Analysis of Temperature Dependence of the Second-order Elastic Constants of PbF_2

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The temperature dependence of the second-order elastic constants of PbF_2 is calculated by using a thermodynamic relation. It is shown that the model reproduces relatively well the experimental values of the elastic constants C_{11}, C_{12} and C_{44} from room temperature to around 600 K. With the increase of temperature, the calculated values of the elastic constants start to deviate accompanying the increase of the ionic conductivity. The result indicates that in the case of PbF_2, the material parameters evaluated at a reference temperature, the room temperature in the present case, can not be extrapolated to high temperatures and that the model for the elastic constant used widely in the literature should be used carefully.

§1. Introduction

It is well known that PbF_2 shows superionic conductivity in the temperature range T_c = 705 K < T < T_m = 1143 K, where T_c is the superionic transition temperature and T_m is the melting temperature.1) The superionic conductivity of PbF_2 arises from the large defect concentration. PbF_2 has a fluorite structure at room temperature and ambient pressure. Concerning the origin of superionic behavior, many models have been proposed.2) For instance, one of the authors proposed the bond fluctuation model of superionic conductors. According to this model, the fast ion movement in solids occurs accompanied by local change of the chemical bonding.3)

In the present report, the temperature dependence of the elastic constant of PbF_2 is examined based on a thermodynamic relation. In cubic crystals, there are three independent elastic constants, C_{11}, C_{12} and C_{44}. These elastic constants describe the longitudinal, transverse and shear stiffness, respectively. Study on the behavior of elastic constant is important, because it provides useful information concerning cohesive energy and interatomic interaction of the materials. The result of our analysis reveals that the relation widely used in the literature does not describe adequately the temperature dependence of the elastic constants of PbF_2.

§2. Temperature dependence of elastic constants

The Anderson-Grüneisen parameter which is used widely in the discussion of elastic properties of solids is given by

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P , \tag{2.1}$$

where α is the thermal expansion coefficient and K_T is the isothermal bulk modulus. By using the definition of the thermal expansion coefficient, the above equation becomes

$$\delta_T = -\frac{V}{K_T}\left(\frac{\partial K_T}{\partial V}\right)_P . \tag{2.2}$$

Some years ago, Tallon[4)] showed that (2.2) can be generalized as

$$\delta_{\mathrm{M}} = -\frac{V}{M}\left(\frac{\partial M}{\partial V}\right)_P , \tag{2.3}$$

where M is any of the elastic moduli such as bulk modulus and elastic constants.

Among various equations of state for solids proposed till now, the equation of Murnaghan is one of the most widely used. In the framework of Murnaghan's equation, the quantity δ_{M} defined in (2.3) is assumed to take a constant value. Under this assumption, the elastic modulus can be written as

$$M(T) = M_0\left(\frac{V(T)}{V_0}\right)^{-\delta_{\mathrm{M}}^0} , \tag{2.4}$$

where the suffix 0 denotes that the quantity under consideration is evaluated at the temperature of reference. In the past, (2.4) was used to analyze the temperature dependence of the elastic constants of ionic solids such as NaCl, KCl, MgO, etc.[5)] The study revealed that (2.4) reproduces quite well the behavior observed experimentally over wide range of temperatures. (2.4) was also applied to study the temperature dependence of elastic constants of AgBr.[6)] There, it was shown that the agreement between the calculated and the measured data are good for C_{44}. However, concerning C_{11} and C_{12}, deviations were observed at high temperatures. On the other hand, in the parent compound AgCl, (2.4) reproduced well the temperature dependence of C_{11} and C_{12} reported experimentally, while a deviation was observed in C_{44} at high temperatures.[7)] AgCl and AgBr are known for their high ionic conductivity that exhibit at high temperatures. These observations motivated us to apply (2.4) to study the temperature dependence of the elastic constant of PbF_2 which exhibits also a large defect concentration and high ionic conductivity at high temperature. For the evaluation of (2.4), $V(T)/V_0$ is obtained from lattice parameter measurements.[8)] For the Anderson-Grüneisen parameters, the calculated values from (2.1), δ_{11}=5.7, δ_{12} =7.2 and δ_{44}=1.5 were used.

§3. Results and discussion

Figs. 1 - 3 show the temperature dependences of the elastic constants C_{11}, C_{12} and C_{44} of PbF_2. The solid line represents the calculated curve by (2.4) and the circles are the experimental data.[9)]

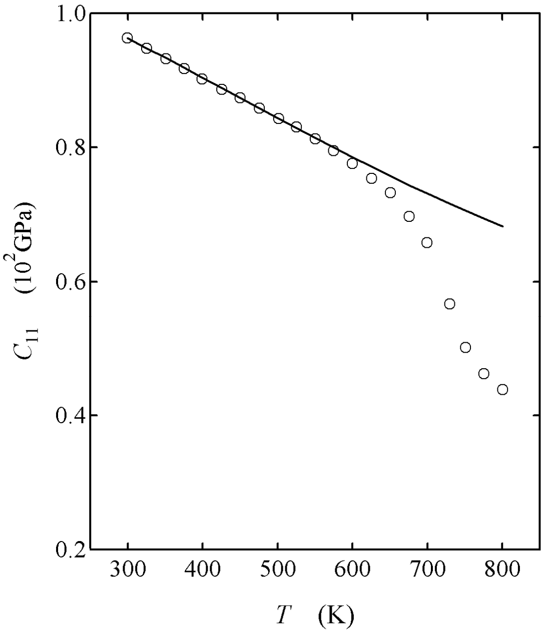

Fig. 1. The temperature dependence of the elastic constant C_{11} of PbF_2.

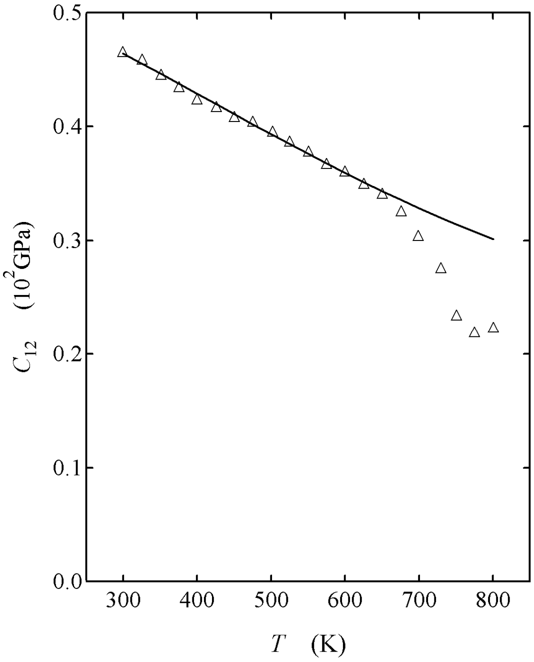

Fig. 2. The temperature dependence of the elastic constant C_{12} of PbF_2.

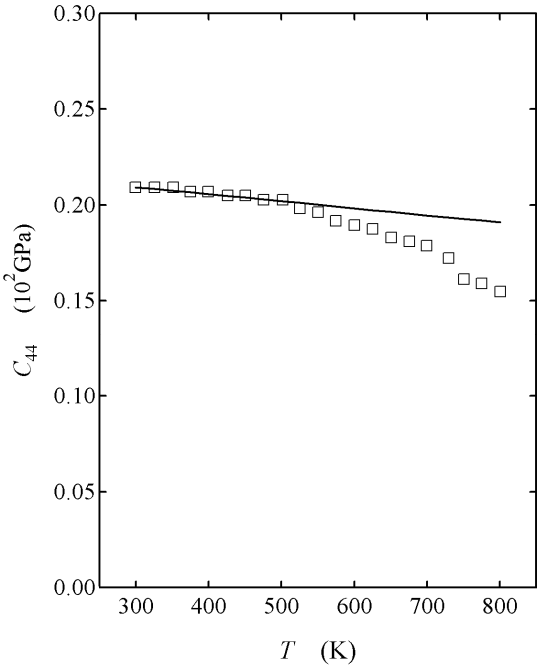

Fig. 3. The temperature dependence of the elastic constant C_{44} of PbF_2.

As shown in Figs. 1-3, the agreement between the measured and calculated values is good at low temperature. In the high temperature part, large deviations from the theoretical prediction are apparent above 700 K. We note that the theoretical curves start to overestimate the measured values of elastic constants at around 600 K. This means that there is a softening in the elastic constants of the crystals above this temperature. The result indicates also that the material parameters evaluated at the reference temperature of room temperature cannot be used at high temperatures as in the case of typical ionic crystal NaCl.5) This observation was also noted in our previous works.6), 7)

It is interesting to note that the superionic phase transition in PbF_2 occurs at 705 K. The phase transition in PbF_2 is diffuse, that is, the ionic conductivity increases gradually with the increase of temperature. Fig. 4 shows that a clear correlation exists between the temperature dependencies of the ionic conductivity and the elastic constants. The ionic conductivity in PbF_2 starts to increase at around 600 K. As noted above, at around the same temperature, the elastic constants start to deviate from the theoretical estimation based on (2.4). At around 700 K, an abrupt increase of the ionic conductivity and large change in the elastic constants are discernible.

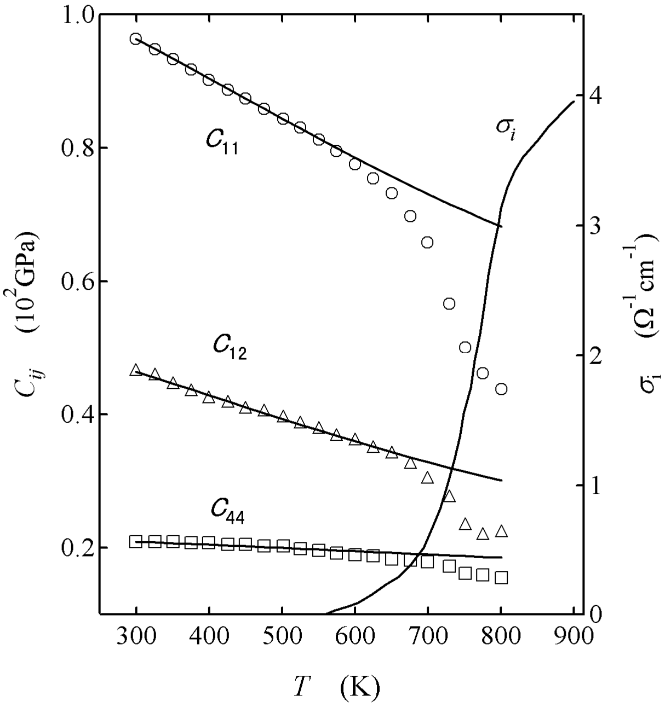

Fig. 4. The temperature dependence of the elastic constant C_{ij} and ionic conductivity σ_i of PbF_2.

Through the phase transition, the concentration of Frenkel defects increases dramatically. Therefore, a part of the large deviations observed in the elastic constants at high temperatures is caused undoubtedly by these defects. In the microscopic theory of elastic constants, the effect of these defects should be included. In the phenomenological theory as used in our analysis, the effect of defects enters through the material parameters used, δ_M^0 in our case. On the other hand, some lattice dynamical properties of ionic conductors have been interpreted in the light of bonding nature of the compounds.10-12) Thus, another cause that results in the large deviation shown in the figures could be related to this observation. To separate the contributions of defects from the bonding effects and other effects if any, is a subject left for a future study.

§4. Conclusion

The temperature dependences of the elastic constants of PbF_2 were calculated from room temperature to above the superionic transition temperature through an expression derived from the Murnaghan equation of state. The comparison with the experimental data revealed that the theory overestimates the values of elastic constants by large amounts above 700 K. Possible origins of the deviation was discussed briefly.

The result of the analysis, together with the previous ones[6), 7)] indicate that the evaluation method of the elastic constants used widely in the literature should be used carefully when it is applied to high ionic conducting materials.

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