

## Temperature variations of the elastic constants of $\text{CaF}_2$ and $\text{SrF}_2$ crystals

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We have investigated the temperature variations of the second-order elastic constants of  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals by means of a three-body-interaction potential model which earlier has successfully described such variations exhibited by the other members of the fluorite family [Phys. Rev. B **39**, 13 493 (1989)]. Our results, obtained from the three-body-interaction potential model, have shown reasonably good agreement with their experimental neutron-scattering data. On the basis of these successful descriptions, we have concluded that three-body interactions and lattice anharmonicity play an important role in revealing the anomalous behavior and temperature variations of the elastic constants of fluorites.

In an earlier paper,<sup>1</sup> we successfully described the temperature dependence of the second-order elastic constants (SOEC's) of some superionic solids ( $\text{BaF}_2$ ,  $\text{PbF}_2$ , and  $\text{SrCl}_2$ ) by means of a three-body-interaction potential model.<sup>2,3</sup> This model has been developed by incorporating the effects of anharmonicity in the framework of the three-body potential (TBP) consisting of the long-range Coulomb and three-body interactions (TBI's) and the short-range van der Waals attraction due to dipole-dipole ( $d-d$ ) and dipole-quadrupole ( $d-q$ ) interactions and overlap repulsive interactions effective up to the second-neighbor ions. This TBP model has been found successful in predicting the anomalous behavior and the temperature dependence of the elastic constants in these materials. The TBI's in these crystals also arise from the charge-transfer mechanism<sup>3</sup> caused by the deformation of the electron shells of the overlapping adjacent ions.

A survey of literature reveals that the anomalous temperature dependence of elastic constants, observed in fluorite crystals, has been attributed to three main physical reasons,<sup>1,4-6</sup> namely, lattice anharmonicity, increase in Frenkel defects near transition temperature  $T_c$ , and hopping motion of these defects. Earlier,<sup>4</sup> we satisfactorily explained the anomalous temperature dependence of elastic constants and assessed the significance of TBI's and anharmonicity. However, the effects of the formation of Frenkel defects at transition temperatures could not be

incorporated in this investigation mainly because their contribution to the anomalous behavior is much smaller than that of the anharmonicity. This fact is obvious from a qualitative analysis which reveals that the pressure of these defects reduces the lattice energy maximum up to 20–25%. Thus, even around the transition temperature, the major factor governing the temperature dependence of elastic constants is the contribution from the anharmonicity. Moreover, the TBI have an appreciable influence on the anharmonicity<sup>1-3</sup> and a proper account of the Cauchy discrepancy, which cannot be predicted from the two-body potentials.

Motivated from the success of the earlier TBP model,<sup>1</sup> we thought it pertinent to study the temperature variations of SOEC's of  $\text{CaF}_2$  and  $\text{SrF}_2$  in order to complete such investigations for the remaining members of the fluorite family. In this paper, we have adopted the same procedure to determine the model parameters [ $b$  and  $f(r)$ ] and the SOEC's (both at room temperature and above) as is discussed in our earlier paper.<sup>1</sup> The values of the model parameters at room temperature are listed in Table I. The values of hardness parameters ( $\rho_{ij}$ ) at room temperature have been taken directly from Ra<sup>7</sup> for  $\text{CaF}_2$  and  $\text{SrF}_2$ . The measured values of thermal expansion and lattice parameters required for model parameter calculations are taken from Schumann and Neumann<sup>8</sup> for  $\text{CaF}_2$  and from Kominichau *et al.*<sup>9</sup> for  $\text{SrF}_2$ . The values of the

TABLE I. Values of model parameters at room temperature.

Solids	$\rho_{+-}$ ( $10^{-1}$ N m)	$\rho_{++}$ ( $10^{-1}$ N m)	$\rho_{--}$ ( $10^{-1}$ N m)	Ref.	$b$ ( $10^{-19}$ J)	$10^2 f(r)$	Models
$\text{CaF}_2$	0.277	0.166	0.357	7	0.541	-0.488	Model I
					0.738		Model II
					0.549	-0.488	Model III
$\text{SrF}_2$	0.290	8.199	0.364	7	0.565	-0.505	Model I
					0.786		Model II
					0.586	0.505	Model III

TBI parameter,  $f_0$ , have been obtained from Cochran's relation<sup>10</sup> [ $f(r)=f_0 \exp(-r_0/\rho)$ ] for both  $\text{CaF}_2$  and  $\text{SrF}_2$  and their values are the same as those reported by Shanker *et al.*<sup>11</sup>

The variations of SOEC's ( $C_{ij}$ ) with temperature ( $T$ ) in  $\text{CaF}_2$  and  $\text{SrF}_2$  have been plotted in Figs. 1 and 2 and compared with their available experimental data,<sup>4</sup> obtained from the relation  $C_{ij}=\sigma v_s^2$  with  $\sigma$  as the measured value of the density and  $V_s$  as the temperature-dependent velocity of sound waves causing Brillouin scattering.

It is seen from Figs. 1 and 2 that the temperature variations of the elastic constants obtained from the TBP model I (with TBI's and anharmonic effects) for  $\text{CaF}_2$  and  $\text{SrF}_2$  are in reasonably good agreement with their experimental data.<sup>4</sup> In these figures, we have plotted our results on temperature variations of SOEC's obtained from three potential models to demonstrate the individual significance of TBI and anharmonicity. Model I includes the effects of both TBI's and anharmonicity while models

II and III exclude the effects of TBI's and anharmonicity, respectively. It is seen that the values of  $C_{ij}$  in the cases of models I and III vary linearly with temperature without showing any rapid decrease. The results from model II though, show trends similar to those exhibited by the measured data, but they are large in magnitudes. This shows that the TBI plays a significant role in predicting the temperature variations of SOEC's of  $\text{CaF}_2$  and  $\text{SrF}_2$  as it has done in the cases of other members of the fluorite family. This can be further verified by considering the fact that, in fluorite structure supersonic solids,<sup>12</sup> the ions are not situated at the center of inversion symmetry, and hence, they undergo displacement whenever the lattice is strained. This phenomena is responsible for the Cauchy violation<sup>3</sup> and hence for giving rise to the many-body forces<sup>3</sup> of which the three-body components are most significant.<sup>3</sup> Thus, it may be remarked that, besides anharmonicity, the contributions from the TBI at high temperatures are quite significant in explaining the

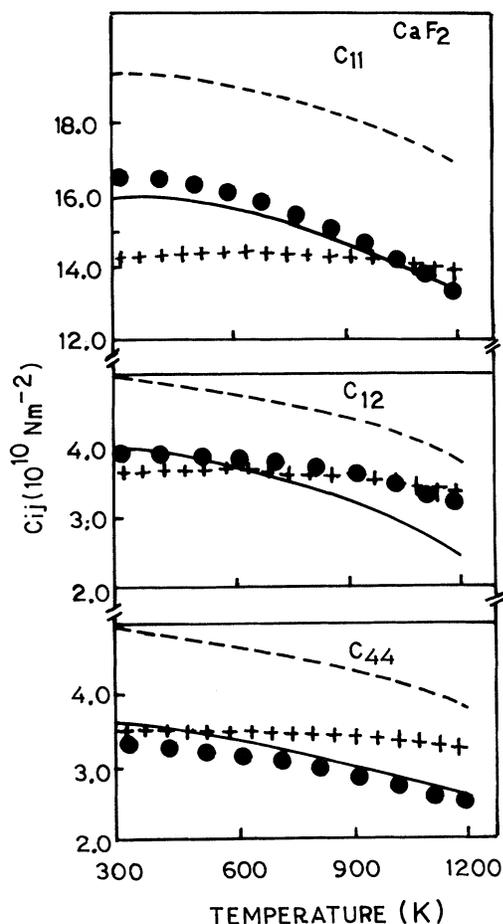


FIG. 1. Temperature variation of second-order elastic constants ( $C_{ij}$ ) of  $\text{CaF}_2$  from 300 to 1200 K obtained from model I (—), model II (---), model III (+++), and experimental results (●●●) from Ref. 4.

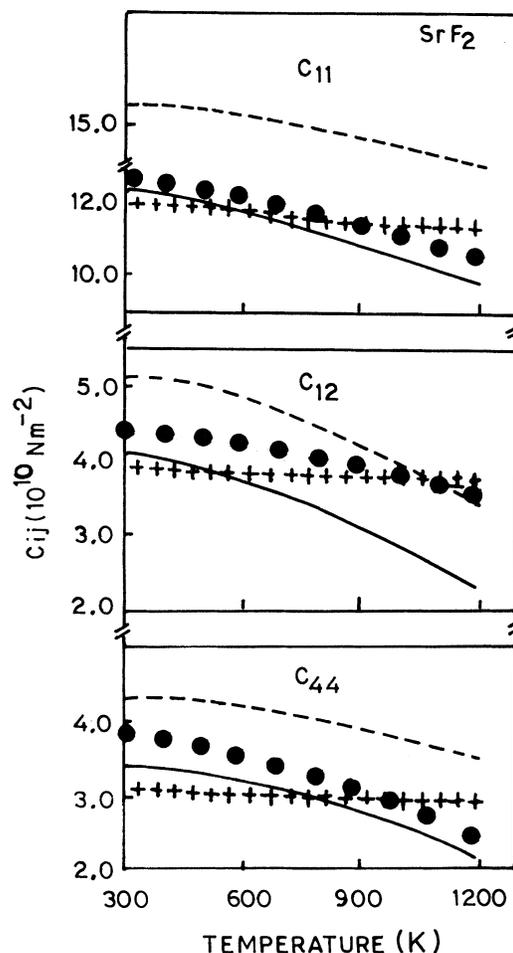


FIG. 2. Temperature variation of second-order elastic constants ( $C_{ij}$ ) of  $\text{SrF}_2$  from 300 to 1200 K obtained from model I (—), model II (---), model III (+++), and experimental results (●●●) from Ref. 4.

temperature variations of elastic constants.

A successful description of the temperature dependence of elastic constants, achieved here and elsewhere,<sup>1</sup> for the complex fluorite structure crystals can be considered remarkable in view of the inherent simplicity of the TBP model and its less parametric nature. The small deviations appearing in our results might be eliminated by incorporating the effects of the concentration of inter-

stitials<sup>4</sup> formed near the transition temperature.

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<sup>1</sup>R. K. Singh, C. N. Rao, and S. P. Sanyal, *Phys. Rev. B* **39**, 13 493 (1989).

<sup>2</sup>R. K. Singh and C. N. Rao, *Nuovo Cimento D* **11**, 10 (1989).

<sup>3</sup>R. K. Singh, *Phys. Rep.* **85**, 259 (1982).

<sup>4</sup>C. R. A. Catlow, J. D. Comins, F. A. Germano, R. T. Harley, and W. Hayes, *J. Phys. C* **11**, 3197 (1978).

<sup>5</sup>J. Garber and A. V. Granato, *Phys. Rev. B* **11**, 3990 (1975).

<sup>6</sup>S. Ghosh and S. Dasgupta, *Phys. Rev. B* **35**, 4416 (1987).

<sup>7</sup>Ø. Ra, *J. Chem. Phys.* **52**, 3765 (1970).

<sup>8</sup>B. Schumann and H. Neumann, *Cryst. Res. Technol.* **19**, 1 (1984).

<sup>9</sup>G. Kommichau, H. Neumann, W. Schmitz, and B. Schumann, *Cryst. Res. Technol.* **21**, 1583 (1986).

<sup>10</sup>W. Cochran, *CRC Crit. Rev. Solid State Sci.* **2**, 1 (1971).

<sup>11</sup>J. Shanker and J. P. Singh, *Phys. Status Solidi B* **110**, 697 (1982).

<sup>12</sup>W. Hayes, *Crystals with Fluorite Structure* (Clarendon, Oxford, 1976).