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Raman spectroscopy of $BaF_2:R^{3+}$ and $SrF_2:R^{3+}$ solid solutions between 300 and 1400 K

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In this paper we present results of Raman scattering experiments on BaF_2 and SrF_2 single crystals, doped with trivalent La ions, in the temperature range 300–1400 K. The linewidth of the Raman peaks in heavily doped materials is partly due to time-dependent effects from hopping interstitial fluoride ions, which are present in large numbers because of the excess positive charge of the La ions. From a comparison of experiment with the results of a theoretical treatment we find that the hopping energy of interstitial fluoride ions in a BaF_2 crystal doped with 3.1 mol% LaF_3 is 0.60 eV, whereas the corresponding value for a crystal with 7.3 mol% LaF_3 is 0.35 eV. For crystals with higher La concentrations the activation energy is lower. This decrease can be explained in terms of defect-defect interactions.

I. INTRODUCTION

The alkaline-earth fluorides are interesting materials because they can accomodate relatively large quantities of trivalent impurities while the long-range order is maintained.[1–3] It appears that without any difficulties crystalline materials containing up to 20–25 mol% rare-earth (RE) fluorides can be produced. On the other hand we know that fluorite-type alkaline-earth fluorides have superionic properties above a certain temperature T_c, which is well below the melting point. At high temperatures the defect concentrations are quite considerable and the ionic conductivity and diffusion constants are comparable to those of liquids. With increasing concentration of trivalent impurities the ionic conductivity increases to values which are close to those in the superionic state.[4,5] This occurs for RE concentrations between 5 and 10 mol% at temperatures well below T_c.

We have employed the Raman techniques to study the jump behavior of defects in pure and doped alkaline-earth fluorides at high temperatures. It will be shown that our experimental results provide information about the conduction and diffusion mechanism below the order-disorder transition temperature T_c.

In the alkaline-earth fluorides one observes only one Raman peak which has been associated with the excitation or annihilation of T_{2g} phonons. The positions of these lines for SrF_2 and BaF_2 at 300 K are 280 and 240 cm^{-1}, respectively. The width of the Raman lines increases with increasing temperature; this appears to be due to anharmonic effects, but also jumping defects (interstitial fluoride ions) may, especially at high temperatures where the jump rates can be very high, contribute significantly to the linewidth. It is expected that this mechanism only contributes if the concentration of defects is sufficiently high. We have carried out experiments on heavily doped materials with large concentrations of fluoride interstitials. Solid solutions of alkaline-earth fluorides and rare-earth fluorides have been investigated by means of various experimental techniques.[6–8] It appears that the description of the defect structure of heavily doped materials is far from complete. There is some evidence for extensive clustering of two or more charge-compensation complexes.[2,6–8] For some materials, however, we have found that a statistical description of the defect structure is sufficient to explain the experimental observations.[9,10] It therefore is not likely that clusters consisting of two or more charge compensation defects contribute significantly to the very large mobility of the fluoride interstitials.

A possible mechanism for the very large ionic conductivity at moderate temperatures (1000–1400 K) is a hopping sequence where bound interstitial fluoride ions jump from one charge-compensation complex to another. If this mechanism is active at high temperatures the activation energy obtained from an ionic conductivity experiment will be determined by the jumps of interstitial fluoride ions which are incorporated in dipolar complexes. It is obvious that this conduction mechanism can be dominant only if we are dealing with a percolation-type conduction, which occurs only for large dipole concentrations.

As mentioned above hopping may influence the width of the T_{2g} Raman peak in SrF_2 and BaF_2. From the temperature behavior of this additional broadening effect, which will be described theoretically, we have found effective jump energies for the conduction process in heavily doped fluorides and it appears that there is good agreement between the Raman-jump energies and those obtained from dielectric experiments.

II. EXPERIMENTAL PROCEDURES

The single-crystal materials $Ba_{1-x}La_xF_{2+x}$ with x up to 0.20 have been prepared with a modified Bridgman setup. The materials were heated in highly pure carbon crucibles with a 25-kW high-frequency furnace under He atmosphere (700 Torr). In order to remove the O^{2-} impurities we have added to the mixture of BaF_2 and LaF_3 from which the crystalline material is grown 1–2% PbF_2. It appears that after growth there is no Pb present and during growth the O^{2-} impurities are removed by the reaction

$$BaO + PbF_2 \rightarrow BaF_2 + PbO\uparrow \ .$$

The single-crystal materials have been prepared at a growth rate of 3 mm/h.

The high-temperature Raman experiments were carried out with a Spex Ramalog Raman spectrometer setup in conjunction with a resistance furnace which could be operated under vacuum of 10^{-4} Torr. With the furnace used for these experiments it is possible to carry out Raman experiments up to temperatures as high as 1450 K. We found that it is necessary to employ phase-lock techniques for temperatures above 1100 K, because of the thermal radiation of the heating element of the furnace (a Ta coil). For these measurements the laser beam is chopped at a frequency of 100 Hz; phase-sensitive detection has been carried out with a PAR 128 lock-in amplifier.

The concentration of the La impurities in the various samples has been determined with x-ray fluorescence measurements. A disadvantage of this method is that the fluorescence peaks that can be used for the analysis are always very close to each other. Consequently, for samples containing small amounts of La (less than 1 mol%) this method cannot be employed.

III. EXPERIMENTAL RESULTS

In Fig. 1(a) we show the Raman spectrum for nominally pure BaF_2 at 300 K. It reveals one single line located at 240 cm^{-1}. The position of this peak is in good agreement with observations of Mead and Wilkinson and Elliott *et al.*[11,12] It appears that with increasing temperature the position and width of the Raman line varies. In Fig. 2 we have plotted the behavior of the linewidth as a function of temperature. Mead and Wilkinson[11] have measured the Raman lines up to about 1100 K and their results are in good agreement with ours in this temperature range.

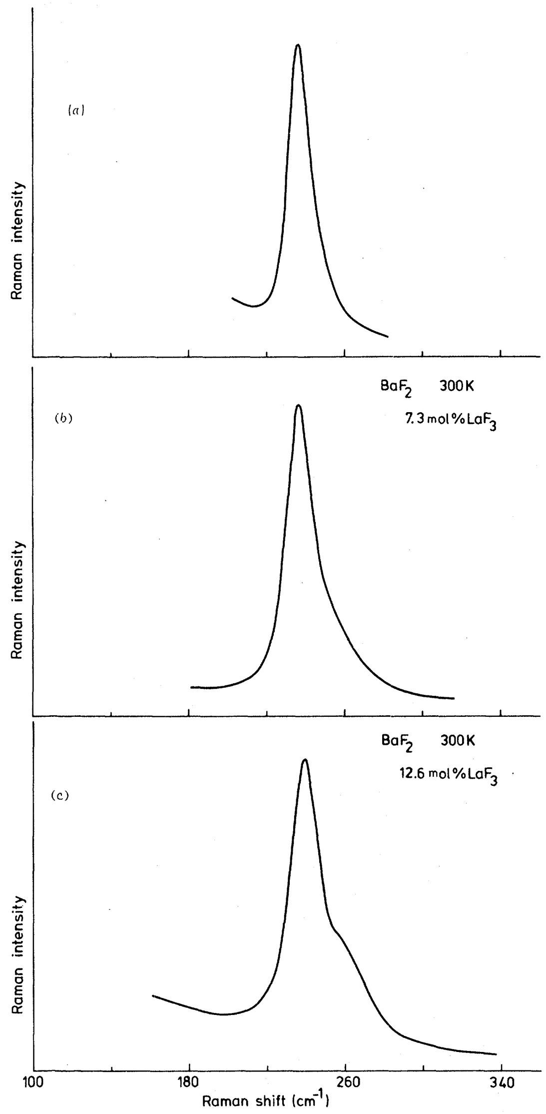

FIG. 1. (a) Raman spectrum of pure BaF_2, measured at room temperature. (b) Raman spectrum of a BaF_2 crystal doped with 7.3 mol% LaF_3 showing the T_{2g} peak. The presence of additional peak at 260 cm^{-1} is indicated by the shoulder observed in the high-frequency tail of the T_{2g} peak. (c) The Raman spectrum of a BaF_2 sample doped with 12.6 mol% LaF_3. It can be seen that the additional peak at about 260 cm^{-1} is higher than in Fig. 4.

For BaF_2 doped with LaF_3 we have observed a similar Raman line as in pure BaF_2 at approximately the same position, but this line behaves differently as a function of temperature. At low temperature T_{2g} peak width increases, just as for pure BaF_2, slowly with temperature, but above a certain temperature the width of the peak in doped materials increases more rapidly. In Fig. 2 we show a few Raman spectra observed for a BaF_2 crystal doped with 3.1 mol% LaF_3 in the temperature range 300–1400 K. An analysis of the spectra provides us with the widths of the individual lines, the intensities, and the relative positions. In Fig. 3 we have plotted the width of the T_{2g} line as a function of temperature. An interesting

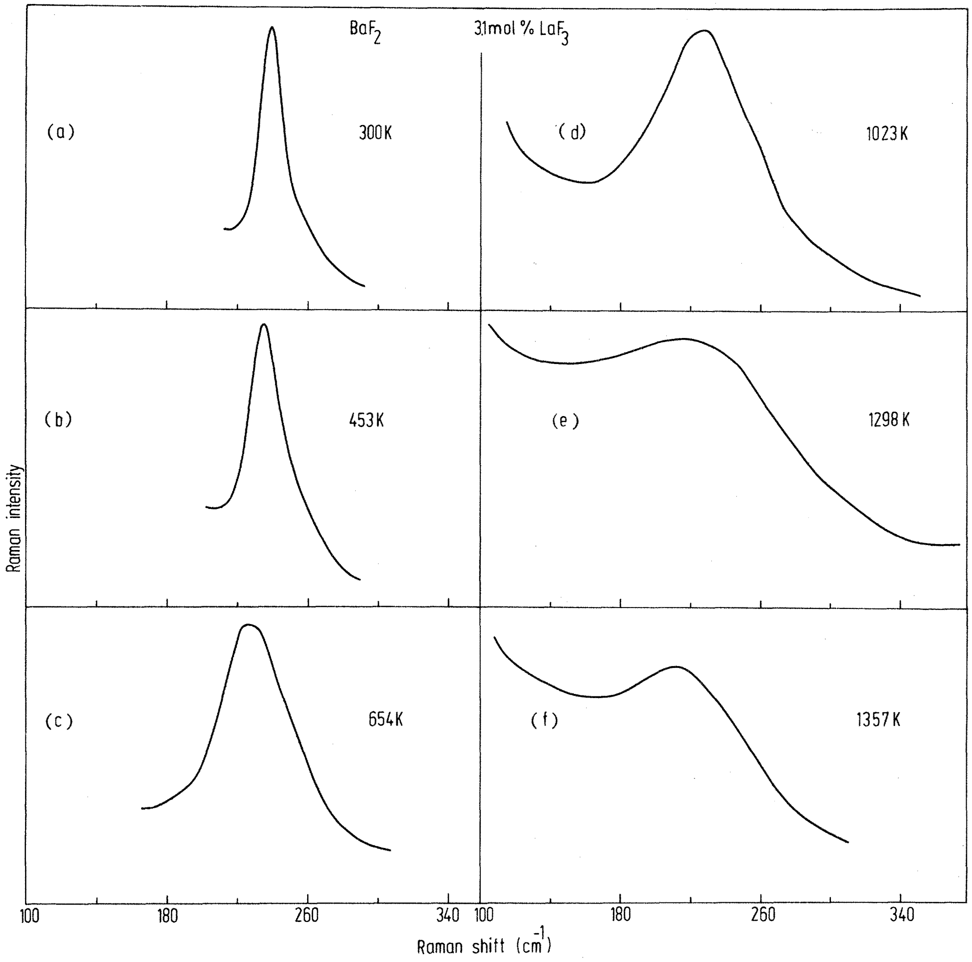

FIG. 2. Behavior of the T_{2g} Raman line in a BaF_2 sample doped with 3.1 mol% LaF_3 as a function of temperature.

feature of these results is that at temperatures higher than approximately 1300 K the linewidth appears to decrease with increasing temperature. Unfortunately, we have been able to observe the Raman line at temperatures higher than T_c only for a few samples, due to the decreasing signal-to-noise ratio and the increasing background signal (see Fig. 2).

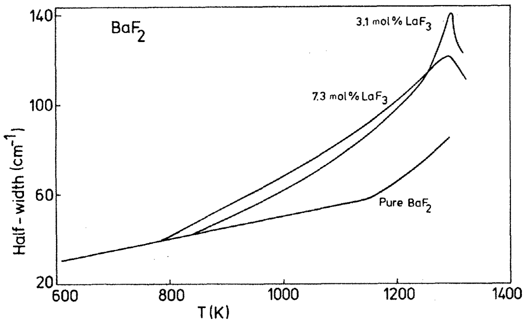

FIG. 3. Survey of the results obtained for the width of the Raman lines in pure BaF_2 and samples doped with 3.1 and 7.3 mol% LaF_3 as a function of temperature.

In Fig. 3 we also show a review of the results for the linewidth of BaF_2 crystals doped with 0, 3.1, and 7.3 mol% LaF_3. Comparing the results for the different samples we see that the extra contribution to the line broadening, which is due to hopping defects, increases with increasing La concentration. The temperature at which this additional contribution becomes observable shifts to lower temperatures. Another result obtained from the analysis of the Raman spectra is that the intensity of the additional Raman line, located at 260 cm^{-1} increases with increasing La concentration. This is demonstrated by comparing the Raman spectra of samples with 0, 3.1, 7.3, and 12.6 mol% LaF_3 [see Figs. 1(a), 2(a), 1(b), and 1(c)] at 300 K. This trend is continued for BaF_2 samples with more LaF_3; we note that at very large La concentrations the T_{2g} Raman line even disappears (see Ref. 4) while the extra line at 260 cm^{-1} is still present.

We have also investigated SrF_2 samples doped with LaF_3 and we found that it behaves similar to the

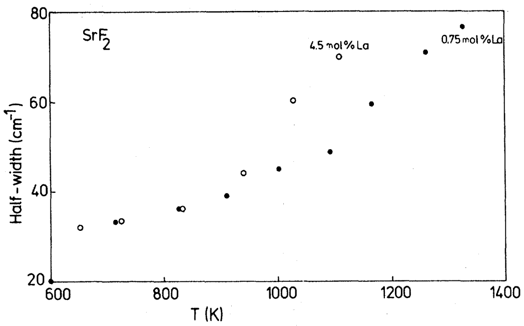

FIG. 4. Plots of the linewidths of the T_{2g} Raman line in SrF_2 crystals doped with 0.75 and 4.5 mol% LaF_3 as a function of temperature.

BaF_2 samples. In Fig. 4 we show the results for the Raman linewidth for SrF_2 doped with 0.75 and 4.5 mol% LaF_3. Here too, we find a slowly varying low-temperature behavior for the linewidth and a deviation at higher temperatures.

IV. DISCUSSION

The nature of the main Raman line observed in BaF_2 has been described at several places in the literature.[11,12] It has been well established that this Raman line is connected with the T_{2g} Raman-active phonon of the fluorite crystal structure. We have observed that with increasing concentrations of LaF_3 the extra Raman line situated at approximately 260 cm^{-1} grows. Because the T_{2g} peak is associated with the excitation of the F^- sublattice we speculate that the additional line is not due to vibrations of the La impurities but that it should be ascribed to local vibrations of the interstitial F^- ions, which are present in BaF_2 crystals doped with LaF_3. This interpretation is in agreement with results of the calculations of Nerenberg, Haridasan, Govindarajan, and Jacobs.[13] These authors have calculated the frequencies of the local modes associated with interstitial fluoride and hydride ions in alkaline-earth fluoride crystals. Nerenberg *et al.* find several excitation frequencies in the close vicinity of the T_{2g} phonon frequency and in this regard especially the Raman-active E_g excitation, which is calculated to occur at approximately 284 cm^{-1}, is of interest.

The behavior of the T_{2g} peak for increasing temperatures can be explained by anharmonic effects if we confine ourselves to the low-temperature region (400–1200 K for pure BaF_2); see also Elliott *et al.*[12] for a treatment of third- and fourth-order anharmonicities, which give rise to a shift and broadening of the Raman line. We have observed both effects during our experiments as can be seen from Fig. 2. In addition to the appreciable broadening of the Raman line with increasing temperature we observe a shift towards lower energies.

At temperatures above 1200 K for pure BaF_2 we have found that the Raman line is broadened by an additional mechanism, which is strongly temperature dependent (see Fig. 3). On the other hand it has been observed that this additional broadening mechanism is operative in doped BaF_2 at lower temperatures. We therefore conclude that this mechanism is associated with the defects, which are introduced into the BaF_2 lattice when this material is doped with LaF_3. A second conclusion which can be drawn from our observations is that the extra broadening should be due to motional effects. If they were due to interactions between the phonon and the static defect system there would also be appreciable contributions to the broadening from this mechanism at low temperatures.

Probably the interstitial fluoride ions, which are present in large quantities in BaF_2:La^{3+}, are the origin of the broadening at high temperatures. The La impurities are not expected to contribute to the broadening at high temperatures, because we know that the hopping frequencies of cations in the fluorite lattice are very small. On the other hand, the mobility of fluoride ions is large.

Diffusion and ionic conduction of fluorite-type crystals are controlled by interstitialcy jumps of fluoride ions. Similar processes take place during the reorientational jumps of dipolar systems in doped fluorite materials (see Fig. 5).[14] The activation energies associated with the jumps of interstitial fluoride ions are 0.8 eV for free interstitials and ~0.4 and 0.6 eV for tetragonal (C_{4v}) and trigonal (C_{3v})R^{3+}-F_i^- complexes, respectively. The hopping dipoles and interstitial fluoride ions give rise to a time-dependent interaction with the phonons and will therefore reduce the lifetime of the T_{2g} phonon. Consequently, the T_{2g} peak broadens with increasing hopping rates,

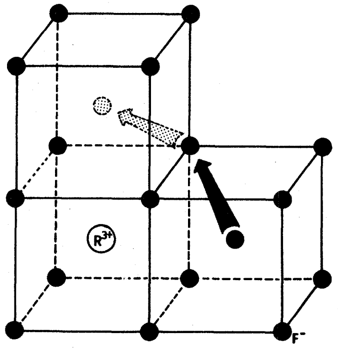

FIG. 5. Schematic representation of the jump process of a NN R^{3+}-F_i^- dipolar complex in the fluorite lattice structure.

which are described by the formula

$$\nu=\nu_0\exp(-E_a/kT) \quad . \tag{1}$$

From the reasoning given above it can be concluded that from a detailed study of the width of the T_{2g} Raman line one can obtain information about the hopping processes at high temperatures.

We shall now analyze the results in terms of time-dependent phonon-defect interaction. In order to do so we have to propose a model for the interaction between phonons and defects. We confine ourselves to first-order perturbation theory and furthermore we only take into account the effects due to the first derivatives of the electric potentials. In addition we assume that the jumps of different anions are uncorrelated, implying that the electric field intersities associated with the hopping ions are additive. It is obvious that at high defect concentrations this assumption is not valid. In our treatment we have ignored the effect of screening and we have assumed that during the interstitialcy hop the two anions, which are involved in the process, move with the same velocity.

We approximate the time-dependent perturbation potential due to the hopping interstitial fluoride ion by square pulses. Because the hops are determined by statistics we have to take into account that the length of the square pulses is distributed about an average value $\langle t\rangle$ ($\sim 1/\nu$). We assume that the distribution of square pulses with length t can be described by

$$p(t)=\frac{1}{\langle t\rangle}\exp(-t/\langle t\rangle) \quad . \tag{2}$$

The Fourier transform of this distribution of these pulses is equal to

$$\overline{|V(\omega)|^2}=2\frac{\pi^{-1}\langle t\rangle}{1+\omega^2\langle t\rangle^2} \quad , \tag{3}$$

and the corresponding transition probability describing the excitation from a state with n T_{2g} phonons to a state with n' phonons

$$T_{n\to n'}=\frac{2\pi}{\hbar}|\langle n|V^*|n'\rangle|^2 \times\int_{-\infty}^{+\infty}\frac{\frac{1}{2}\hbar\Gamma_1\pi^{-1}|V(\omega)|^2d\omega}{\hbar^2(\omega_R-\omega)^2+\frac{1}{4}\hbar^2\Gamma_1^2} \quad , \tag{4}$$

where the matrix element

$$\langle n|V^*|n'\rangle=\left\langle n\left|-e\sum_{l,k}\vec{\mathrm{E}}(l,k)\cdot\vec{\mathrm{u}}(l,k)\right|n'\right\rangle \quad , \tag{5}$$

Γ_1 is the width of the Raman line due to anharmonic effects and ω_R is the Raman excitation frequency. In (5) $\vec{\mathrm{u}}(k,l)$ is the displacement of the kth ion of lth unit cell from its lattice position and $\vec{\mathrm{E}}(k,l)$ is the electric field strength at this lattice site. The summation (5) is carried out over a part of the crystal that contains one hopping interstitial. This region depends upon the La^{3+} concentration and the temperature. In accordance with the nomenclature of Wallis *et al.*[15] we can write

$$u_\alpha(k,l)=\left(\frac{\hbar}{2NM}\right)^{1/2}\sum_{\vec{q},j}\frac{e_\alpha(k|\vec{q}j)}{\sqrt{\omega_j(\vec{q})}} \times\exp[2\pi i\vec{q}\cdot\vec{R}(l,0)]A_{\vec{q}j}$$

and

$$A_{\vec{q}j}=b^{\dagger}_{-qj}+b_{\vec{q}j} \quad . \tag{6}$$

N is the number of unit cells considered. As mentioned above we approximate the electric field due to the defect; therefore we confine ourselves to first-order processes in the description with creation and annihilation operators. Consequently we only consider transitions between states where the number of T_{2g} quanta differ by one. I.e.,

$$\langle n|V^*|n'\rangle=\frac{-ie\sqrt{\hbar}}{\sqrt{2M\omega_R}}\left(\sum_{l=2}^{N}\sum_{k\neq 0}^{2}\frac{(-)^k}{\sqrt{2N-1}}E_\alpha(\vec{\mathrm{R}}(l,k))\right)(\sqrt{n'+1}\,\delta_{n,n'+1}-\sqrt{n'}\,\delta_{n,n'-1}) \quad . \tag{7}$$

Taking into account that the excited states containing different numbers of T_{2g} quanta are distributed in accordance with the Bose-Einstein statistics, we sum the different contributions.

The shape of the Raman line is determined by two processes: (a) the process of anharmonic broadening as treated by Elliott *et al.*[12] and (b) the hopping defects. The damping associated with the second mechanism can now be written as

$$\Gamma_2=\frac{\pi e^4}{\hbar\omega_R^2Ma^4}\frac{1+\exp(-\hbar\omega_R/kT)}{1-\exp(-\hbar\omega_R/kT)}\left|\sum_{l,k}\frac{(-)^k}{\sqrt{2N-1}}\frac{a^2}{e}E_\alpha(\vec{\mathrm{R}}(l,k))\right|^2\int\frac{\frac{1}{2}\Gamma_1\omega_R\pi^{-1}|V(\omega)|^2}{(\omega_R-\omega)^2+\frac{1}{4}\Gamma_1^2}d\omega \quad .$$

The summation in Eq. (8) has been carried out and gives approximately $0.745/\sqrt{N}$. Because $1/N$ is approximately the probability of finding a fluoride ion under hopping conditions and because this probability is equal to the product of the concentration of the defects (La^{3+}-F^- dipoles) and the hopping probability of these dipoles, which are referred to as η and p, respectively, we can now rewrite Eq. (8) as

$$\Gamma_2 = \frac{2\pi e^4}{\hbar\omega^2 M a^4}\frac{1+\exp(-\hbar\omega_R/kT)}{1-\exp(-\hbar\omega_R/kT)}0.555\eta p \times \frac{\pi^{-1}(\frac{1}{2}\Gamma_1 + \langle t\rangle^{-1})}{\omega_R^2 + (\frac{1}{2}\Gamma_1 + \langle t\rangle^{-1})^2}\ , \qquad (9)$$

which can, for our applications, be approximated by the following form [because the second factor in (9) behaves as T at high temperatures; the same applies to the final factor; p behaves as $\exp(-E_a/kT)$]

$$\Gamma_2 = AT^2\exp(-E_a/kT)\ . \qquad (10)$$

We note that especially the hopping probability p shows a temperature dependence which is of importance for the analysis of the results presented in this paper.

The total linewidth of the Raman peaks due to the two mechanisms indicated above can be found by adding Γ_1 and Γ_2. Γ_1 is due to anharmonic effects, while Γ_2 is associated with hopping dipoles. In order to analyze the results we assume that we can calculate the effects due to the latter mechanism by subtracting the width observed for the pure BaF_2 sample from the doped one. Especially, for temperatures below 1150 K this is easy to do because in this temperature region the width of the Raman line for pure BaF_2 behaves approximately linearly with temperature. For the sample containing 3.1 mol% LaF_3 we found for the activation energy a value of 0.57 eV and for the sample with 7.3 mol% LaF_3, 0.35 eV (see Fig. 6). For concentrations higher than 7.3 mol% the activation energy is reduced further. This is not unexpected. Also from ITC experiments we found that the activation energy decreases with increasing concentration.[16,17] Wapenaar[18] has found similar effects in ionic conductivity experiments. In an earlier paper we have proposed an explanation for the decreasing activation energy in terms of defect-defect interactions.[16]

In addition we note that at concentrations as high as 7.3 mol% there will be large numbers of F^- interstitials, which are located in the first shell of interstitial positions with respect to a La^{3+} impurity. These interstitials have very large hopping rates as compared to free interstitial fluoride ions and fluoride ions which are situated in the second shell of interstitial positions (NNN interstitial sites). The large hopping rate associated with these interstitial fluoride ions is due to a significantly lower activation energy; the activation energy of the jumps of NNN interstitials is ~0.6 eV whereas the one connected with NN interstitials is ~0.4 eV! From Fig. 6 we see that for temperatures higher than 1050 K the slopes of the curves decrease with increasing temperature. This can be explained by two reasons. First, it is possible that the approximations made to derive Eq. 10 are no longer valid. As a result, deviations from the linear behavior in Fig. 6 are expected to occur. Another possible origin of the deviations might be that above 1050 K the defect-defect interactions become stronger due to dissociation of clusters of dipolar defects. The electrostatic interactions between the hopping interstitial fluoride ions give rise to the line broadening, and simple dipoles are larger than the corresponding values for interstitial fluoride ions and dipole clusters. This increased interaction gives rise to a decrease of the measured activation energy. We note that ionic superconductors generally have low hopping energies.

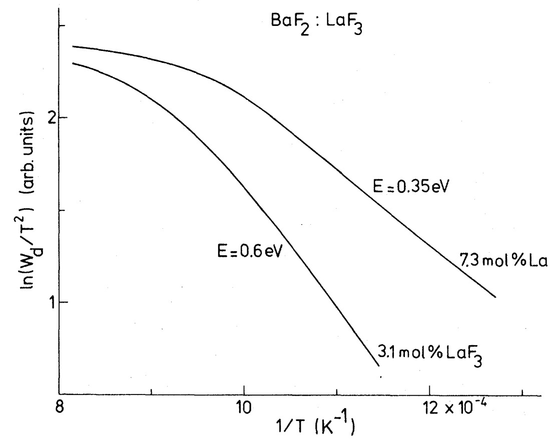

FIG. 6. The analysis of the results of the linewidth of T_{2g} Raman peaks in terms of the model described in Sec. IV [Eq. (9)].

We have found that the contribution to the total linewidth as described by Eq. (9) is approximately equal to the experimentally observed one, if we substitute the values for τ_0, E_a and the La concentration. This leads us to the conclusion that the model presented in this paper describes the additional line broadening of the T_{2g} peak at high temperature correctly.

[1] L. S. Garashina and B. P. Sobolev, Kristallografiya 16, 307 (1971) [Sov. Phys. Crystallogr. 16, 254 (1971)].

[2] A. K. Cheetham, B. E. F. Fender, and M. J. Cooper, J. Phys. C 4, 3107 (1971).

[3] D. Steele, P. E. Childs, and B. E. F. Fender, J. Phys. C 5, 2677 (1972).

[4] J. Schoonman, in *Fast Ion Transport in Solids,* edited by P. Vashishta, J. N. Mundy, and G. K. Shenoy (North-Holland, Amsterdam, 1979).

[5] L. E. Nagel and M. O'Keeffe, in *Fast Ion Transport in Solids,* edited by W. van Gool (North-Holland, Amsterdam, 1973).

[6] R. J. Booth, M. R. Mustafa, and B. R. McGarvey, Phys. Rev. B 17, 4150 (1978).

[7] A. R. Alnatt and P. S. Yuen, J. Phys. C 9, 431 (1976).

[8] D. R. Tallant and J. C. Wright, J. Chem. Phys. 63, 2075 (1975).

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

[10] H. W. den Hartog, J. Phys. (Paris) 41, C6-275 (1980).

[11] D. G. Mead and G. R. Wilkinson, J. Phys. C 10, 1063 (1977).

[12] R. J. Elliott, W. Hays, W. G. Kleppman, A. J. Rushworth, and J. F. Ryan, Proc. R. Soc. London, Ser. A 360, 217 (1978).

[13] M. A. H. Nerenberg, T. M. Haridasan, J. Govindarajan, and P. W. M. Jacobs, J. Phys. Chem. Solids 41, 1217 (1980).

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

[15] R. F. Wallis, I. P. Ipatova, and A. A. Maradudin, Fiz. Tverd. Tela 8, 1078 (1966) [Sov. Phys. Solid State 8, 850 (1966)].

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

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

[18] K. E. D. Wapenaar, J. Phys. (Paris) 41, C6-220 (1980).