LATTICE DYNAMICS AND SPECIFIC HEATS OF FLUORITE STRUCTURES

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ABSTRACT

Lattice Dynamics of calcium fluoride, strontium fluoride and barium fluoride have been worked out employing (1) the rigid ion model first used by Ganesan and Srinivasan and (2) the shell model, the parameters being taken from the work of Axe, With the phonon branches at forty-eight representative points in the Brillouin zone, the frequency distribution and the specific heats are calculated and the variation of Θ_D *with temperature is compared with the experimental data. The frequencies for the* L.*O.,* L.*A. and T.A. phonons at the critical point X in the case of* SrF_2 *and* BaF_2 *have been compared with the Raman frequencies observed by Mitra and Brafman. it is found that the rigid ion model explains* (i) *the experimental dispersion curves of* CaF_2, (ii) *the observed Raman effect data in* SrF_2 *and* BaF_2 *aud* (iii) *the experimetal specific heat data of the fluorites, better than the shell model.*

INTRODUCTION

The dynamics of the fluorite lattice was worked out by Ganesan and Srinivasan[1] on the basis of the rigid ion model. They used general force constant tensors, for the short range interaction upto second neighbours and reduced the number of independent parameters by the application of symmetry of the fluorite lattice. The violation of the Lyddane, Sachs, Teller formula in CaF_2, reported by Cribier[2] was shown by Ganesan and Srinivasan to arise from an error due to the nonapplication of a symmetry operations in the second neighbour fluorine-flourine interactions in Crebier's work. They derived the expressions for the elastic constants and infrared and Raman frequencies in terms of the force constants. In their investigations using model I, they showed that the diffuse X-ray scattering was in accordance with the LST formula, but found that the specific heat calculations were in disagreement with the experiment. The Θ_∞ obtained on this model was 473°K as against the experimental value of 500°K observed by Todd[3]. Since there is a close correlation between Θ_∞ and the infrared absorption frequency, they attributed the disagreement of Θ_∞ as arising from a wrong choice of the infrared absorption frequency. From the data of infrared reflection in CaF_2 and using the relation between infrared reflection maxima the absorption frequency as given by Born and Huang[4], they obtained a value of 40.6 μ for the principal infrared absorption frequency. This value was further supported by the data on refractive index. Accordingly the parameters were recalculated using this value of the absorption frequency and this model, denoted by them as Model II explained the specific heat data at least in the low and high temperature region. It is to be mentioned that the calculated dispersion curves along [100] and [111] directions on this model were found to agree with the dispersion curves obtained from neutron scattering experiments carried out much later by Criber *et al*[5]. They also showed that the diffuse X-ray scattering measurements of Cribier were consistent with the LST formula in model II as well.

Recently Axe[6] worked out the long wave lattice dynamics of fluorites on the basis of the shell model. He derived expressions for the long wavelength eigen frequencies and elastic constants. Using the concept of the effective charge, relations analogous to Szigeti's relation in a diatomic lattice were derived for the fluorities. He found that these relations could explain the elastic and dielectric properties much better. Axe used a central force model for the short range interaction matrix and assumed a repulsive exponent of 9 for CaF_2 and SrF_2 and a Vander Waals type exponent of 6 in the case BaF_2, for the second neighbour F-F interaction. The values of the shell model parameters for the three fluorities were tabulated by him.

Pryor[7], extended the calculations on the rigid ion model of CaF_2 to compute the Debye Waller factors of CaF_2 and UO_2 by obtaining the eigen frequencies at a large number of wave vector points in the Brillouin zone. Except for the pioneering work of Ganesan and Srinivasan, so far no calculations have been made on the frequency distribution of the fluorite lattice. The lack of agreement between their theoretical values and the experimental data on the specific heat in the intermediate temperature region prompted us to compute the frequency distributions of CaF_2, SrF_2 and BaF_2, employing the more elaborate Blackman's method and to compare the computed temperature variation of specific heats with the available experimental results. This would enable us to get some information on the relative merits of the two types of model, employed in the computation.

2 METHODS OF CALCULATION

2.1. *Rigid ion model*

The electrostatic coupling coefficients of fluorite lattice have been computed for the 48 wavevector points in the irreducible part of the Brillouin zone using the Ewald's method. The non-Coulomb coupling coefficients are taken from Ganesan *et al*[1]. The parameters entering are evaluated by using the expressions given by them for the elastic constants, Raman and infrared frequencies.

The dynamical matrix is a (9×9) Hermitian matrix and has been diagonalised to obtain the eigen frequencies for the 48 wave-vector points which by symmetry generates 9000 frequencies. A modified Jacobi's method is used for diagonalisation in the CDC computer at Tata Institute of Fundamental Research.

2.2 *Shell Model*:

The dynamical matrix in the shell model is given by

$$\widetilde{M}\,[\,(R+ZCZ)-(\widetilde{T}+YCZ)\,(s+YCY)^{-1}\,(T+ZCY)\,]\,M$$

where M is the inverse of the square roots of mass matrix, R is the short range interaction matrix, C is the Coulomb interaction matrix and Z and Y are the matrices of the ion and shell charges. The matrix s is given by

$$s_{\alpha\beta} = S_{\alpha\beta} + k\,\delta_{\alpha\beta}$$

where k is the isotropic spring constant between the core and its shell and S and T are the short range interaction matrices among the cores and shells. The values of Y are taken from the values of isoelectronic rare gases deduced by Dick and Overhausser[8]. Then k is obtained from the relation $\alpha = Y^2e^2/k$ where α is the electronic polarisability. Assuming that the short range interaction acts only through the shells one gets $T=S=R$. Using the shell model parameters given by Axe, the dynamical matrix was diagonalised as in the rigid ion case for the 48 wave vector points in the case of CaF_2, SrF_2 and BaF_2.

2.3 *Frequency Distributions*:

As mentioned earlier the computed frequencies generate 9000 frequencies by symmetry and by using Blackman's root sampling procedure the frequency distributions for the three flourite crystals both in the rigid ion and shell models were worked out and the results are shown in Figs. 1, 2 and 3. The dotted line corresponds to the rigid ion model.

It is seen that the high frequency cut off in the frequency distribution is slightly more in the shell model than in the rigid ion case. The main peaks in the frequency distributions agree with the observed infrared maximum. Since the dispersion curves are available only for CaF_2, detailed comparison between theoretical and experimental frequencies could be made for this case. It is found that the rigid ion model gives a better agreement with the experimental data than the shell model. This behaviour is similar to the case of KI where Dolling *et al.*[9] found that the rigid ion model gave a better fit with the experimental dispersion curve. The shell model gives in the case of fluorites, consistently higher values. Since Cribier *et al.* have indicated the positions of theoretical values of Ganesan and Srinivasan's model on the dispersion curves obtained experimentally, we do not reproduce the dispersion curves again here.

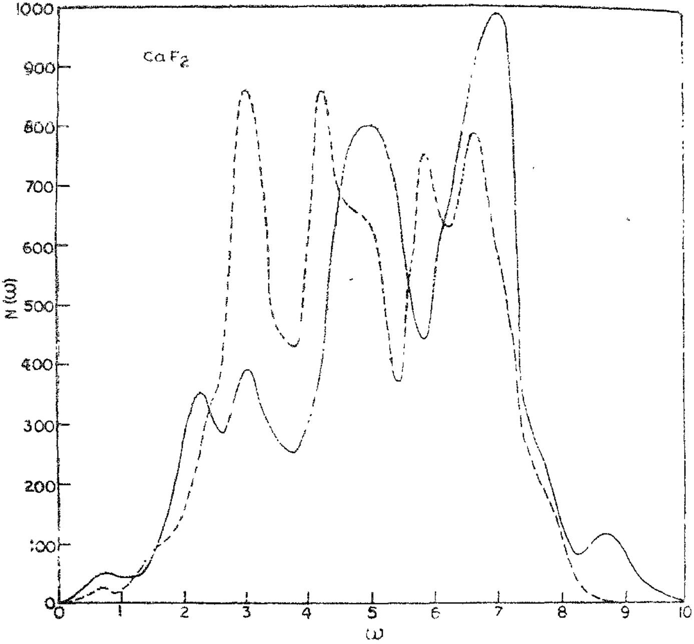

FIG. 1

Frequency distribution in CaF_2

2.4 *Comparison with Raman effect data*:

The first order Raman spectrum of fluorites consists of a single line corresponding to the LO phonon of the zone centre (Γ point) and this has been used in the evaluation of the parameters of the rigid ion model. The frequencies corresponding to the critical point X evaluated on the two models are entered in Table I. Recently data concerning the first order Raman spectra of SrF_2 and BaF_2 have been obtained by Mitra and Brafman[10]. They succeeded in doing so by additively colouring SrF_2 and BaF_2 with Ca and thereby breaking the selection rule. They recorded 3 additional Raman lines in SrF_2 and two in BaF_2 They have given the proper assignments also. The values of the frequency shifts are entered in Table I.

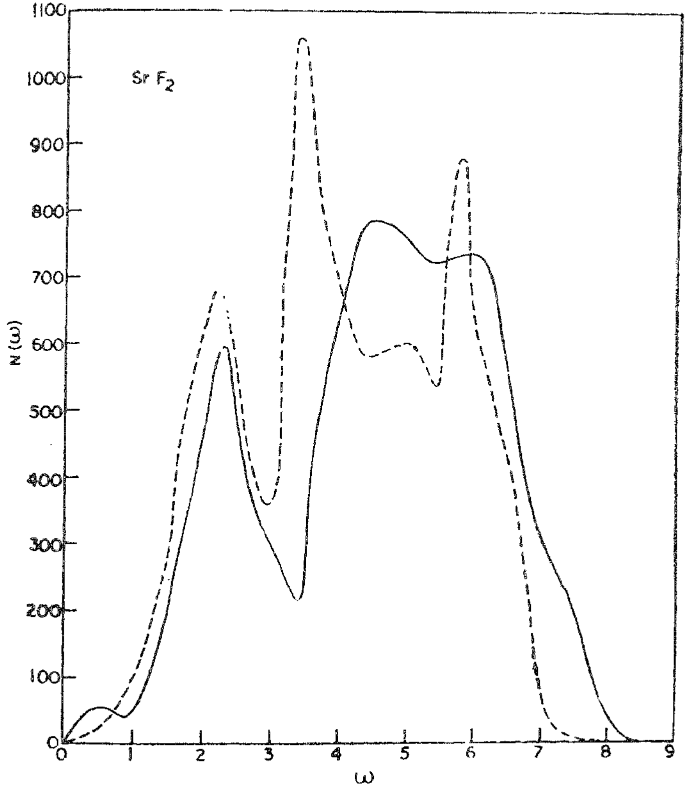

FIG. 2

Frequency distribution in SrF_2

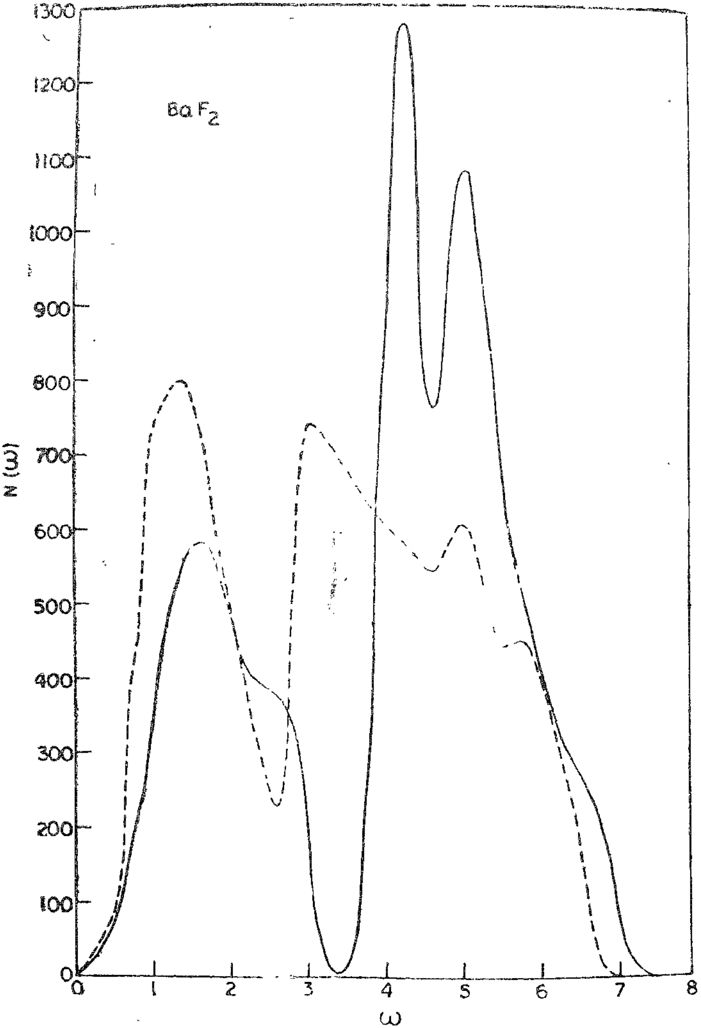

FIG. 3

Frequency distribution in BaF_2

TABLE 1

Frequencies at the *X* point for SrF_2 and BaF_2 (in cm^{-1})

	LO_1	LO_2	TO_1	TO_2	LA	TA
SrF_2 (shell)	375	211	323	207	197	134
SrF_2 (Rigid ion)	361	167	315	171	163	129
SrF_2 (Expt.)	336	—	—	—	171	115
BaF_2 (shell)	342	201	291	206	160	100
BaF_2 (Rigid ion)	334	134	272	147	114	81
BaF_2 (Expt.)	300	—	—	—	—	81

A comparison of the experimental Raman frequencies with those calculated on the two models shows that rigid ion model gives a better agreement with the experimental data.

2.5 *Specific heat* :

Using the theoretical frequency distribution curves, the specific heats of these crystals have been calculated over a wide range of temperature. From the specific heats, the variation of Debye characteristic temperature θ_D with temperature is obtained. Figs. 4, 5 and 6 show the results obtained for CaF_2, SrF_2 and BaF_2 respectively. Experimental values of specific heats C_p are available from the work of Huffman *et el.*[11] and Todd[3], for CaF_2 from the work of Smith *et al.*[12] for SrF_2 and from the work of Pitzer *et al.*[13] for BaF_2. From thermal expansion measurements Bailey and Yates[14] have computed $(C_p - C_v)$ over a wide range of temperature. Using all these data, fairly accurate values of experimental C_v and consequently the Θ_D were evaluated. In Figs. 4, 5 and 6 experimental points are also shown for comparison.

It can be noted that in all these cases the $\theta_D - T$ curves obtained using the shell model lie below the experimental points in the low temperature region and above in the high tempereture region. For CaF_2 and SrF_2 the experimental points up to 160°*K* are close to the theoretical curve calculated on the rigid ion model, whereas in BaF_2, they lie in between the rigid ion and shell model curves. In Fig. 4 is also included the θ_D versus T curve obtained by Ganesan and Srinivasan using a model denoted by them as II *b*. In this model they assumed a wave vactor dependence for one of the force constants β_1, of the form $\beta_1 = \beta_1^0 \, (1 - C_1/q\,|^2)$ in order to get better agreement with experimental results.

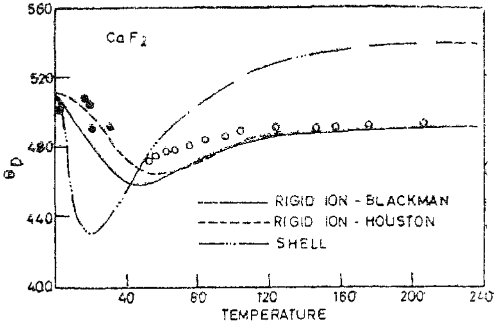

FIG. 4

Variation of θ_D with temperature of CaF_2

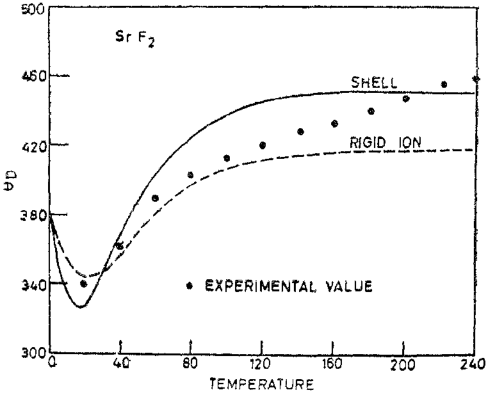

FIG. 5

Variation of θ_D with temperature of SrF_2

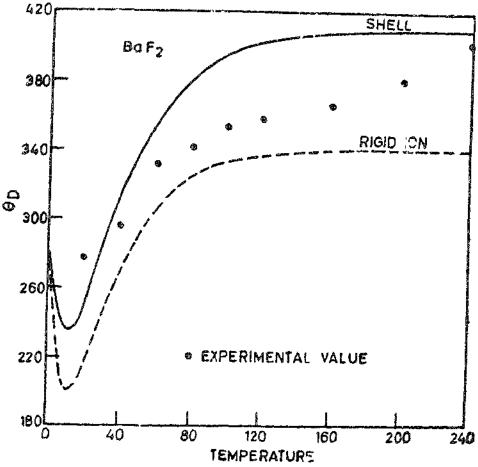

FIG. 6

Variation of θ_D with temperatare of BaF_2

CONCLUSIONS

The $\theta_D - T$ curve evaluated on the basis of a frequency distribution by Blackman's method on the model II of Ganesan and Srinivasan, without a wave vector dependance of the force constant agrees fairly well with the $\theta_D - T$ curve of Ganesan and Srinivasan on model *IIb*, computed on Houston's procedure, especially above 40°K and both these curves are close to the experimental points. Houston's method gives better results for specific heat at low temperatures and that may be due to the coarse mesh of wave vector points used by us in the present calculation.

The fact that the shell model in the case of fluorites do not yield as good a result as the rigid ion model is a very surprising result. The reason for this strange behaviour is under further study. We feel that the assumption that the short range interaction acts only through the shells is not very sound in the case of fluorites, unlike in the alkalihalides. The fact that the model II of Ganesan and Srinivasan, gave correct values of specific heats at low temperatures shows the adequacy of the harmonic approximation at low temperatures and consequently the absence of anharmonicity. It is not surprising to have the specific heat agreement at high temperature since in that region calculation was checked with value of the second moment. The small deviation of theoretical values in the intermediate temperatures can be mainly due to the contribution from anharmonicity which, as pointed out by Axe[1], can arise from the central and noncentral two body interactions and from the more complex many body interaction apart from the "internal strain" contribution.

The experimental data on the dispersion relation of CaF_2, the defect induced first order Raman spectra of SrF_2 and BaF_2 and the data on specific heat of these flourites favour the rigid ion model rather than the shell model. The availability of experimental data of third order elastic constants of these fluorites makes it possible to recalculate the dynamics of these crystals, taking also into account the anharmonic interactions. Additional experimental data especially on the dispersion relations of SrF_2 and BaF_2 would be very helpful to confirm the conclusions detailed above.

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