

Remarks on the Assignment of Vibronic Satellites Exhibited by CaF_2 , SrF_2 , and BaF_2 Containing Substitutional Divalent Rare-earth Ions

ØYSTEIN RA

Tinius Olsens Tekniske Skole, N-3600 Kongsberg, Norway

When reexamined on the basis of lattice dynamics calculations some earlier vibronic assignments turn out to be questionable. A well known type of analysis involving local XY_6 complexes is shown to be of dubious validity even when restricted to satellites known to originate from semilocalized modes. Theoretical perfect lattice frequency distributions are reported for the three alkaline-earth fluorides.

Valuable information on the vibrations of even perfect crystals may often be uncovered by applying imperfections as probes. This paper, which is a sequel to previous lattice dynamics studies,¹⁻⁶ contains defect calculations concerning the frequency distributions of CaF_2 , SrF_2 , and BaF_2 . The following remarks relate to substitutional rare-earth ions in the mass defect limit. Force field models and the attendant diagonal Green's functions put to use below are those reported on earlier occasions.¹⁻⁶ Information about phonon spectra may be obtained from vibronic satellites (satellite bands associated with electronic transitions of impurity atoms due to the combination of the electronic transition with the creation or annihilation of one or more phonons). In this respect CaF_2 , SrF_2 , and BaF_2 have been receiving some considerable attention. These fluorides frequently serve as host lattices for paramagnetic ions, and the simultaneous excitations of lanthanide ions and lattice waves have been studied by a number of authors. However, as I hope to demonstrate below, it is desirable to reconsider some of the earlier assignments. Preferably, a few conjectures should be put on a safer basis by relating them to detailed lattice dynamics calculations.

THE LOW LYING $\text{CaF}_2:\text{Tm}^{2+}$ VIBRONIC

To begin with, we turn to the vibronic spectrum of Tm^{2+} in CaF_2 where the predominant contribution to the electronic transition appears to be of the $4f^n \rightarrow 4f^n$ type.⁷ This system shows a strong vibronic satellite at an energy

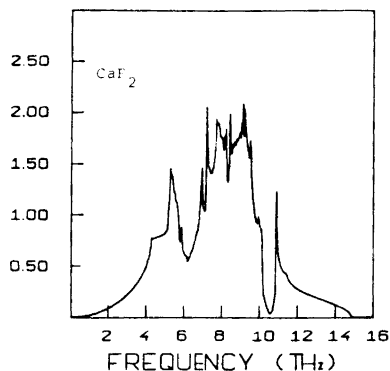


Fig. 1a. Unsmoothed computer plot of the frequency spectrum for CaF_2 as calculated by the method of Gilat and Raubenheimer¹⁷ on the basis of the central force shell-model described in Ref. 6. The spectrum is normalized to one chemical unit.

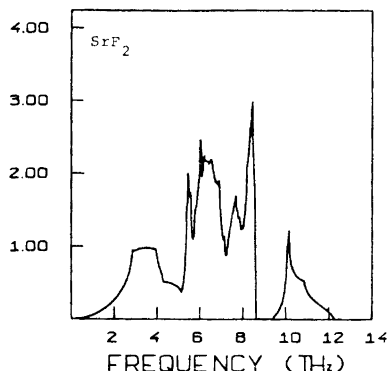


Fig. 1b. Unsmoothed computer plot of the frequency spectrum for SrF_2 as calculated by the method of Gilat and Raubenheimer¹⁷ on the basis of the central force shell-model described in Ref. 6. The spectrum is normalized to one chemical unit. The gap is possibly an artifact of the model (see the discussion of parameter fitting in Ref. 6).

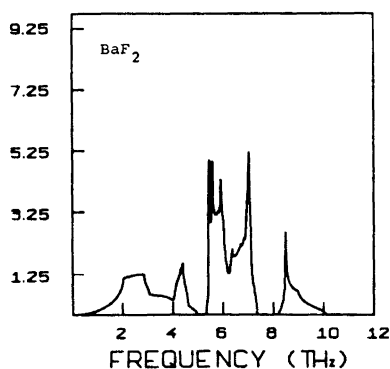


Fig. 1c. Unsmoothed computer plot of the frequency spectrum for BaF_2 as calculated by the method of Gilat and Raubenheimer¹⁷ on the basis of the central force shell-model described in Ref. 6. The spectrum is normalized to one chemical unit. Note that the model predicts a complete separation of acoustic and optical frequency branches throughout the Brillouin zone. The acoustic part of the spectrum has the typical shape of the frequency distribution function for an f.c.c. monoatomic solid (see for instance the Ni spectrum calculated by Gilat and Raubenheimer¹⁷ and shown in their Fig. 2)

shift of 93 cm^{-1} from the purely electronic line. However, there is probably no critical point in the perfect lattice, one-phonon density of states at this low energy value as indicated by the theoretical spectrum shown in Fig. 1a. It has been suggested by Loudon⁸ that the satellite in question may originate in a quasilocized mode brought about by the comparatively large mass difference between Ca and Tm. As far as symmetry arguments are concerned only odd-parity phonons can contribute a vibronic satellite for a $4f^n \rightarrow 4f^n$ transition. Thus, a Γ_{15} type resonance mode would be effective (a Γ_{15} semilocalized vibration is the only kind of resonance mode which can appear in the mass defect limit). Can such a mode exist? Invoking Figs. 2a, b we tentatively

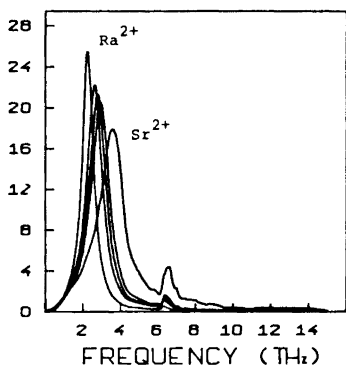


Fig. 2a. $\omega_L^2 M_{01} \text{Im } G(l1\alpha, l1\alpha; \omega_L^2 x + i0)$, $0 < x < 1$, for Ra^{2+} , Tm^{2+} , Sm^{2+} , Ba^{2+} , and Sr^{2+} in CaF_2 . The curve for Dy^{2+} is intermediate between those for Tm^{2+} and Sm^{2+} . Here ω_L is the largest (circular) frequency of the host lattice, M_{01} is the alkaline-earth ion mass, and $G(l1\alpha, l1\alpha; \omega_L^2 x + i0)$ is the limiting Green's function obtained for the impurity in the mass defect approximation on approaching the real axis from above. For a comparison with the perfect lattice cation Green's function, which differs from impurity Green's functions by the absence of a resonance denominator, the reader should consult Fig. 1a in Ref. 4. On so doing one will note the reappearance of perfect lattice features in the Sr^{2+} case for which the mass difference between the host cation and the impurity cation is the least.

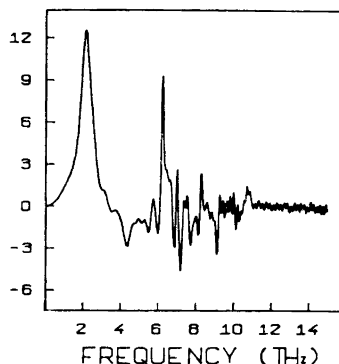


Fig. 2b. Large N (= the number of unit cells in a cyclic macrocell) limit of the CaF_2 , $3nN\Delta F(\omega^2) \times 10^{-1} \omega_L^2$; where n (=3) is the number of ions in a unit cell, and where $\Delta F(\omega^2)$ is the perturbation in the distribution of squared frequencies caused by a substitutional Ra^{2+} ion. The structure appearing for frequency values above ~ 11 THz consists of spurious fluctuations resulting from a representation of the imaginary part of the perfect lattice Green's function in terms of truncated sine series expansions (Ref. 4). The shapes assumed by the corresponding function for divalent rare-earth substitutions are similar, although the heights of the two main peaks decrease when the impurity mass approaches that of Ca^{2+} . Also, on decreasing the impurity mass through the sequence Ra^{2+} , Tm^{2+} , Dy^{2+} , Sm^{2+} the position of the low-frequency peak maximum shifts from 2.41 THz ($\sim 80.5 \text{ cm}^{-1}$) through 2.88 THz ($\sim 96.2 \text{ cm}^{-1}$) and 2.96 THz ($\sim 98.6 \text{ cm}^{-1}$) to 3.11 THz ($\sim 103.8 \text{ cm}^{-1}$). In units of ω_L^2 , the corresponding widths are 0.02, 0.04, 0.04, and 0.04, respectively. On lowering the impurity mass from Ra^{2+} to Sm^{2+} the peak maximum of the other main maximum changes from 6.32 THz ($\sim 210.9 \text{ cm}^{-1}$) to 6.45 THz ($\sim 215.0 \text{ cm}^{-1}$). Nominal widths can be calculated, but would not be very instructive, the peak shapes differing considerably from a Lorentzian for this resonance.

answer this question in the affirmative and attribute the vibronic satellite to a pseudolocalized mode; the wavenumber value predicted for this mode by the mass defect approximation being 96 cm^{-1} .

THE $\text{CaF}_2:\text{Dy}^{2+}$, $\text{SrF}_2:\text{Dy}^{2+}$, AND $\text{BaF}_2:\text{Dy}^{2+}$ SYSTEMS

The above assignment receives support from the existence of a similar phenomenon in the fluorescence spectrum obtained by Kiss⁹ for a $4f \rightarrow 4f$ transition in $\text{CaF}_2:\text{Dy}^{2+}$. Again, there is a low-lying satellite, the peak maximum of which is separated from the no-phonon line by an amount of energy being significantly smaller than the predicted energy of any host crystal critical point phonon. This time the shift amounts to $\sim 100 \text{ cm}^{-1}$. In the mass defect approximation the replacement of a Ca^{2+} ion by a Dy^{2+} ion brings about a pseudolocalized mode at $\sim 99 \text{ cm}^{-1}$. However, an interpretation involving a Γ_{15} type vibration is at variance with Kiss' own explanation of his $\text{CaF}_2:\text{Dy}^{2+}$ results. Kiss adheres to the type of analysis devised by Axe and Sorokin¹⁰ and classifies several of the vibronics in terms of a vibrating XY_8 cluster constituted by the substitutional rare-earth and a cage of nearest neighbour F^- ions. Although

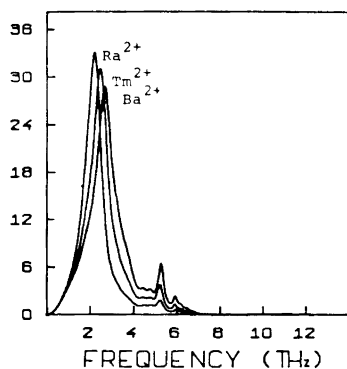


Fig. 3a. $\omega_L^2 M_{01} \text{Im } G(11\alpha, 11\alpha; \omega_L^2 x + i0)$ (the significance of the symbols involved is obtainable from the legend to Fig. 2a) for Ra^{2+} , Tm^{2+} , and Ba^{2+} in SrF_2 . The curves for Dy^{2+} and Sm^{2+} impurities are intermediate between those for Tm^{2+} and Ba^{2+} . The two minor peaks show impurity resonances superposed on the perfect lattice structure shown in Fig. 2a of Ref. 4, the resonance frequencies being nearly coincident with two perfect lattice critical point frequencies as discussed in the text.

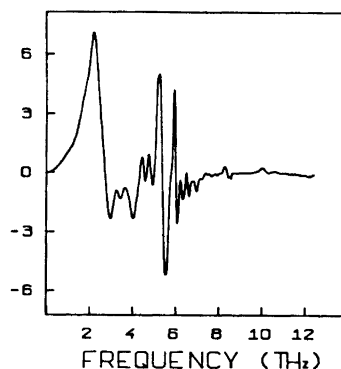


Fig. 3b. $3nN\Delta F(\omega^2) \times 10^{-1} \omega_L^{-2}$ for a substitutional Ra^{2+} in SrF_2 (the significance of the symbols is explained in the legend to Fig. 2b). Due to the reduced difference between impurity and host ion mass the (dimensionless) width ($=0.07$) of the low-frequency maximum is more than three times that of its $\text{CaF}_2:\text{Ra}^{2+}$ counterpart shown in Fig. 2b. For substitutional lanthanides in SrF_2 the perturbancies in frequency spectra are similar to the above curve, apart from the fact that the low-frequency peaks are more diffuse and the asymmetry in the peak shapes becomes more pronounced. In fact, the usual resonance condition is not fulfilled for any of the lanthanides since the appropriate multiple of the real part of the perfect lattice cation Green's function does not quite equal unity at peak maximum. However, in view of the crudeness of the mass defect approximation there is, in the present context, little difference in physical significance between resonance and near resonance.

this kind of interpretation has been rejected by Richman¹¹ on the grounds that the majority of vibronics discussed by Axe and Sorokin can be accounted for by host lattice phonons alone, Kiss maintains that an XY_8 analysis still applies to those experimentally detected effects which he ascribes to semilocalized vibrations. This reasoning makes him attach an E_u label to the 100 cm^{-1} vibronic of $\text{CaF}_2:\text{Dy}^{2+}$. However, for reasons to become clear shortly an XY_8 interpretation is of dubious validity even when the interest is confined to quasilocated effects. Of the vibronics observed by Kiss in the fluorescence spectra of $\text{SrF}_2:\text{Dy}^{2+}$ and $\text{BaF}_2:\text{Dy}^{2+}$ there is for each compound one regarded by Kiss as originating in semilocalized vibrations and being of symmetry E_u . The frequency values are $\sim 85 \text{ cm}^{-1}$ and $\sim 79 \text{ cm}^{-1}$, respectively. If, as a consequence of the doubt expressed above concerning the XY_8 analysis, we change the E_u assignment and take these modes to be of the Γ_{15} type (T_{1u} in the notation used by Kiss) then their wavenumbers are in fair agreement with those obtained for the lowermost semilocalized modes in the mass defect limit; namely 80 cm^{-1} ($\text{SrF}_2:\text{Dy}^{2+}$) and 72 cm^{-1} ($\text{BaF}_2:\text{Dy}^{2+}$). As indicated by Figs. 3 and 4a,b these resonance modes decay more rapidly into the neighbouring part of the phonon continuum than the corresponding ones occurring in the $\text{CaF}_2:\text{Tm}^{2+}$ (Dy^{2+}) cases. As for $\text{BaF}_2:\text{Dy}^{2+}$, part of the lowermost observed vibronic peak may possibly be contributed also by lattice phonons since according to the lattice dynamics calculations described previously⁶ (see also Fig. 1c) there is an L_3' phonon with odd-parity components at $\sim 69 \text{ cm}^{-1}$.

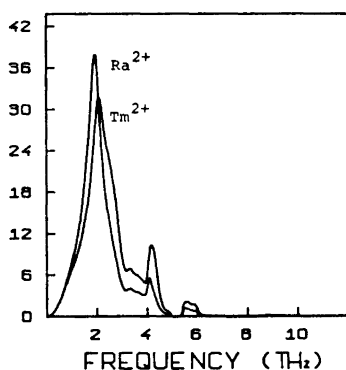


Fig. 4a. $\omega_L^2 M_{01} \text{Im } G(l1\alpha, l1\alpha; \omega_L^2 x + i0)$ (the significance of the symbols involved is obtainable from the legend to Fig. 2a) for Ra^{2+} and Tm^{2+} in BaF_2 . The Dy^{2+} and Sm^{2+} curves are rather similar to the shown Tm^{2+} graph. The perfect lattice case is displayed in Fig. 3a of Ref. 4.

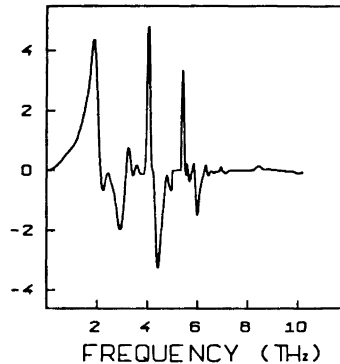


Fig. 4b. $3nN\Delta F(\omega^2) \times 10^{-1} \omega_L^2$ for a substitutional Ra^{2+} in BaF_2 (the significance of the symbols is explained in the legend to Fig. 2b). Since the critical impurity mass for (true) low-frequency resonance to take place is 337 (a.u.), the resonance condition is not satisfied even in the Ra^{2+} case. The rare-earth plots are similar to the one shown here. On decreasing mass the impurity mass from that of Ra^{2+} , the low-frequency maximum does, however, become even broader, and less symmetrical.

THE $\text{SrF}_2:\text{Sm}^{2+}$ AND $\text{BaF}_2:\text{Sm}^{2+}$ SYSTEMS

Having introduced L_3' phonons into the discussion, we turn to the systems $\text{SrF}_2:\text{Sm}^{2+}$ and $\text{BaF}_2:\text{Sm}^{2+}$ both of which have fluorescence spectra associated with parent transitions within the $4f$ configuration.¹² This may be contrasted with $\text{CaF}_2:\text{Sm}^{2+}$ where all the low-temperature emission originates at a $4f^5 5d$ level.¹² The fluorescence spectra of Sm^{2+} in SrF_2 and in BaF_2 have been studied experimentally by Wood and Kaiser.¹² Their $\text{SrF}_2:\text{Sm}^{2+}$ work has later been confirmed and extended by Cohen and Guggenheim¹³ who reported data also on the Zeeman effect on the transitions. In the spectrum of $\text{SrF}_2:\text{Sm}^{2+}$ the two lowest lying vibronics are situated on the wavenumber axis at 86 cm^{-1} and 97 cm^{-1} , respectively. From symmetry and the Zeeman effect the 97 cm^{-1} vibronic may be ascribed to lattice vibrations which prior to the breakdown of translational symmetry carried labels L_3' or $X_3'(M_3')$. According to the calculations of dispersion relations reported earlier⁶ there is a critical point phonon with symmetry label L_3' at $\sim 96 \text{ cm}^{-1}$, see also Fig. 1b. I tentatively identify this phonon with the 97 cm^{-1} observed vibronic line. However, there is in the dispersion relations for high symmetry k 's and in the predicted frequency distribution, Fig. 1b, no sign of another perfect lattice critical point in the vicinity of and below this energy value. In fact, ignoring the possibility of an unresolved critical point due to branch crossing at a general k -value, the second lowest theoretical critical point, which is of the $X_5'(M_5')$ type, appears at $\sim 133 \text{ cm}^{-1}$. This critical point can be identified as the second slope discontinuity from the left in Fig. 1b. Now, 133 cm^{-1} is rather close to the wavenumber of the third lowest vibronic line of $\text{SrF}_2:\text{Sm}^{2+}$, 131 cm^{-1} . Upon the reduction $O_h^5 \rightarrow O_h$ an irreducible $O_h^5 - X_5'$ amplitude subspace splits into $O_h - \Gamma_{15}$ and $O_h - \Gamma_{25}'$ spaces. The symmetry assigned to the odd-parity 131 cm^{-1} level by Cohen and Guggenheim¹³ is Γ_{15} . I consider this to be sufficient reason for asking whether the lowest vibronic observed at 86 cm^{-1} might not possibly be due to an impurity effect on the lattice vibrations, *i.e.* a semilocalized mode. As pointed out by Cohen and Guggenheim the similar "sizes" of host and impurity cations makes it reasonable to assume that the SrF_2 lattice becomes only mildly distorted on replacing a few and well separated Sr^{2+} ions with Sm^{2+} ions. By invoking the results of Bron and Wagner¹⁴ and of Timusk and Buchanan¹⁵ on pseudolocalized modes generated by lattice distortions, Cohen and Guggenheim conclude that for the system $\text{SrF}_2:\text{Sm}^{2+}$ the phonons contributing to the vibronic spectra are those of the host crystal. On the other hand, in keeping with the "moderate distortion" hypothesis we may take the mass defect approximation to be quite good in this case. The mass defect model leads to a comparatively broad and not quite symmetric, yet discernible, peak in the perturbed frequency spectrum, Figs. 3a, b, with a maximum increase in the density of one-phonon states at $\sim 87 \text{ cm}^{-1}$. Consequently, I believe a semilocalized mode to provide a plausible explanation for the observed 86 cm^{-1} level. In the $\text{BaF}_2:\text{Sm}^{2+}$ case the difference between impurity and host mass is smaller than for $\text{SrF}_2:\text{Sm}^{2+}$, and the calculated low-frequency maximum in the perturbed frequency spectrum is more diffuse and of lower height than the corresponding $\text{SrF}_2:\text{Sm}^{2+}$ peak, Fig. 4a, b. If there should be a feeble resonance effect in the real system, it would probably

occur at an energy value close to that of the previously mentioned $\text{BaF}_2 L_3'$ phonon at 69 cm^{-1} , and might be difficult to resolve.

SHORTCOMINGS OF THE XY_8 TYPE ANALYSIS

At this point a few comments are in order regarding the validity of the XY_8 type analysis. In so far as the mass defect approximation can be trusted, Figs. 2, 3, and 4a, b show that for a substitutional lanthanide ion in an alkaline-earth fluoride the possibility of the occurrence of a T_{15} resonance is not exhausted by the low-lying and main maximum in the diagonal lanthanide ion Green's function. Among the additional maxima in the perturbed frequency spectra, some are fairly narrow and of appreciable height. The fact that these do not show up very clearly in the Green's function plots is a direct consequence of the closure conditions on the eigenvectors of the dynamical matrix in conjunction with the appreciable rare-earth amplitude in modes located on the frequency axis in the proximity of the lowermost peak in the Green's function. It is still possible for the other semilocalized modes to take part in vibronic formation, though, since for an electronic transition to couple to lattice waves it is not necessary for the rare-earth itself to move provided the remaining part of the lattice can furnish a suitable and oscillating crystal field. In view of the crudeness of the mass defect model, the predicted width, height, and peak position of even the major maxima occurring in Figs. 2b, 3b, and 4b are probably inaccurate. In fact, seemingly important peaks may represent mass defect artifices rather than physical occurrences. Nevertheless, our results serve to show that more than two distinct T_{15} resonances *could* very well turn up in alkaline-earth fluorides doped with rare-earth ions. This points to a serious shortcoming of the kind of analysis based on a local XY_8 complex, at least in the form proposed by Axe and Sorokin.¹⁰ Their oscillatory space contains only two irreducible T_{15} (in their notation T_{1u}) subspaces.

It may be noted that rare-earth induced peaks in the density of one-phonon states may easily appear quite close to frequency values for perfect lattice critical point phonons, as evidenced by $\text{SrF}_2:\text{Sm}^{2+}$. In addition to the previously mentioned semilocalized mode at $\sim 87 \text{ cm}^{-1}$ there are two predicted T_{15} type semilocalized vibrations both of which occur in the vicinity of peaks in the host crystal frequency spectrum, Figs. 1b, 3b. The two semilocalized modes have frequency values $\sim 178 \text{ cm}^{-1}$ and $\sim 199 \text{ cm}^{-1}$, respectively, while the two critical points, having symmetry labels Σ_1 and Σ_4 , are at 183 cm^{-1} and 202 cm^{-1} . This proximity of frequencies is in the present case of some consequence since Cohen and Guggenheim have observed vibronic levels corresponding to frequencies which coincide with those of the two Σ_1 and Σ_4 critical points.¹³ Upon the reduction $O_h^5 \rightarrow O_h$, carrier spaces for irreducible O_h^5 representations of the Σ_1 and the Σ_4 type both precipitate point group carrier spaces with labels compatible with what is known about the two above-mentioned vibronics. However, since the latter may both be of the T_{15} type,¹³ the two quasilocalized modes may also contribute.

In ending these remarks on vibronic satellites it seems safe to assert that additional and refined theoretical calculations may be useful in extracting

further information on vibrational properties from the quite ample experimental data already in existence.

AVAILABLE MATERIAL PREREQUISITE TO FURTHER CALCULATIONS

The author hopes to find the opportunity to indulge in further and more detailed studies of defective alkaline-earth fluorides in the future. It may be mentioned that extensive numerical material (*e. g.* numerical eigensystems for Fourier transformed dynamical matrices corresponding to a grid of 64 000 *k*-values + additional wave vector triplets going into the procedure used in Ref. 4 for generating Green's functions) needed in performing Kanzaki-type lattice statics¹⁶ and Green's function lattice dynamics calculations has been stored on magnetic tape for use as required. This material is available from the author on request.

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