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Clustering in thermally treated BaF_2:Y^{3+} crystals

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BaF_2 crystals doped with yttrium with molar concentrations ranging from 10^{-5} to 10^{-3} were studied by ionic thermal-current techniques. Two low-temperature peaks *A* and *B* were observed for all the concentrations located at 161 and 183.5 K. The relaxation parameters obtained for peak *A* were $E_A = 0.45$ eV and $\tau_{0A} = 5.7\times10^{-13}$ s. For peak *B* a model assuming a Gaussian distribution of the reorientation energy around a mean value E_0 and with a width σ was assumed and gave $E_{0B}(\sigma) = 0.56$ eV, $\sigma_B = 0.009$ eV, and $\tau_{0B} = 3.3\times10^{-14}$ s. Peaks *A* and *B* were attributed to the relaxation of nearest-neighbor and next-nearest-neighbor dipoles, respectively. Thermal treatments were made on these crystals in order to study the clustering of defects and the dissolution of the nonpolarizable clusters existing in the samples. After quenchings from increasing temperatures, from 700 to 1200 K, the number of free dipoles was determined. Assuming the nonpolarizable clusters to be the 2:2:2 dimer, the dissolution energy was estimated and compared to the theoretical calculations. However, the dissolution mechanism could be better understood if the cluster were the linear $Y^{3+}F_{i2}^-$ and this possibility is discussed herein.

I. INTRODUCTION

It is a well-established fact that fluorite crystals doped with trivalent rare-earth (*R*) fluorides show the existence of substitutional cations, R^{3+}, and interstitial fluorine ions, F_i^-, as the charge-compensating defects. Depending on the distance between the R^{3+} and the F_i^- ions, several types of defects can coexist in the matrix. If there is a local charge compensation by means of a F_i^- anion in first or second neighbor of the impurity, the pair has a dipolar moment and will be named NN or NNN dipole, respectively. If there is an aggregation of several of these dipoles, different clusters can be formed, for which Catlow[1] has proposed several models. In Fig. 1, the 2:2:2 cluster formed by two NN dipoles, is represented. This cluster has the lowest calculated energy of the three types of dimers studied by Catlow and he concludes that the 2:2:2 cluster is the basic structural unit for the fluorite crystals with molar impurity concentrations of $c \simeq 10^{-2}$. For higher dopant concentrations, Catlow[2] has postulated more complicated clusters such as the symmetric tetramer and the 4:3:2 cluster in which there is a relaxation of the F_i^- in the ⟨111⟩ and ⟨110⟩ directions. A significant amount of the trivalent impurity ions can also be isolated from their compensating defects as has been proposed by several authors.[3-4] Recently some experimental results have been interpreted in terms of a defect formed by a dipole which has trapped a mobile F_i^- as suggested by Crawford *et al.*[3] These YF_{i2}^- complexes could be linear or *L*-shaped in a {100} plane.[5]

The R^{3+} doped fluorites have been the object of extensive experimental work with the most diverse techniques. In all the fluorites, dipoles have been observed, the predominant type depending on the impurity size and the matrix. Defects larger than the NN and NNN dipoles have been postulated by Andeen *et al.*[6] to explain the five peaks observed in the complex dielectric-constant curve, as a temperature function, of rare-earth-doped CaF_2. They suggest that the negative dimer, the positive dimer, and a larger cluster are responsible for three of the peaks observed in as-given crystals with an impurity molar concentration of 10^{-3}. More recently Jacobs *et al.*[7] concluded from combined ionic thermocurrents (ITC) and ionic conductivity experiments on

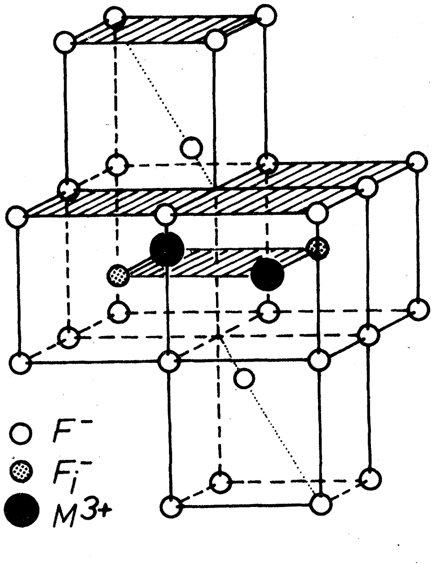

FIG. 1. 2:2:2 cluster. F_i^- are relaxed in the ⟨110⟩ direction.

CaF_2:$10^{-3}Y^{3+}$ crystals, quenched from 1100 K, that possibly there exist the two types of dipoles, the 2:2:2 dimer, and more complicated clusters responsible for four other relaxation peaks. On the CaF_2:Gd system Capelletti *et al.*[8] published ITC results on thermally treated crystals that enabled them to clarify the cluster origin of the second relaxation peak observed by them. They suggested that this aggregate could be a negative dimer, a neutral dimer, or a more complicated aggregate.

In the SrF_2:R^{3+} system and for the temperature range we are concerned with (77–350 K), the ITC spectrum has been interpreted by Lenting *et al.*[9] in terms of NN and NNN dipoles. In SrF_2:La^{3+}, Figueroa *et al.*[10] have studied an ITC relaxation peak located at 220 K which is possibly due to clusters because of its observed behavior after thermal treatments, for the crystal with 10^{-2} impurity concentration, and as a function of the impurity concentration for the other samples.

In the BaF_2:R^{3+}, Laredo *et al.*[11] assigned the two low-temperature peaks present for all the impurities studied (La, Ce, Pr, Nd, Sm, Gd, Y, Ho, Tm) to NN and NNN dipoles. For all the impurities, the calculated concentration of impurities under dipolar form was lower than the nominal concentration of the crystal. The remaining trivalent cations, if any, could be free in the lattice or in nonpolarizable clusters that do not give any signal in an ITC spectrum ranging from 77 to 350 K.

In this paper, we present experimental evidence which suggests that in BaF_2:Y^{3+} and for intermediate impurity concentrations ($c \leqslant 10^{-3}$) some kind of nonpolarizable cluster exists which undergoes a dissociation process at high temperature. Similar conclusions could be made for the BaF_2:La^{3+} system.

II. EXPERIMENTAL PROCEDURE

The BaF_2 single crystals were provided by Optovac Inc.; the nominal impurity concentration c ranged from 10^{-5} to 10^{-3} expressed in molar fractions. The samples were slices of approximately 1 cm^2 in area and 1 mm thick.

The experimental technique already has been described.[12] The polarizing field ϵ_p is of the order of 10 000 V/cm. The polarizing time $t_p \simeq 3$ min when the polarization is made at a temperature $T_p > T_M$, where T_M is the temperature at which the maximum current occurs for the peak under study. The final temperature is 77 K, and the heating rate is typically 0.1K/sec.

The crystals were the object of thermal treatments in order to modify the state of aggregation of the defects in the crystal. The cell used was made of quartz and was filled with dry helium gas. Two kinds of treatments were performed: First an annealing at high temperature (1285 K) followed by a slow decrease in temperature at a rate of 10 K/h; second, the crystals were heated to a temperature T_q and kept for five hours at this temperature, before being quenched to room temperature. The quenching was made by pulling the cell out of the furnace and cooling it with a powerful stream of water. These quenchings were made from 693 to 1184 K by steps of 50 K approximately between two successive experiments. The samples reached room temperature in about 1 min; they did not present evidence of surface attack or loss of transparency.

III. RESULTS

In Fig. 2, the ITC spectra of three BaF_2:Y^{3+} crystals are shown, the molar concentration of the samples being 10^{-5}, 10^{-4}, and 10^{-3}. The three spectra have similar characteristics, that is, they show three peaks A, B, and C whose maxima occur at 161 K, 183.5 K and at a variable temperature for peak C. The intensity of peak A is always lower than the intensity of peak B, in agreement with the previous observations[11] in BaF_2 crystals doped with various rare-earth ions (La, Ce, Pr, Nd, Sm, Gd, Ho, Tm). After an efficient cleaning of the B peak, the relaxation parameters E and τ_0 were determined using the standard model for ITC introduced by Bucci and Fieschi,[13] which is based on the assumption of a unique value for the disoreintation energy E. The result obtained with this monoenergetic model is shown in Fig. 3, curve a. The experimental points lie on a curve wider than that calculated. By using

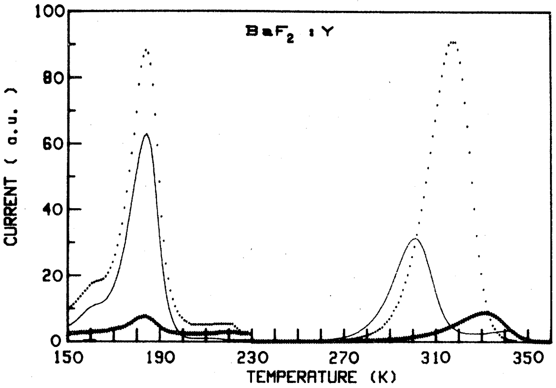

FIG. 2. ITC spectra of BaF_2 crystals with different Y^{3+} concentrations (+++: $c=10^{-5}$; ⋯ : $c=10^{-4}$; —: $c=10^{-3}$).

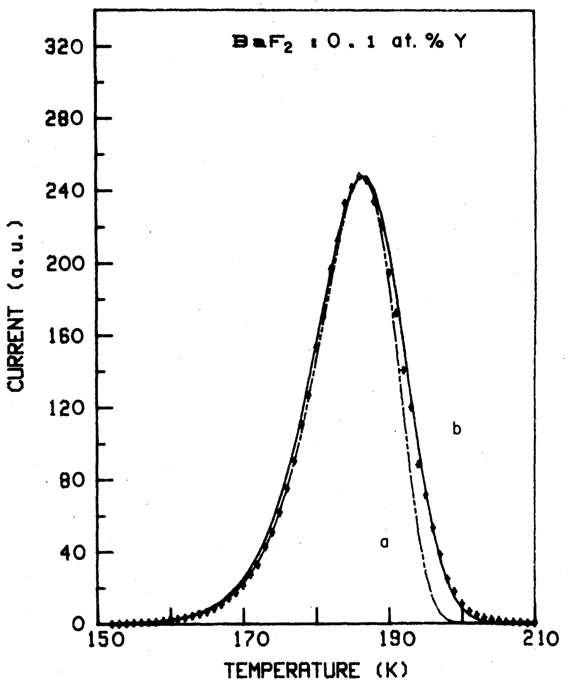

FIG. 3. Relaxation peak attributed to NNN dipoles after different analysis (+++: experimental points; ------: analysis with $\sigma=0$; ——: analysis with $\sigma=0.009$ eV).

a computer model that assumes a Gaussian energy distribution of width σ around a mean value $E_0(\sigma)$,[14] a good agreement was obtained between the calculated curve (Fig. 3, curve b) and the experimental points. The final relaxation parameters values were $E_{0B}(\sigma)=0.56$ eV, $\sigma_B=0.009$ eV, and $\tau_{0B}(\sigma)=3.3\times10^{-14}$ sec. For peak A, which is strongly influenced by peak B, this kind of analysis is not possible as we need very efficiently cleaned peaks. The estimated parameters are in the monoenergetic model $E_A=0.45\pm0.03$ eV and $\tau_{0A}=5.7\times10^{-(13\pm0.4)}$ sec. We observe that E_A is lower than E_{0B}, and both are lower than the free interstitial migration energy E_m as determined by ionic-conductivity experiments in the same system ($E_m=0.76$ eV).[15] For this reason one can assign peak A to the more bound NN dipole and peak B to the less bound NNN dipole whose disorientation energy should be closer to E_m. Using the undistorted point-ion model, the dipolar moment of the two species is calculated. The concentration of NN and NN dipoles is then estimated, following the method indicated by us.[12]

In Fig. 4, the variation of the concentration of the two types of dipoles is represented as a function of the nominal impurity concentration c for as-given crystals. As can be observed, the dipole concentration is an increasing function of c. The concentration ratio between the two species is preserved for the concentration range studied.

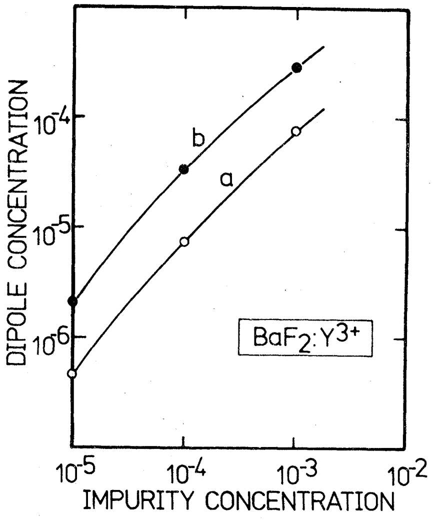

FIG. 4. Variation of the concentration of NN dipoles (curve a) and NNN dipoles (curve b) as a function of the nominal impurity concentration for $BaF_2:Y^{3+}$ crystals.

Afterwards, the crystals with $c=10^{-3}$, were subjected to thermal treatments. This series started with an annealing at 1285 K followed by a slow cooling. The ITC spectrum after the annealing is represented in Fig. 5 (curve a). The intensity of the maximum of peak B decreased by a factor of 2.4. The intensity ratio between peaks A and B was preserved. Then, the quenchings were made from 693 to 1183 K, by steps of 50 K. In Fig. 5, curves b and c represent the ITC spectrum after quenching from 904 and 1183 K, respectively. An increase in the intensity of the dipolar peaks can be observed. This effect is best visualized in Fig. 6 where we have plotted

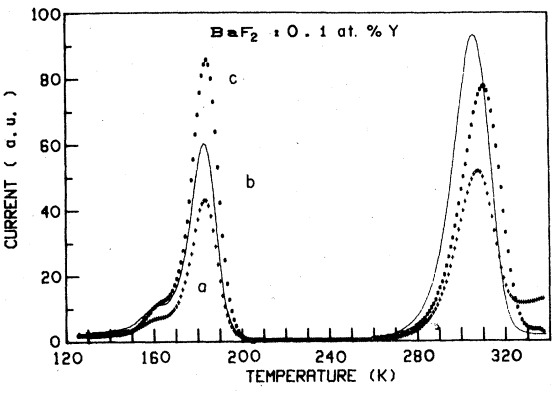

FIG. 5. Variation of the ITC spectrum of a crystal of $BaF_2:Y^{3+}$ ($c=10^{-3}$) after thermal treatments [(a) ++++: crystal annealed; (b) —: quenched from 904 K; (c) oooo quenched from 1183 K].

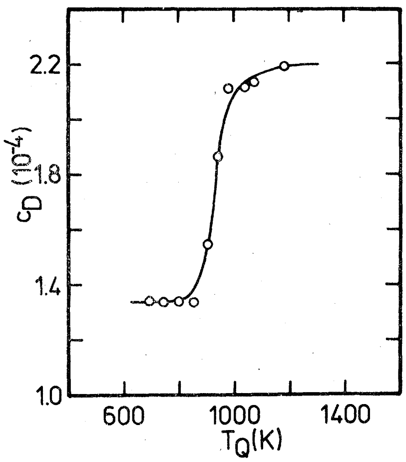

FIG. 6. Variation of the NNN-dipole concentration in a $BaF_2:Y^{3+}$ ($c=10^{-3}$) crystal as a function of the quenching temperature.

the variation of the concentration of NNN dipoles as a function of the quenching temperature.

In addition to the A and B peaks, the ITC spectra of BaF_2 crystals doped with yttrium show the presence of a third peak whose behavior is distinct from that of the low-temperature peaks. The position of the maximum of this C peak depends on the impurity concentration of the crystal as well as on the thermal and mechanical treatments applied to the sample. In a previous paper[12] on $BaF_2:La^{3+}$ the C peak has been discussed and has been related to the polarization of the dislocations present in the crystal. In this system we have reached the same conclusion as in the case of $BaF_2:La^{3+}$.

IV. DISCUSSION AND CONCLUSIONS

As Y^{3+} is not paramagnetic, the assignment of each dipolar relaxation to peaks A and B is worth discussing. In all the BaF_2 crystals doped with impurities of the lanthanide series, two low-temperature relaxation peaks were observed.[11] These two peaks are well separated only in the case of La^{3+} and Ce^{3+}. In the $BaF_2:Ce^{3+}$ system EPR lines with tetragonal symmetry have been reported.[16] In BaF_2 doped with other paramagnetic impurities the line with trigonal symmetry is predominant. Therefore the less intense peak is tentatively assigned to NN dipoles while peak B is assigned to NNN dipoles. If peak A were due to a polarizable aggregate, the intensity ratio of peak A and B should not be constant as the concentration increases; one peak should grow at the expense of the other, as was observed by Capelletti *et al.*[8] in CaF_2:Gd where the higher-temperature peak was attributed to a cluster. The fact that the intensity ratio I_A/I_B does not depend significantly on the nominal impurity concentration of the crystals reinforces the assumption that these peaks are due to the relaxation of NN and NNN dipoles. The equilibrium between the two types of dipoles depends on the difference in free energies involved in the two configurations. This difference has been calculated by Crawford *et al.*[17] in SrF_2:Gd and was found to be 0.046 eV. Thus, if the as-given crystals correspond to the same quenched equilibrium state, the ratio I_A/I_B should be concentration independent as shown in Fig. 4.

The high-temperature annealing in the case of $BaF_2:La^{3+}$ and $BaF_2:Y^{3+}$ gave different results. For lanthanum-doped crystals after the annealing, the dipole peaks A and B disappeared from the spectrum (Fig. 7 in Ref. 12). In the case of yttrium impurities, the dipole signal is significantly reduced as compared to the as-given crystals. This result indicates that the rate of the temperature decrease was not low enough to reach equilibrium at all temperatures. The impurities that are no longer under a simple dipolar form must be now in nonpolarizable clusters, as the ITC spectrum does not show any new relaxation peak from 80 to 300 K. The existence of these nonpolarizable clusters present in the annealed crystals can explain the results shown in Fig. 6. The increase in the number of NNN dipoles is due to the dissolution of these clusters when the quenching temperature is increased. The dipolar signal has a constant intensity up to temperatures of 850 K, which is the lowest equilibrium temperature reached during the annealing. For higher values of the quenching temperature, the clusters start dissolving, therefore increasing the number of free dipoles and consequently the height of the respective ITC peaks.

The plateau observed at high temperatures can be interpreted in two different ways: It can be due to the exhaustion of the clusters present in the crystal, in which case 2.2×10^{-4} is the limit for the concentration of NNN dipoles in the crystal; or this plateau can be explained as the result of a quenching which is not quick enough to freeze equilibrium states of temperatures higher than 1000 K. In this case the total impurity concentration in clusters c_c is no longer a known parameter. One can only say that the quenchings we performed on the crystals were able to dissolve clusters until a concentration of free NNN dipoles of 2.2 $\times10^{-4}$ was reached. The total impurity concentration c_T under NN and NNN dipoles and clusters has a value between 2.8×10^{-4} and 10^{-3}, the latter being the nominal impurity concentration of the crystal.

Now, if an attempt to estimate the energy involved in this cluster dissolution is made, the structure of these clusters must be assumed. Catlow[1] has calculated the binding energies for different possible clusters in this system. In $BaF_2:Y^{3+}$ the cluster with the lower energy is the 2:2:2 shown in Fig. 1, in which the relaxation of F_i^- along the ⟨111⟩ and ⟨110⟩ direction stabilizes the structure. The dipolar moment of this dimer is zero. The binding energy is −1.22 eV with respect to the pair $Y^{3+}-F_i^-$.

If we suppose that for the concentrations reported here, $c_T \leq 10^{-3}$, there is only one type of cluster, which is the nonpolarizable 2:2:2, upon dissociation this cluster will originate free dipoles easily detected by ITC techniques. If these dipoles are in equilibrium with the dimers at a temperature T, the following equilibrium reaction can be written:

$$(Y^{3+}-F_i^-)_2 \rightleftarrows (Y^{3+}-F_i^-)+(Y^{3+}-F_i^-).$$

From this equation we can write the relation between the impurity concentration in clusters, c_c, and the concentration of NNN dipoles as a function of the cluster dissolution enthalpy, E, and the entropy change involved in the reaction, ΔS, as

$$\frac{c_c}{c_D^2}=e^{E/kT}e^{-\Delta S/k}.$$

The impurity concentration in clusters c_c can be calculated from

$$c_c=c_T-(c_D'+c_D),$$

where c_D' is the impurity concentration in NN dipoles calculated by assuming that the ratio c_D'/c_D is constant and equal to 0.26. The above expression can be written as

$$c_D^2e^{-\Delta S/k}e^{E/kT}+(c_D'+c_D)-c_T=0.$$

Least-squares fittings for calculating E and ΔS as a function of the parameter c_T, which can vary from 2.8×10^{-4} to 10^{-3}, were performed. The results of these fittings are plotted in Fig. 7. As ΔS represents the change in entropy between the dipolar state and the cluster, its value should be positive; this limits us to values of $c_T < 7\times10^{-4}$, or for the dissociation energy, to values between 0.79 and 2 eV. The calculated value of 1.22 eV is within these limits and would correspond to a value of 3.5×10^{-4} for c_T. The impurity concentration under dipolar form calculated from the high-temperature plateau of Fig. 6 will then correspond to 80% of the total impurity concentration, which is a reasonable value.

However, this model presents a difficulty due to the cluster dissociation mechanism. When the cluster dissociates into two dipoles and contributes then to the ITC signal, the Y^{3+} ions must leave their original sites in the cluster. These ions are now farther apart than they were in the 2:2:2 cluster. Owing to the very low mobility of these substitutional trivalent cations,[2] the jumps of these cations occur with a very low probability. It is possible that the positions occupied by the Y^{3+} are those they acquired at a very high temperature during the crystal growth. In this quenched sublattice of Y^{3+}, the only change can be originated by the redistribution of interstitial fluorines that are very mobile at these temperatures. The cluster that can fulfill the conditions of being nonpolarizable, and at high temperature originate a dipole without involving any motion of the trivalent cation, is a dipole that has trapped an extra F_i^-. This type of complex has been previously discussed[3-5-7] in CaF_2. It has been calculated[5-7] that the linear complex $F_i^--Y^{3+}-F_i^-$ which has no dipolar moment is less stable than the L-shaped $Y^{3+}F_{i2}^-$ in a {100} plane which has a nonzero dipolar moment. With these two types of $Y^{3+}F_{i2}^-$, the dissolution of aggregates in fluorites with intermediate impurity concentrations can be understood without any impurity jump being involved. In BaF_2 the linear complex would be more stable, and at high temperature the increase in the number of dipoles will be due to the loss of one F_i^-. If the L-shaped complex occurs, its relaxation should occur at temperatures lower than 77 K. In $SrF_2:La^{3+}$ a cluster relaxation peak has been observed by us together with the NN dipole relaxation, and the complex responsible for this

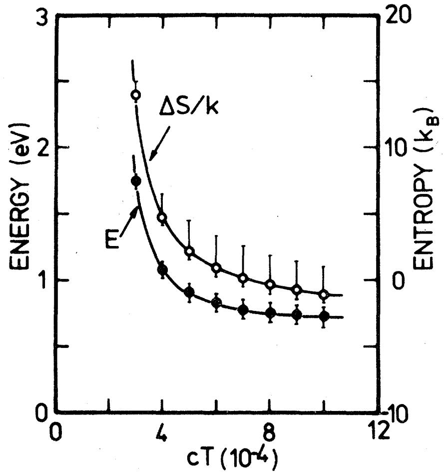

FIG. 7. Variation of the dissolution enthalpy and the dissolution entropy as a function of the total impurity concentration under dimer and dipolar form.

relaxation could be then the L-shaped $Y^{3+}F_{i2}^-$. In $CaF_2:La^{3+}$ we have observed the presence of a single relaxation peak below 280 K; this peak is attributed to NN dipoles, but its intensity indicates a very low impurity concentration under dipolar form; for example, in CaF_2 crystals with 10^{-3} La^{3+}, only 1.5×10^{-5} lanthanum ions in NNN dipoles are found.[10] The excess La^{3+} concentration could be, as in the case of $BaF_2:La^{3+}$, in nonpolarizable complexes, possibly the linear $La^{3+}F_{i2}^-$.

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

[2] C. R. A. Catlow, J. Phys. C 9, 1859 (1976); *ibid.* 9, 1845 (1976).

[3] J. H. Crawford and G. E. Matthews, Semiconductors and Insulators 2, 213 (1977).

[4] D. R. Tallant, D. S. Moore, and J. C. Wright, J. Chem. Phys. 67, 2897 (1977).

[5] C. R. A. Catlow, J. D. Comins, F. A. Germano, R. T. Harley, and W. Hayes, Phys. Lett. 71A, 97 (1979).

[6] C. Andeen, D. Link, and J. Fontanella, Phys. Rev. B 16, 3762 (1977).

[7] P. W. M. Jacobs and S. H. Ong, J. Phys. Chem. Solids 41, 431 (1980).

[8] R. Capelletti, E. Okuno, G. E. Matthews, and J. H. Crawford, Jr., Phys. Status Solidi 47, 617 (1978).

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

[10] D. Figueroa, M. Puma, E. Laredo, and N. Suárez, in *Simposio de Física de la Materia Condensada-Parte Experimental*, leras. Jornadas Cientificas de la U. S. B., edited by E. Laredo (Equinoccio, Caracas, 1980).

[11] E. Laredo, D. R. Figueroa, and M. Puma, J. Phys. (Paris) (in press).

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

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

[14] M. Puma, E. Laredo, D. Figueroa, and N. Suárez, in *Simposio de Física de la materia condensada-Parte Experimental*, Iras. Jornadas Científicas de la U.S.B., edited by E. Laredo (Equinoccio, Caracas, 1980).

[15] D. R. Figueroa, A. V. Chadwick, and J. H. Strange, J. Phys. C 11, 55 (1978).

[16] A. Kiel and W. B. Mims, Phys. Rev. B 6, 34 (1972).

[17] G. E. Matthews and J. H. Crawford, Jr., Phys. Rev. B 15, 55 (1977).