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Temperature dependence of elastic constants of some fluorite crystals

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The temperature dependence of elastic constants of some fluorite-structure crystals (namely BaF_2, PbF_2, and $SrCl_2$) has been investigated by means of potential models that include the effects of three-body interactions (TBI) and lattice anharmonicity arising from thermal-phonon pressure. The agreement between the experimental and present theoretical model I (with TBI) is better than that obtained from model II (without TBI) and is comparable with those calculated from measured Brillouin-scattering frequencies [Catlow *et al.*, J. Phys. C **11**, 3179 (1978)]. It has been found that the lattice anharmonicity is responsible for an anomalous change in elastic constants with temperature for the fluorites.

I. INTRODUCTION

There has been considerable interest in the study of materials showing superionic behavior. The fluorite crystals constitute the simplest superionic conductors,[1-3] and they are the model systems for the study of a variety of solid-state phenomena. One of the most interesting features of the fluorites is the temperature dependence of their elastic constants[4-8] and specific heats.[9,10] Some of these crystals (CaF_2, BaF_2, $SrCl_2$, and PbF_2) are well known to exhibit elastic and specific-heat anomalies at temperatures T_c well below the melting temperature T_m. This anomaly is understood to be associated with the development of extensive disorder in the anion sublattice. The effects of such high-temperature disorders have been investigated on Raman-scattering,[10] the elastic constants[5] using Brillouin scattering, and the acoustic-phonon modes[7] using neutron scattering. Both the Brillouin-scattering[5] and neutron-scattering[7] studies have shown large decreases of the elastic constants C_{11} near T_c without any marked change in C_{12} and C_{44}.

The anomalous temperature dependence of the elastic constants has been attributed to three main physical reasons: (i) the normal lattice anharmonicity,[11] (ii) the increase in concentration of interstitials[5] near the transition temperature T_c, and (iii) the hopping motion of defects. In the past three have been several attempts to study the variation of the elastic constants with temperatures using different experimental probes[4,6,7] and theoretical models.[5,7,12]

Catlow *et al.*[5] have derived the elastic constants from the Brillouin-scattering measurements assuming that the square of the scattering frequency is directly proportional to the elastic constants. They have found that the Coulomb interactions between anion vacancies and interstitials are primarily responsible for the cooperative anion disorder in the fluorites. Ghosh and Dasgupta[12] have considered the effects of both anharmonicity and the Frenekl disorder to explain the temperature dependence of bulk modulus. On the other hand, Kleppmann[13] has investigated the effects of the change in nearest-neighbor central force constants on vacancies and interstitials and found that they alone cannot account for the experimentally observed difference in the temperature dependence of C_{11} (large decrease) and C_{12} and C_{44} (no measurable decrease) near T_c. He has shown from his analysis that the changes in the long-range Coulomb forces due to the lowest-order perturbation might be responsible for the difference in their behavior. It is, however, now well established that the inclusion of many-body forces arising from the deformation of electron charge density[13] acts as a small perturbation to the Coulomb forces. The three-body potential[14,15] is also capable of taking account of the violation of the Cauchy relation ($C_{12}=C_{44}$) which is an interesting property of ionic crystals and cannot be predicted from two-body potentials used by Catlow *et al.* and Ghosh and Dasgupta. Another fact which needs attention is that no attempt, so far, has been made to estimate the individual effects of the anharmonicity on the variation of elastic constants with temperature.

In the present paper we incorporate the effects of anharmonicity, probably for the first time, in the framework of three-body potentials[14] of fluorite crystals. We have derived the temperature dependence of the second-order elastic constants (SOEC) from this potential in which the three-body interactions (TBI) arise from the charge-transfer mechanism[14-16] caused by the deformation of the electron shells of the overlapping ions. These TBI have appreciable influence on the anharmonicity exhibited by the elastic constants at higher temperatures in ionic crystals.[17]

In order to assess the significance of TBI, we have analyzed the temperature dependence of SOEC from the potentials with (model I) and without (model II) TBI effects. It has been found that the predictions obtained from the model I are better than those revealed from model II. It is interesting to note that the agreements between the experimental and present theoretical results on temperature variations of SOEC are comparable with the results calculated from the data reported by Catlow *et al.* on the temperature variation of Brillouin-scattering frequencies. Also, it is seen that the anharmonicity has considerable influence on SOEC at higher temperatures well up to T_c

and it seems that a gradual decrease of C_{11} around transition temperatures primarily depends on the lattice anharmonicity. This feature has been analyzed by performing calculations with (models I and II) and without (model III) the anharmonicity effects.

We have given a brief description of the TBP model and method of calculations in Sec. II. The results of computations have been presented and discussed in Sec. III.

II. THEORY AND METHOD OF CALCULATIONS

The anomalous elastic behavior of fluorites has been analyzed by Catlow *et al.*[5] and Ghosh and Dasgupta.[12] The model of Catlow *et al.* incorporates the effect of the Frenkel disorder using two-body potentials in the framework of the shell model. On the other hand, Ghosh and Dasgupta have considered similar two-body potentials including defects and anharmoncity in their approach. Such two-body (or pairwise) potentials cannot explain the elastic properties of solids as they fail to explain the Cauchy violation ($C_{12} \neq C_{44}$). Moreover, it is not obvious how the anharmonicity influences these elastic constants.

In order to understand the anharmonic effects on the elastic constants at higher temperatures, we have used the Hilderbrand equation of state as[18]

$$P = -\frac{d\phi}{dv} + T\alpha_v B_T , \tag{1}$$

with P as the pressure, T the temperature, α_v the volume thermal-expansion coefficient, and B_T the isothermal bulk modulus. The last term in Eq. (1) is the so-called thermal phonon pressure. Here, ϕ is the three-body potential (model I) expressed as[15]

$$\begin{aligned}\phi = &-\sum_{i,j}{}' \frac{Z_i Z_j e^2}{r_{ij}} - \sum_{i,j}{}' \frac{Z_i Z_j e^2 f(r_{ik})}{r_{ij}} - \sum_{i,j} c_{ij} r_{ij}^{-6} \\ &- \sum_{i,j} d_{ij} r_{ij}^{-8} + 8bf_{ij} \exp\left[\frac{r_i + r_j - r_{ij}}{\rho_{ij}}\right] + 6bf_{ii} \exp\left[\frac{2r_i - \kappa_2 r_{ij}}{\rho_{ii}}\right] \\ &+ 6bf_{jj} \exp\left[\frac{2r_j - \kappa_1 r_{ij}}{\rho_{jj}}\right] + 12bf_{jj} \exp\left[\frac{2r_j - \kappa_2 r_{ij}}{\rho_{jj}}\right] ,\end{aligned} \tag{2}$$

where the first term is the Coulomb energy and the second term is the three-body interaction energy added as perturbation to the Coulomb energy. The TBI parameter $f(r_{ik})$ is the measure of the overlap between the adjacent ions. The third and fourth terms represent the van der Waals (vdW) energy contributions due to the dipole-dipole and dipole-quadrupole interactions, respectively. The remaining terms correspond to the short-range repulsive energy due to the first- and second-neighbor ions.

The expressions for the SOEC for the fluorites can be derived from Eqs. (1) and (2) and using the method of homogeneous deformation as

$$\begin{aligned}C_{11} = 1.573T\alpha_v B_T + L[\tfrac{1}{3}A_1 - 0.90B_1 - 1.57B_2 \\ + 8.9558(r\,df/dr)_0] ,\end{aligned} \tag{3}$$

$$\begin{aligned}C_{12} = -1.786T\alpha_v B_T + L[\tfrac{1}{3}A_1 + 1.45B_1 + 1.78B_2 \\ + 8.9958(r\,df/dr)_0] ,\end{aligned} \tag{4}$$

$$\begin{aligned}C_{44} = -0.786T\alpha_v B_T + L[\tfrac{1}{3}A_1 + 1.45B_1 \\ + 1.78B_1 - \tfrac{1}{3}\Delta] ,\end{aligned} \tag{5}$$

with

$$\begin{aligned}\Delta = [A_1 + 6.77B_1 + 7.78B_2 \\ - 7.77(T\alpha_v B_T/L)]/[A_1 + 2B_1) + 3(A_2 + 2B_2)] ,\end{aligned} \tag{6}$$

$$\begin{aligned}T\alpha_v B_T = L\{1.9395Z[Z' + 8f(r_0)] + (B_1 + B_2)\} , \\ L = e^2/4r_0^4 .\end{aligned} \tag{7}$$

TABLE I. Values of model parameters at room temperature.

Solids	ρ_{+-} (10^{-1} nm)	ρ_{++} (10^{-1} nm)	ρ_{--} (10^{-1} nm)	b (10^{-19} J)	$f(r)$ (10^{-2})	Ref.
BaF_2	0.310	0.226	0.367	0.557	−0.494	model I
				0.465		model II
				0.577	−0.494	model III
PbF_2	0.295	0.430	0.160	0.977	−0.487	model I
				0.615		model II
				0.996	−0.487	model III
$SrCl_2$	0.336	0.200	0.472	0.553	−0.372	model I
				0.408		model II
				0.572	−0.372	model III

The abbreviations appearing in these expressions have been defined elsewhere[15] including the short-range force constants A_i and B_i $(i=1,2)$. Their values can be obtained from the knowledge of the range (b) and hardness (ρ_{ij}) parameters. In the present calculations the values of ρ_{ij} at room temperature have been taken directly from Ra[19] for BaF_2 and from the additivity rule[20] for PbF_2 and $SrCl_2$. Using these values, we have determined the TBI parameter $f(r)$ by considering it to depend exponentially on r as[21]

$$f(r_{ij})=f_0\exp(-r_{ij}/\rho_{ij}),\quad i\neq j \tag{8}$$

with f_0 as a constant taken from Shanker *et al.*[20] Considering the values of ρ_{ij} to be temperature independent, we have evaluated the temperature-dependent parameter (b) from the equilibrium condition

$$\left[r\frac{d\phi}{dr} \right]_0 = 3T\alpha_v V B_T \,, \tag{9}$$

where V is the unit-cell volume of the solid. The thermal-expansion coefficients are taken directly from Robert and White[22] for BaF_2 and from Palchaudhari and Bichile[23] for PbF_2 and $SrCl_2$ at different temperatures. The values of the model parameters $[\rho_{ij}, b, f(r)]$ have been listed in Table I for BaF_2, PbF_2, and $SrCl_2$ at room temperature and for higher temperatures b and $f(r)$ are calculated from Eqs. (8) and (9) and are used to compute

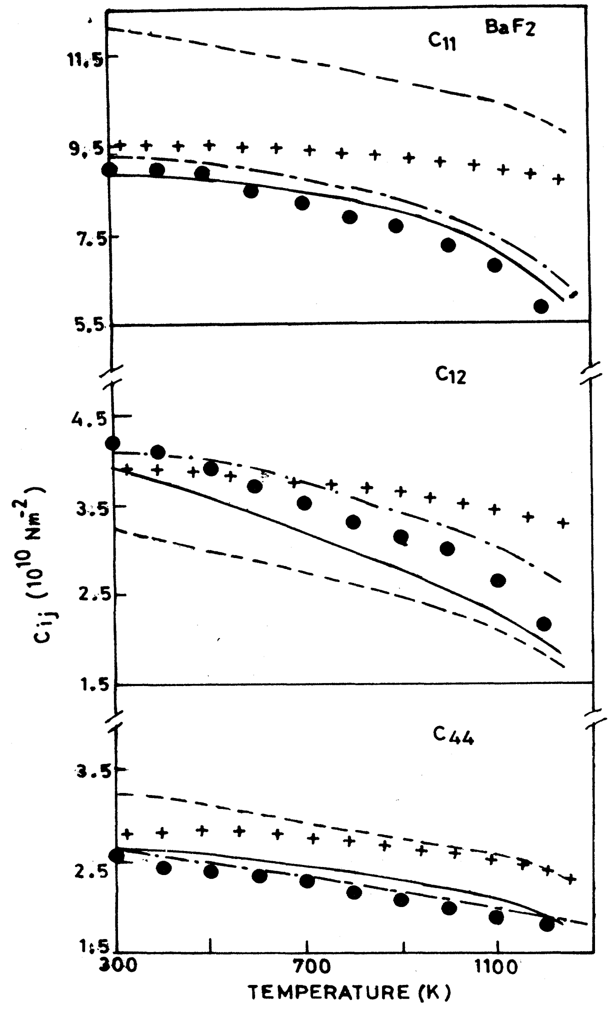

FIG. 1. Temperature variation of second-order elastic constants (C_{ij}) of BaF_2 from 300 to 1200 K obtained from model I (with TBI, ——), model II (without TBI, — — —), model III (without anharmonicity, + + +), and calculated results (—·—·—·) from Ref. 5. The solid circles represent the experimental data (Ref. 4).

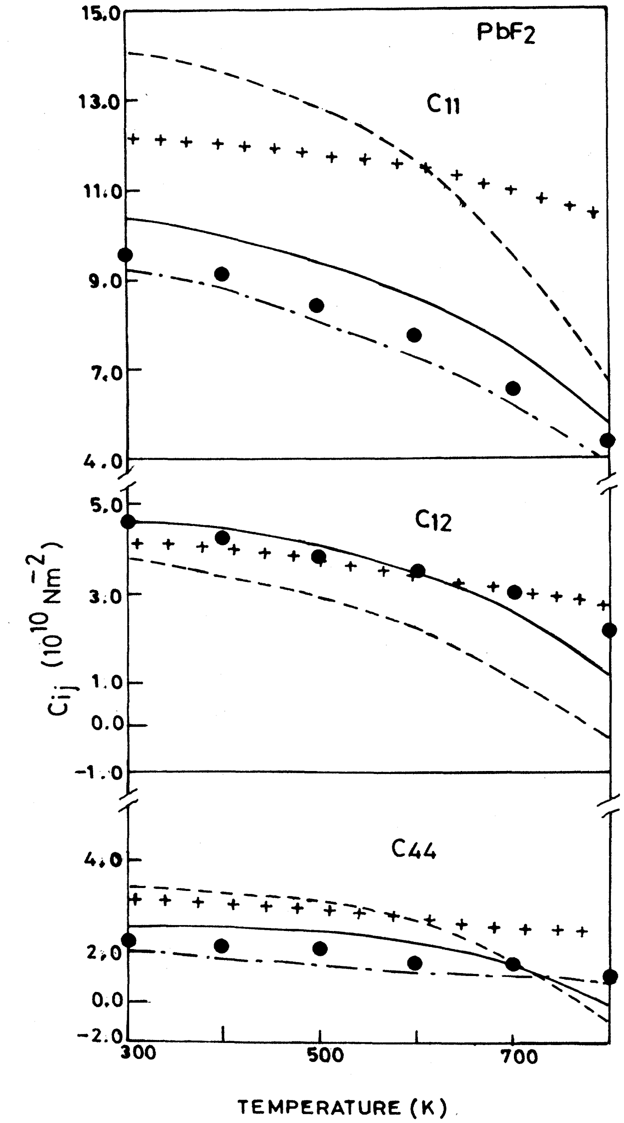

FIG. 2. Temperature variation of second-order elastic constants (C_{ij}) of PbF_2 from 300 to 800 K obtained from model I (with TBI, ——), model II (without TBI, — — —), model III (without anharmonicity, + + +), and calculated results (—·—·—·) from Ref. 5. The solid circles represent the experimental data (Ref. 4).

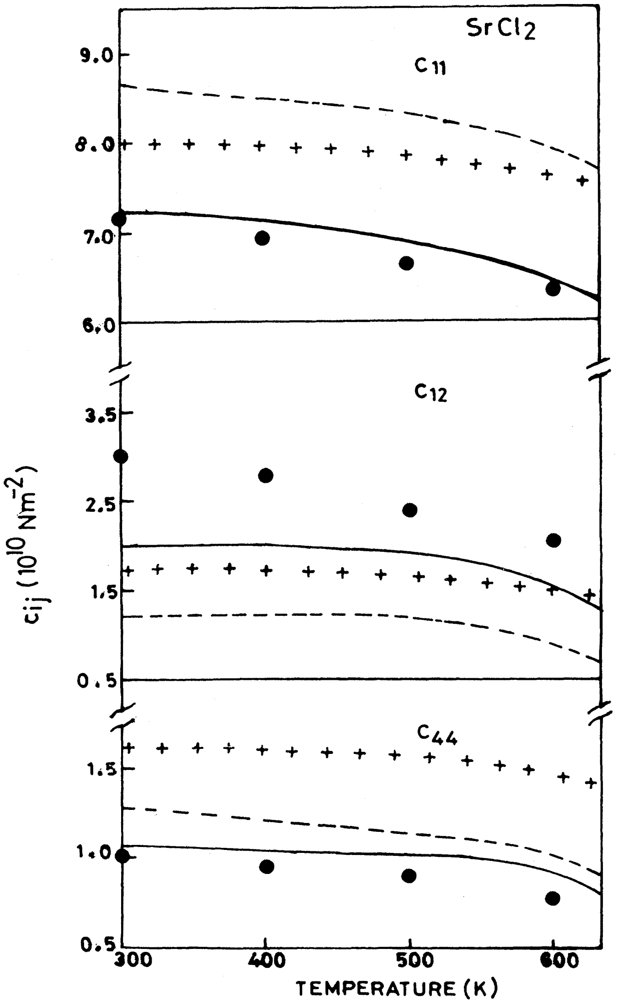

FIG. 3. Temperature variation of second-order elastic constants (C_{ij}) of $SrCl_2$ from 300 to 600 K obtained from model I (with TBI, ——), model II (without TBI, — — —), and model III (without anharmonicity + + +). The solid circles represent the experimental data (Ref. 6).

the temperature variation of SOEC's (C_{11}, C_{12}, and C_{44}). These variations of C_{ij} with temperatures (T) have been plotted in Figs. 1–3, respectively, for BaF_2, PbF_2, and $SrCl_2$ and compared with their available experimental data[4–6] and theoretical results calculated from the relation $C_{ij} = \rho V_s^2$ using the experimental values of the density (ρ) and the temperature variation of the velocity (V_s) of the sound waves,[5] which are available only for BaF_2 and PbF_2 crystals.

III. RESULTS AND DISCUSSIONS

It is seen from Figs. 1–3 that the variations of the elastic constants (C_{ij}) with temperature (T) obtained by us from the model I for BaF_2, PbF_2, and $SrCl_2$ are in reasonably good agreement with their experimental data.[4,6] Also, a critical analysis reveals that the predictions of the temperature variations of the C_{11} and C_{44} obtained from our TBP (model I) are more satisfactory than those for C_{12} in almost all the solids under consideration. Moreover, these variations are smaller at lower temperatures and larger at higher temperatures particularly for C_{11} in all the cases. These features are identical to that exhibited by the experimental observations[4–6] and theoretical calculations.[5]

Another interesting feature observed from Figs. 1–3 is that the agreements between theoretical and experimental results are remarkably better from model I than those obtained from model II. This shows that the three-body interactions have played a vital role in describing the temperature variations of the second-order elastic constants (C_{ij}). The deviations appearing in the agreements of C_{12} particularly at lower temperatures in almost all the cases and the minor deviations seen in C_{11} and C_{44} in some cases at the higher temperatures might be due to the exclusion of the effect of the concentration of interstitials. Also, the magnitudes of the temperature variations of C_{ij} obtained from model I are quite comparable to those achieved from the calculations (as indicated in Sec. II) performed by us from the knowledge of the measured data on the density (ρ) and the velocity (V_s) of the sound waves causing the Brillouin scattering in which the effects of the Frenkel disorder have been included by Catlow *et al.*[5] However, the decrease of C_{11}, C_{12}, and C_{44} around 600 K in the case of PbF_2 is more sharp from our theoretical results than the experimental data. This might be so because the lattice parameter (r) of PbF_2 shows no anomaly nearly up to 540 K, but above this temperature[23] it increases somewhat abruptly. This is the reason why the short-range force constants (A_i and B_i, $i = 1,2$), especially A_1 and B_1 decrease rapidly around 600 K, resulting in a sharp decline of the values of C_{12} and C_{44} along with C_{11}. The elastic constants for $SrCl_2$ could be calculated only up to 560 K and the agreements between theory (TBP) and measured data are generally good.

The anharmonicity has been found to play an important role, as is obvious from Figs. 1–3, in which the results obtained from a model without anharmonicity effects have been plotted for a visual comparison. This plot shows that the anharmonicity is mainly responsible for predicting the anomalous behavior (sudden decrease) of elastic constants at higher temperatures.

The present study has an important finding. We have noted a large contribution of lattice anharmonicity to the anomalous behavior of elastic constants as temperature is increased (see Figs. 1–3). This finding is based on the fact that the present model fits thermal expansion (α) to derive its one parameter. Up to the transition temperature T_c, thermal expansion of the fluorites does not show any anomalous behavior and thus it is not markedly influenced by the Frenkel disorder. Therefore, up to the transition temperature, anharmonicity is a major contributor to the temperature dependence of C_{ij} (see Figs. 1–3). Around T_c, however, the ions gain sufficient energy and more anion Frenkel defects are formed. The interaction of these defects with lattices sufficiently reduces the Coulomb energy. As is seen from the literature,[5] at T_c the concentration of defects amounts to about 15–20 %. A qualitative analysis reveals that the presence of these defects can reduce the energy of the lattice maximum up to 20–25 %. Thus even around T_c anharmonicity must be a major factor governing the temperature dependence of elastic constants. The limitations of the present model restrict us to comment on the contributions from the hopping motion of interstitials.

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