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# Elastic behaviour of lead fluoride under pressure

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**Abstract.** The variation of the second-order elastic constants (SOECs) and the longitudinal and shear modulii with hydrostatic pressure for the lead fluoride ($PbF_2$) has been investigated for the first time by means of a three-body force potential (TBP) model. The significance of three-body interactions (TBI) has been clearly demonstrated in reproducing the elastic constant variations and the pressure derivatives of SOECs of $PbF_2$. The equation of state for this crystal has also been reported.

**Keywords.** Fluorite; anharmonic; three-body interactions; Cauchy discrepancy.

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## 1. Introduction

Recently, the equation of state and anharmonic elastic properties of the fluorite crystals have been extensively studied by several theoretical (Goyal and Sharma 1988; Goyal *et al* 1988; Gupta *et al* 1987; Rimai and Sladek 1980) and experimental (Rimai and Sladek 1979; Wong and Schuele 1968; Derrington *et al* 1976) workers. Most of these theoretical investigations are confined to three fluorite crystals ($CaF_2$, $SrF_2$ and $BaF_2$) without giving much attention to lead fluoride ($PbF_2$), which is an important member of the fluorite family and exhibits many interesting temperature and pressure dependent elastic properties (Samara 1976). The most remarkable among them are the transition to superionic state at moderately elevated temperatures between 600 and 800 k, the ferroelectric transition (Samara 1976) below room temperature, the first order transition to orthorhombic structure at 4 kbar and the large Cauchy discrepancy (Srinivasan 1968; Ramachandran and Srinivasan 1972). Earlier, the pressure derivatives of SOECs of $PbF_2$ were calculated from the shell model (Srinivasan 1968; Ramachandran and Srinivasan 1972) without much success. This might be so because the shell model (Srinivasan 1968) is inadequate to account for the Cauchy discrepancy which owes its origin to three-body interactions (Singh 1982).

Motivated from the above necessity and the facts brought out by Srinivasan (1968) and Singh (1982), the present authors have tried to predict, probably for the first time, the pressure variations of the second-order elastic constants (SOECs) of $PbF_2$ using the three-body interaction potential (TBP) which has currently been found to explain the temperature variations (Singh *et al* 1989) of SOECs in fluorite crystals. To demonstrate the effects of TBI, we have computed elastic constant variations from two models I and II developed with and without the inclusion of TBI effects. It has been found that model I has given much better agreement with the experimental data (Rimai and Sladek 1980) than that obtained from model II. This clearly indicates the

significance of the TBI effects in the prediction of pressure variations of SOECs in $PbF_2$ crystal.

The essentials of TBP model and the method of computations are given in §2. The results and their discussions have been presented in §3.

## 2. TBP model and method of computations

The stability of a particular lattice structure is well known to be achieved at the minimum value of the Gibbs free energy ($G$) defined as

$$G = U + PV = U(r) + 2r^3P \tag{1}$$

for the fluorite structure crystals at the pressure, $P$, volume $V$ and temperature $T = 0°K$. Here, $U$ is the lattice energy consisting of the long-range Coulomb and three-body interactions (Singh 1982) and the short-range van der Waals (vdW) attraction (Tosi 1964) and overlap repulsion effective up to the second neighbour ions (Benson and Dempsey 1962). Its relevant expression is given by Singh *et al* (1989)

$$\begin{aligned} U(r) = &-\sum_{ij}\frac{Z_iZ_je^2}{r_{ij}}\left(1+\sum_k f(r_{ik})\right)-\sum_{ij}c_{ij}r_{ij}^{-6}-\sum_{ij}d_{ij}r_{ij}^{-8} \\ &+8b\beta_{ij}\exp(r_i+r_j-r_{ij})/\rho_{ii}+6b\beta_{ii}\exp(2r_i-k_2r_{ij})/\rho_{ii} \\ &+6b\beta_{jj}\exp(2r_j-k_1r_{ij})/\rho_{jj}+12b\beta_{jj}\exp(2r_j-k_2r_{ij})/\rho_{jj} \end{aligned} \tag{2}$$

with $Z_i(Z_j)$ as the ionic charges for fluorites, $c_{ij}$ and $d_{ij}$ as the vdW dipole-dipole and dipole-quadrupole interaction coefficients (Pauling 1960), $b$ and $\rho_{ij}$ as the range and hardness parameters, $r_i(r_j)$ as the ionic radii of ions $i(j)$ and $f(r_{ik})$ as the TBI parameter (Singh 1982). The details of the first term are reviewed elsewhere (Singh 1982).

The TBP model described above contains only two parameters ($b$ and $f(r)$) as the values of relaxed hardness parameters ($\rho_{ij}$) are known (Shanker and Singh 1982). The values of these two parameters ($b$ and $f(r)$) are determined from the equilibrium condition

$$(r\,\mathrm{d}U(r)/\mathrm{d}r)r = r_0 = 0 \tag{3}$$

and the analytical expression (Cochran 1971)

$$f(r_{ik}) = f_0\exp(-r_{ik}/\rho_{ik}) \tag{4}$$

respectively corresponding to those nearest neighbour separations ($r$) for which the Gibbs free energy given by (1) is minimum. Here, $f_0$ is a constant and for $PbF_2$ its value is $-29{\cdot}8$ (Shanker and Singh 1982). In model II, the value of the parameter $b$ will be obtained from (3) by regarding the TBI parameter $f(r)$ and its derivatives to be zero.

The values of the present model parameters ($b$, $f(r)$) as listed in table 1 have been determined from the above mentioned procedure by making use of the input data listed by Singh *et al* (1989) for $PbF_2$. The values of the vdW coefficients required for these calculations have been estimated by us using the variational approach of Slater and Kirkwood (1931). The values of the second-order elastic constants have been

**Table 1.** Values of model parameters at different pressures (the units in kbar).

| Parameters | $P=0{\cdot}0$ | $P=1{\cdot}0$ | $P=2{\cdot}0$ | $P=3{\cdot}0$ | Ref. Model |
|---|---|---|---|---|---|
| $r$ (Å) | 2·572* | 2·507 | 2·491 | 2·480 | I |
| $r$ (Å) | 2·572* | 2·474 | 2·473 | 2·471 | II |
| $b$ ($10^{-19}$ J) | 0·841 | 0·841 | 0·841 | 0·841 | I |
| $b$ ($10^{-19}$ J) | 1·044 | 1·044 | 1·044 | 1·044 | II |
| $f(r)(10^{-2})$ | −0·60 | −0·61 | −0·64 | −0·67 | I |

*Experimental value (Palchoudhari and Bichile 1987)

**Table 2.** Values of pressure derivatives of elastic constants at 1 kbar.

| | | | Other theoretical results | | |
|---|---|---|---|---|---|
| Expt.[a] | Model I | Model II | (a) | (b) | (c) |
| $dC_{11}/dp$ 7·40 | 6·33 | 4·90 | 3·90 | 3·54 | 4·27 |
| $dC_{12}/dp$ 7·00 | 5·77 | 4·25 | 5·30 | 5·37 | 6·83 |
| $dC_{44}/dp$ 0·94 | 1·35 | 1·81 | 0·30 | −0·19 | −0·51 |
| $dC_L/dp$ 8·14 | 7·40 | 6·38 | 4·90 | 4·26 | 4·09 |
| $dC_s/dp$ 0·20 | 0·28 | 0·32 | −0·70 | −0·92 | −1·05 |

[a]Rimai and Sladek 1980; [b]Ramachandran and Srinivasan 1972; Srinivasan 1968; [c]Shanker and Singh 1982.

calculated at different hydrostatic pressures ($P$) using their expressions reported by Bedi and Verma (1979).

To demonstrate the effects of TBI, we have calculated the variations of SOEC with pressure ($P$) from two models I (and II) with (and without) TBI effects and depicted them in figure 1 and compared them with their available experimental data (Rimai and Sladek 1980). To guide further merit of the models I and II, we have computed the pressure derivatives of SOECs ($dC_{11}/dp$, $dC_{12}/dp$ and $dC_{44}/dp$) and their combinations ($dC_L/dp$ and $dC_s/dp$) at 1 kbar using their expressions given by Bedi and Verma (1979). We have reported their values in table 2 and compared them with their experimental data (Rimai and Sladek 1980) available only at 1 kbar and other theoretical results (Rimai and Sladek 1980; Shanker and Singh 1982; Srinivasan 1968; Ramachandran and Srinivasan 1972). Here, $C_L = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$ and $C_s = \frac{1}{2}(C_{11} - C_{12})$.

## 3. Results and discussion

It is obvious from the results presented in figure 1 that the TBI play an important role in the description of the pressure variations of the SOECs and their longitudinal and shear modulii of $PbF_2$ crystal. It is evident from figure 1 that the variations obtained from model I are in better agreement with their experimental data than those achieved from model II. This relative success demonstrates the significance of TBI effects.

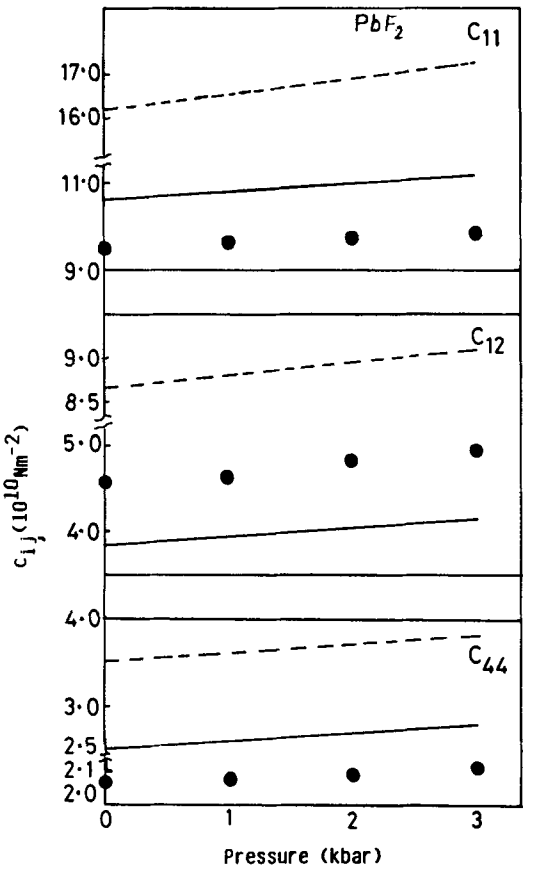


**Figure 1.** The pressure variations of elastic constants up to 3 kbar. The closed circles represents the experimental data (Rimai and Sladek 1980) while the smooth and broken curves correspond to those obtained from models I and II, respectively.

It has been found that SOECs increase linearly with pressure and they do not show any anomalous behaviour as exhibited in the study of their temperature variations (Singh *et al* 1989). $PbF_2$ crystal might exhibit interesting features beyond 3 kbar as it undergoes a structural phase transition from fluorite to orthorhombic phase at about 4 kbar. However, investigations beyond 3 kbar could not be possible due to lack of adequate data for its second phase.

Besides, we have depicted the variation of relative volume ratios $[V(P)/V(0)]$ at pressures $P$ and zero in figure 2. This ratio, which gives the equation of state of $PbF_2$, is found to decrease with pressure and follow the trend similar to that obtained by Wong and Schuele (1968) from the Murnaghan logarithmic equation.

The importance of the role of TBI has been further emphasized from table 2 in which the pressure derivatives of the SOECs and their combinations obtained for $PbF_2$ from model I are in much closer agreement with their experimental data (Rimai and Sladek 1980) than those obtained from the model II and the shell model (Rimai and Sladek 1980) and earlier TBI model (Shanker and Singh 1982). These deviations clearly show that the present two-body potential and the earlier models are inadequate to predict the pressure dependance of the SOECs in $PbF_2$ crystal. This is in keeping with the conclusion drawn by Rimai and Sladek (1980). The main reason for the

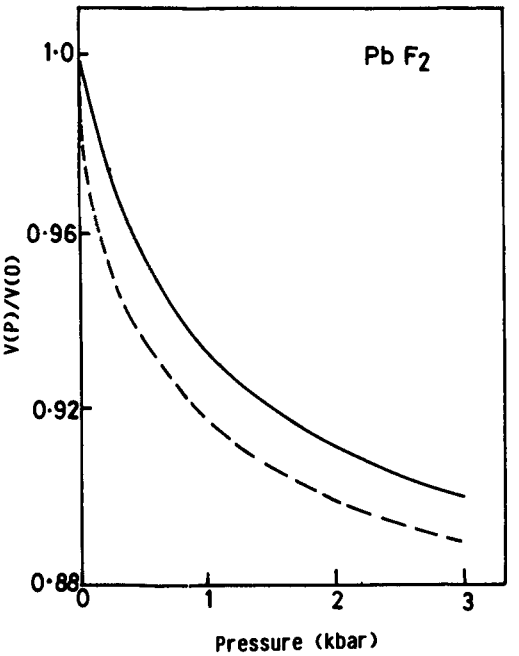


**Figure 2.** The compression curves as calculated from models I (smooth curve) and II (broken curve) for $PbF_2$ crystal.

better agreements from TBP model I as compared to those of Shanker and Singh (1982) is that firstly, it uses those values of vdW coefficients which are obtained from Slater-Kirkwood variational approach (1931) which is considered to be a superior method (Singh *et al* 1984). Secondly, it estimates the pressure derivatives of SOECs at 1 kbar at which experimental data are available.

On the basis of the overall achievements, it may be concluded that the present three-body potential model is adequately suitable for the description of the pressure variations and derivatives of the SOECs of the $PbF_2$ crystal. This TBP model has a promise for such successful description in other members of the fluorite crystal family.

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