity. The ionic radii are taken from the rather recent work of Shannon and Prewitt.[15] Values of the ions are for eightfold coordination in a fluoride structure. They do not give values for the eightfold coordination of aluminum, but as the eightfold radii are normally 0.1 Å larger than the sixfold radii for other trivalent positive ions, an approximate value of 0.8 Å was assumed. As can be seen, the radii appear to decrease slowly as the atomic number increases, but Ce^{3+} and Pr^{3+} have the same radii. Ca^{2+} has a radius of 1.26 Å and F^- has a radius of 1.19 Å. These values therefore imply that the cation is larger than the anion, in contradiction to the older tables of radii, for example those of Pauling, but in good agreement with the electron-density-mapping results.

Figure 1 plots the activation energy of reorientation as a function of ionic radius, where the values are taken from the previous table. The energy appears to increase very slowly with increasing radius (< 10% with a change of 50% in radius) until the radius of the impurity is about equal to the radius of F^-. It then begins to increase much more sharply, about 20% increase for less than a 10% change in radius. Our values and the previous values fit together nicely on our graph. The ITC of CaF_2:Ce by Royce and Mascarenhas[10] was done on RCA-grown crystals and is therefore included as an independent point. Using the Pauling radii would only shift the radii values on the horizontal axis but would not change the form.

We may note at least three interesting features of the above results: (a) The reorientational energies measured are all very small when compared to the observed free-interstitial activation energy (1.04 eV).[9] (b) The dependence of the reorientational energies on ionic radius appears to become important as the radius of the trivalent impurities becomes near to and larger than the F^- radii. (c) The frequency factors are larger than one might reasonably expect for vibrational frequencies in a CaF_2 lattice. (ν_{TO}, the transverse-optical frequency, is approximately 8×10^{12} Hz.)[16]

Concerning the first point, one sees that the activation energy for motion has decreased by between 0.6 and 0.7 eV for the samples used. This is a very large change when one considers that in alkali halides, with binding energies of about 0.35–0.40 eV,[17] the lowering of the energy barrier for motion due to the Coulomb attraction of the members on the complex and lattice distortion

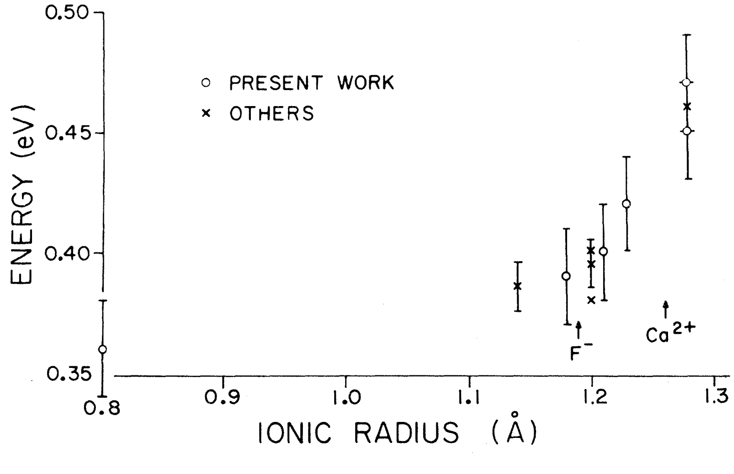

FIG. 1. Dependence of reorientation energy of RE^{3+}-F_i^- complex in CaF_2 on the radius of the rare earth. Radii of Ca^{2+} and F^- are also noted.

TABLE II. Oscillator strength for lowest $4f \rightarrow 5d$ optical transition of some rare earths in CaF_2.

Crystal	Lowest $4f$–$5d$ Transition (nm)	Oscillator Strength
CaF_2: Ce	305	0.014 (Ref. 10) 0.013
CaF_2: Pr	217	0.018
CaF_2: Tb	214	0.011

caused by the complex is normally < 0.15–0.20 eV.[5] In CaF_2: Y, the binding energy of a $Y^{3+}-F_i^-$ complex has been measured to be 0.6 eV,[9] and therefore, one might expect a similar binding energy for the analogous rare-earth-type complex. Thus it would appear that the lowering of the reorientational energy is about the same as if not larger than the binding energy. This is much different than in the alkali halide case. Of course, the complexes are much different. In the latter, reorientation occurs due to the motion of a cation into a cation vacancy. In CaF_2, it is believed that at least for free interstitials motion occurs due to the interstitialcy mechanism. A substitutional fluorine moves into a vacant interstitial site and the interstitial fluorine moves in a substitutional site. The order of events is not clear. The direct mechanism should be harder due to the difficulty the interstitial fluorine will have in moving in the [110] direction because of its size and the size of the other fluorines in the corners of the cube surrounding it. However, remembering the large difference we have observed between the activation of free and bound interstitials, it cannot be assumed that the process and mechanisms are the same for the free and bound interstitial. One must also remember that another ITC peak has been reported in CaF_2:RE with an activation energy less than 0.2 eV.[11,12] This is > 0.8 eV less than the free-interstitial value and reminds one of molecular reorientation rather than ionic. Nonetheless, it would appear that binding a fluorine interstitial to a positive trivalent ion in CaF_2 appears to affect its diffusional properties drastically.

However, though all the values are low with respect to the free-interstitial values, they are self-consistent. In fact, the very slow energy dependence with ionic radii until near a critical value, in this case the radius of F^-, and then the sharp increase for larger radii seem reasonable if positive lattice distortions are an important parameter in governing reorientation. From our results, one would expect that the $La^{3+}-F^-$ dipolar complex in calcium fluoride would have the largest reorientation energy, near 0.5 eV. Unfortunately, there does not appear to be a trivalent cation with a larger ionic radius than lanthanum. Therefore, testing to see if the rapid increase in activation energy continues and if one can determine from this the jumping mechanism would not appear possible with ITC.

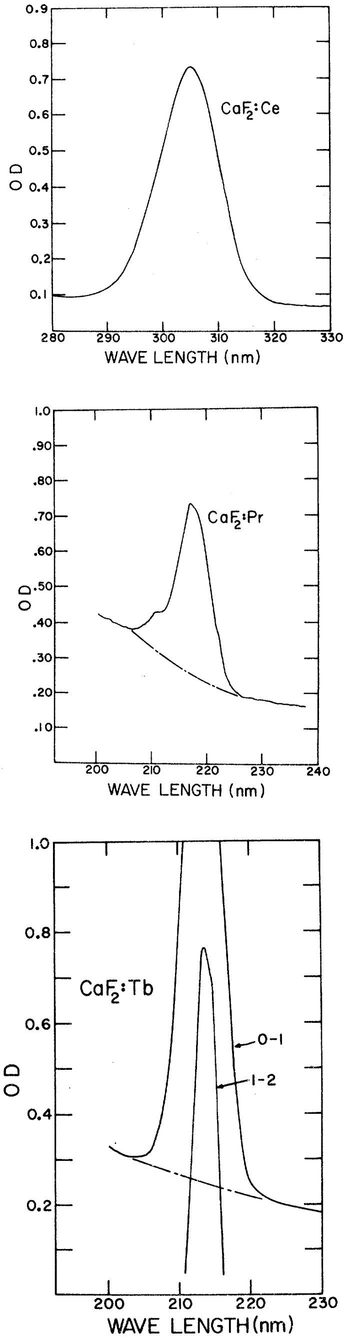

FIG. 2. Optical-absorption band of lowest $4f \rightarrow 5d$ transition in CaF_2:RE. Optical density is abbreviated OD. (a) CaF_2: Ce. (b) CaF_2: Pr. (c) CaF_2: Tb.

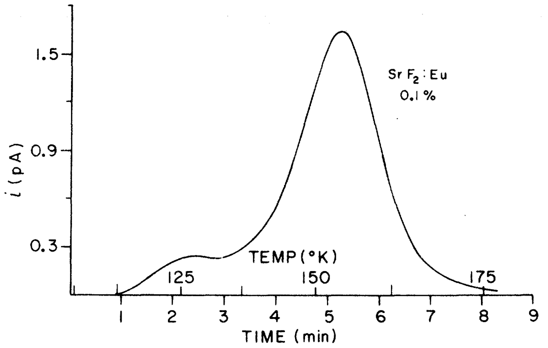

FIG. 3. ITC spectrum of $\mathrm{SrF_2}$: Eu.

A third point that we wish to stress is with regard to the frequency factors or preexponential factors. Although they appear to increase in an orderly fashion with impurity ionic radii, the values for cerium and praesodymium would seem much larger than reasonable if one considers the normal vibrational frequencies in a fluorite lattice. It is unreasonable to put the blame on a wildly increasing force constant between the cation and anion members of the complex. One can resort to using entropy factors and introducing enthalpies instead of energies, but this would imply a difference in entropy factors between reorientation around Pr and reorientation around Tb of approximately 4*k*, where *k* is Boltzmann's constant. It is interesting to note that frequencies associated with motions related to molecular complexes are in general larger than lattice frequencies. Once again, it would be interesting to check the lanthanum complex which could have the largest frequency factor.

B. Oscillator Strengths

Royce and Mascarenhas[10] have determined the oscillator strength *f* of the $4f \rightarrow 5d$ transition of Ce in tetragonal symmetry in $\mathrm{CaF_2}$ using ITC to count the number of Ce^{3+}-F_i^- [100] dipoles.[18] They plotted (optical density)/cm of the 305-nm Ce band vs the number of dipoles as measured using ITC for various concentration samples. That they obtain a straight line ensures that they are correlating the proper band. Unfortunately, we do not have samples with variable concentrations in the three types of crystals ($\mathrm{CaF_2}$ with Ce, Pr, or Tb) in which the lowest $4f \rightarrow 5d$ transition is accessible with a Beckman $\mathrm{DK_2}$ spectrophotometer. However, assuming that the lowest-energy band is the tetragonal band as in Ce, we may determine oscillator strengths for praesodymium and terbium. Assuming Gaussian bands, the results are listed in Table II, as well as the corrected previous result on Ce. We only had samples with a single concentration; the difference between our result for Ce and that of Royce and Mascarenhas is not considered significant. The assumption of simple Gaussian bands is also not very good; the bands are shown in Fig. 2. A calculation of *f* has only been attempted for Ce, and this gives a result in good agreement with the experimental values. Therefore, we do have confidence in our Pr and Tb values even though there are no calculations with which to compare them.

C. ITC of $\mathrm{SrF_2}$: Eu

We have also measured the ITC of $\mathrm{SrF_2}$ doped with a nominal concentration of 0.1 mol% europium. $\mathrm{SrF_2}$ has the same lattice structure as $\mathrm{CaF_2}$ but is much larger, as the strontium is much larger than

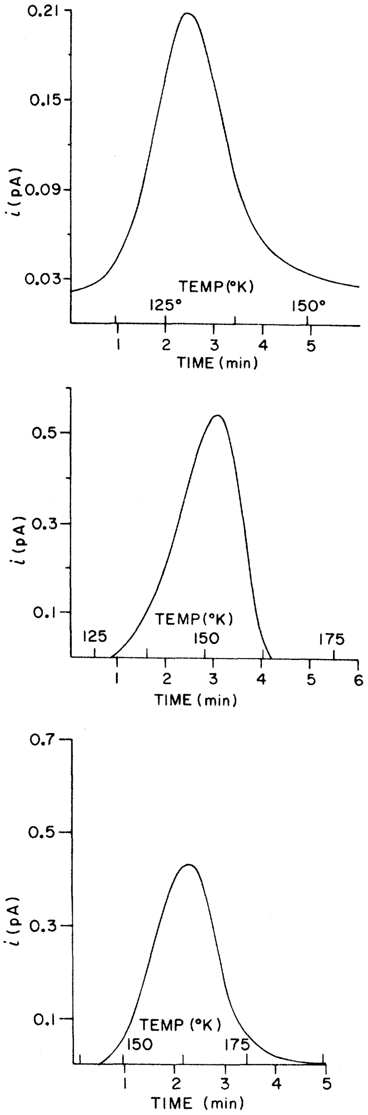

FIG. 4. ITC spectrum of $\mathrm{SrF_2}$: Eu separated experimentally into its three components.

the calcium: 1.39 and 1.26 Å. Therefore, one would expect, and it has been observed, that the dipoles formed with F_i^- present due to charge compensation are less tightly bound in SrF_2 than in the smaller lattice (a binding energy of 0.16 eV in yttrium-doped crystals).[9] But due to the large spacings involved, one would expect easier motion of the interstitial in the free state, and also rather easy reorientation in the bound state. If the important radius is that of the cation for reorientation, one might expect an almost energy-independent behavior of reorientation energy with RE, as all RE's are much smaller than Sr. If the important parameter, for example, is the ratio of the impurity to the anion radii, a significant energy dependence with radius might be present. Also, as the binding energies are small, one would expect that it would be easier to form next-nearest-neighbor (nnn) dipoles and to have transitions between these and the nearest-neighbor (nn) ones.

The ITC spectrum for SrF_2:Eu is shown in Fig. 3. As we see, it is a rather complicated structure, appearing very broad, though in approximately the same temperature range as the ITC spectra of RE-doped CaF_2. Cleaning techniques and different polarization temperatures were tried on the crystals, resulting in the separation of this large structure into three peaks. These are shown in Fig. 4. For the first small peak, the activation energy and frequency factor were measured to be 0.26 eV and 5×10^8 sec^{-1}, respectively. For peak 2, the results are 0.28 eV and 2×10^7 sec^{-1}, and for peak 3, the values are 0.33 eV and 4×10^8 sec^{-1}. The errors involved with the activation energies are probably a bit larger than in the previous work due to the problem of the heavily overlapping peaks and are estimated to be about 0.03 eV. The frequency factors are all very small, less than any characteristic frequency of the system. This could indicate that the peaks are still too broad.

Although it is reasonable to suggest that this more complicated ITC behavior is related to the larger lattice and therefore different binding properties of a rare earth, a better understanding will have to await a more systematic investigation.

III. CONCLUSIONS

In conclusion, due to the systematic investigation of rare-earth-doped calcium fluoride by us and other workers, it now appears that consistent, reliable results are available for the reorientation parameters of the [100]-oriented RE-F dipole. These results imply a large binding energy and a small reorientation energy. An energy dependence on impurity radius is observed, which would be consistent with the idea that positive lattice distortions are more effective in disturbing motions in the lattice. The preexponential factors, although orderly, appear too large with respect to normal lattice vibrational frequencies, although not unreasonable for motion in a molecular complex. The large reorientation energies measured by some earlier groups are hard to interpret.[6] Certainly, their experiments seem valid, and therefore they are measuring the reorientation of something. However, as the values are even larger than the recent values for free-interstitial motion, it is not likely that they are looking at the dominant reorientation mechanism in this complex, if they are looking at this complex. Assuming that they are looking at the proper complex and not some other impurity effect, one might tend to believe that they are looking at reorientation by another mechanism as opposed to the more normal lower-energy one we observed. This type of reorientation would show up using dielectric loss, but not ITC. A systematic investigation of several rare earths using dielectric loss might shed some light on this point.

Our laboratory is also preparing to do a systematic investigation, using our crystals, of the lower-temperature (less than liquid-nitrogen temperature) ITC spectrum that has been reported in Er and Gd. The tentative interpretation proposed for these data will be tested through these studies.

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[1] C. A. Bucci, R. Fiechi, and G. Guidi, Phys. Rev. 148, 816 (1966).

[2] R. Cappelletti and R. Fiechi, Crystal Lattice Defects 1, 69 (1969).

[3] C. Laj and P. Berge, J. Phys. Radium 28, 821 (1967).

[4] J. P. Stott and J. H. Crawford, Phys. Rev. B 4, 639 (1971).

[5] For example, J. S. Dryden and R. I. Meakins, Discussions Faraday Soc. 23, 39 (1957); G. P. Watkins, Phys. Rev. 113, 91 (1958).

[6] J. H. Chen and M. S. McDonough, Phys. Rev. 185, 453 (1969).

[7] A. D. Franklin, J. Phys. C 3, 471 (1970).

[8] R. W. Ure, J. Chem. Phys. 26, 363 (1957).

[9] W. Bollmans, D. Gorlich, W. Hauk, and H. Mothes, Phys. Status Solidi 2, 157 (1970).

[10] B. S. H. Royce and S. Mascarenhas, Phys. Rev. Letters 24, 98 (1970).

[11] J. P. Stott and J. H. Crawford, Phys. Rev. Letters 26, 384 (1971).

[12] J. P. Stott and J. H. Crawford, Phys. Rev. B 4, 668 (1971).

[13] N. Januzzi and S. Mascarenhas, *Electrets and Related Electrostatic Charge Storage Phenomena* (The Electrochemical Society, New York, 1968), p. 41.

[14] R. D. Shelly and G. R. Miller, J. Solid State Chem.

1, 218 (1970).

[15] R. D. Shannon and C. T. Prewitt, Acta Cryst. B25, 925 (1969).

[16] A. D. Franklin, J. Phys. Chem. Solids 29, 823 (1968).

[17] M. P. Tosi and F. G. Fumi, Nuovo Cimento 7, 95 (1958).

[18] There was an error in their calculation, which if corrected gives a value for the oscillator strength f of 0.014.