Analysis of the temperature dependence of elastic constants of AgCl

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Abstract

The lattice dynamical properties of Ag halides are markedly different from those of typical ionic solids such as alkali halides. To gain further understanding on the origin of this difference, studies of elastic properties will be valuable. In the present report, the temperature dependence of the second order elastic constants of AgCl has been calculated by using a formula derived from the Murnaghan model of elastic constants. It is shown that the model reproduces the temperature dependence of C_{11} and C_{12} found experimentally. However, the calculated values of C_{44} deviate from the experimental values at high temperatures. The same model applied to NaCl reproduces quite well the temperature dependence over wide range. The result indicates that the model for the elastic constants used widely in the literature should be used carefully. A discussion concerning the microscopic origin of the differences in the behavior between Ag and alkali halides is given.

Keywords: elastic constants, Cauchy relation, Ag halides, alkali halides, superionic conductors

1. Introduction

Among the silver halide compounds at ambient temperature and pressure, AgF, AgCl and AgBr have the rock-salt NaCl-type structure and AgI exhibits the wurtzite or zinc-blende type structure. The lattice dynamical properties of AgCl and AgBr have been studied by many authors. These studies have revealed that these compounds exhibit different behavior from those of typical ionic crystals such as alkali halides, irrespective they have the same NaCl-type crystal structure. For instance, compared to alkali halides, the Ag halides exhibit low melting temperature, high values of dielectric constants, high ionic conductivity, large thermal expansion coefficient, etc. [1].

According to Phillips theory of bonding [2], the ionicity decreases and the covalency increases in the order AgF, AgCl, AgBr and AgI. In addition, among the various AB-type compounds, the Ag halides occupy a borderline position between covalent and ionic solids. The many interesting behaviors that the Ag halides exhibit are related with this peculiar bonding nature. The bond fluctuation model of superionic conductors proposed by one the authors [3] has been proposed based on these observations.

The studies of elastic properties of materials provide valuable information about cohesive energies, interatomic forces and anharmonic properties such as thermal expansion. Therefore, numerous studies in different materials have been done in the past [4]. For instance, it has been recognized that the elastic properties of alkali halides can be described quite well in terms of Born model, that consists of attractive Coulomb and radially dependent repulsive potentials [5]. On the other hand, it has been revealed that such kind of purely ionic interatomic interaction is not sufficient to describe the properties of compounds that incorporate covalent interactions. The Ag halides are examples of such compounds. In order to describe the properties of Ag halides, various types of interatomic potentials have been used [5-8]. However, it is difficult to find a unified expression for these potentials.

In the present report, with the objective to gain further understanding on the properties of Ag halides, the temperature dependence of the second order elastic constants of AgCl has been calculated by using a formula derived from the Murnaghan model for the bulk modulus. A comparative study with the case of NaCl indicates that the model widely used in the literature should be applied carefully.

2. Temperature dependence of elastic constants

In the investigations of temperature dependence of bulk modulus K_T, the Anderson-Grüneisen parameter defined as

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

are used widely [4]. Here, α is the thermal expansion coefficient,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P . \qquad (2)$$

By inserting Eq. (2) into (1), we obtain

$$\delta_T = -\frac{V}{K_T}\left(\frac{\partial K_T}{\partial V}\right)_P . \qquad (3)$$

Some years ago, Tallon showed that the form of Eq. (3) is of general validity [9]. That is, it holds good for any of the elastic moduli,

$$\delta_M = -\frac{V}{M}\left(\frac{\partial M}{\partial V}\right)_P , \qquad (4)$$

where M represents any of the elastic constants such as K_T, C_{11}, C_{12}, etc.

Among the various equations of states for solids proposed till now, the Murnaghan equation is one of the most widely used [4]. In the framework of this equation, the parameter defined in Eq. (4) is assumed to be constant, i.e., $\delta_M = \delta_M^0 = \text{constant}$. Therefore, by integrating Eq. (4) we obtain

$$M(T) = M_0\left(\frac{V(T)}{V_0}\right)^{-\delta_M^0} , \qquad (5)$$

where M_0, V_0 and δ_M^0 are the elastic constant, volume and Anderson-Grüneisen parameter at the temperature and pressure of reference. The above equation has been proved to works quite well when applied to ionic solids such as NaCl, KCl, MgO, etc. [10]. It has been referred also in many literatures that concern elastic constants of solids [11,12].

On the other hand, it has been reported that the Murnaghan equation does not describe correctly the pressure dependence of the compression of AgCl [13]. The Murnaghan equation underestimates the compression above 40 kbar. These observations and the peculiar lattice dynamical properties as mentioned in the introduction, prompt us to investigate the temperature dependence of the elastic constants of silver halides. In the following, the analysis for the case of AgCl is presented.

3. Results and discussions

The AgCl crystal has a fcc structure. Therefore, it has three independent second order elastic constants, C_{11}, C_{12} and C_{44}. The results of the application of Eq. (5) to AgCl crystal are shown in Figs. 1-3. The melting temperature of AgCl is 723 K. We note that the model reproduces quite well the temperature dependence of C_{11} and C_{12} reported experimentally [14]. However, the calculated values of C_{44} deviate from the experimental values for temperatures above $T = 400$ K. In the calculation, the

volume thermal expansion reported in [15] was used. For the Anderson-Grüneisen parameters, values estimated at the reference temperature of 293 K were used. $\delta_{C_{11}}^0 = 10.84$, $\delta_{C_{12}}^0 = 6.50$ and $\delta_{C_{44}}^0 = 3.84$. The application of Eq. (5) to NaCl, which has the same crystal structure to AgCl is shown in Fig. 4. The melting temperature of NaCl is 1073 K. Numerical data concerning Fig. 4 were taken from [10]. In contrast with AgCl, we note that Eq. (5) describes quite well the temperature dependences of all the elastic constants of NaCl.

By comparing the results for AgCl and NaCl we note certain interesting features that could provide new insights to understand the properties of AgCl. Firstly, we note that in both materials, the temperature variation is large in C_{11} and small in C_{44}. However, concerning C_{12}, the temperature variation is relatively large in AgCl but small in NaCl. The second point concerns about the relative magnitude of C_{12}. From Fig. 4 we recognize that in NaCl the magnitudes of C_{12} and C_{44} are similar. On the other hand, in AgCl the magnitude of C_{12} is much larger than C_{44}. In addition, it should be noted that $C_{12} < C_{44}$ in NaCl but $C_{12} > C_{44}$ in AgCl.

The results shown above reveal many interesting points. The first concerns the applicability of Eq. (5). The result shown in Fig. 3 indicates that it should be used carefully. Previous studies have pointed out that many physical properties of silver halides are anomalous at high temperature [13,14, 16-18]. It has been suggested that their lattice dynamical properties can not be interpreted by a quasiharmonic approximation [16]. The anomalous behavior at high temperature has been associated to a rapid increase in the concentration of Frenkel defects [17]. This peculiarity of AgCl suggests that the values of the physical quantities evaluated at low temperature can not be used at high temperature. Specifically, the deviation observed in Fig. 3 indicates that the assumption $\delta_M^0 = \text{constant}$ used in the derivation of Eq. (5) is not obeyed in the case of AgCl, in particular for the case of C_{44}. In view that Eq. (5) has been used successfully in the analysis of thermodynamic properties of many materials, the result shown in Fig. 3 reveals once again the anomalous nature of AgCl at high temperatures.

In an earlier study of the temperature dependence of elastic constants in Ag halides, the large deviation from the low temperature extrapolation has been accounted by introducing a term proportional to the number of Frenkel defects that increases with temperature. The constant of proportionality was chosen in such a way to fit the experimental data [16]. Concerning the ionic conductivity, the experimental data has been analyzed in terms of Frenkel defects and their interactions [17]. There, it was shown that the long-range Coulomb interactions between the defects are not sufficient to account for the observed large values of ionic conductivity. To fill up the remaining deviation from the experimental values, other physical processes such as softening of the lattice has been invoked. The bond fluctuation model [3] mentioned in the introduction and used in the following discussion is related with such softening process. However, to avoid misunderstanding, it should be mentioned that it is not an independent model from the defect concentrations. It is a model that includes implicitly the formation of defects and their interactions.

Concerning the magnitudes of C_{12} and C_{44} in NaCl and AgCl, it is related with the Cauchy relation. This relation which is expressed as $C_{44}/C_{12} = 1$, is obeyed by crystals governed by central pairwise interactions. Fig. 4 reveals that in NaCl at $T \approx 300$ K, $C_{44}/C_{12} \approx 1.13$, reflecting the dominance of ionic bonding. On the other hand, from Fig. 2 and 3 we have $C_{44}/C_{12} \approx 0.17$ for AgCl. This large deviation from the Cauchy relation has been known for a long time in silver halides. The deviation has been attributed to the presence of covalent interactions in these compounds [5].

Fig. 5 shows the temperature dependence of C_{44}/C_{12} for NaCl and AgCl. For NaCl we note that the deviation from the Cauchy relation increases with temperature. That is, the result indicates that the dominance of ionic interaction decreases with the increase of temperature. On the other hand, although still far from the condition $C_{44}/C_{12} = 1$, the result for AgCl suggests that the bonding becomes more ionic with the increase of temperature.

Some authors have suggested that in AgCl, the transition to the superionic state is frustrated due to melting [14]. This suggestion is understandable if the result shown in Fig. 5 is seen from the point of view of bond fluctuation model of superionic conductors, which claims that in materials such as silver halides, the high ionic motion occurs by the fluctuations of bonds that occur locally within the solid [3]. According to this model, the behavior of Fig. 5(b) arises form the decrease of the covalency due to bond fluctuation processes that increase with temperature. Similar argument was used successfully to understand the temperature dependence of the effective charge of some superionic materials [19]. It should be noted however that in the present case, the bond fluctuation is not accompanied by large change of atomic positions as in the case of AgI which is a four-fold coordinated compound. Detail of the bond fluctuation model is reviewed elsewhere [20].

From Fig. 5 it is clear that $C_{12} < C_{44}$ in NaCl and $C_{12} > C_{44}$ in AgCl. By looking the values of C_{12} and C_{44} for other ionic solids, no general trend seems to exist in the relative magnitudes of C_{12} and C_{44} [21]. Most of the alkali halides with the rock salt structure, excluding NaI, KF, RbF and RbCl, exhibit $C_{12} < C_{44}$ [21]. Concerning the origin of such difference, some authors have approached the problem by using many-body potentials [21,22], other has suggested that it is determined by the competition between three-body potential and breathing mode terms [22]. Although these approaches provide some hint to understand the problem, further studies are necessary to elucidate the origin of the difference.

4. Conclusion

The temperature dependence of elastic constants is of utmost importance to understand the thermodynamic and thermoelastic behavior of solids at high temperatures. In the present study, the temperature dependence of the second order elastic constants of AgCl has been calculated by using a formula derived from the Murnaghan model for the elastic constants. The result revealed that the model reproduces quite well the measured data of C_{11} and C_{12} over a wide range of temperature (from 290 K to 700 K). However, concerning the behavior of C_{44}, a deviation becomes apparent at high temperatures (starting around 400 K). The result indicates that the model should be used carefully in the evaluation of elastic constants. A comparative study of the temperature dependences of elastic

constants between AgCl and NaCl has been presented and the origin of the difference was discussed from the point of view of chemical bonding.

5. References

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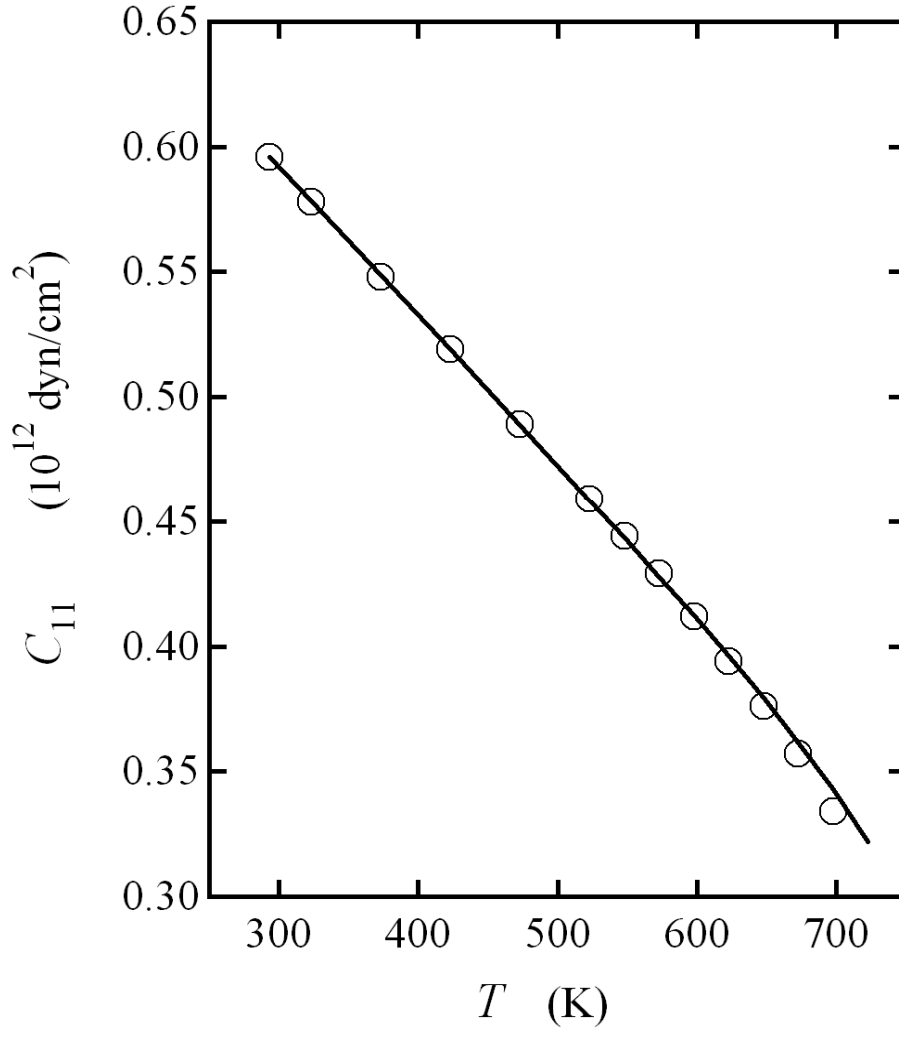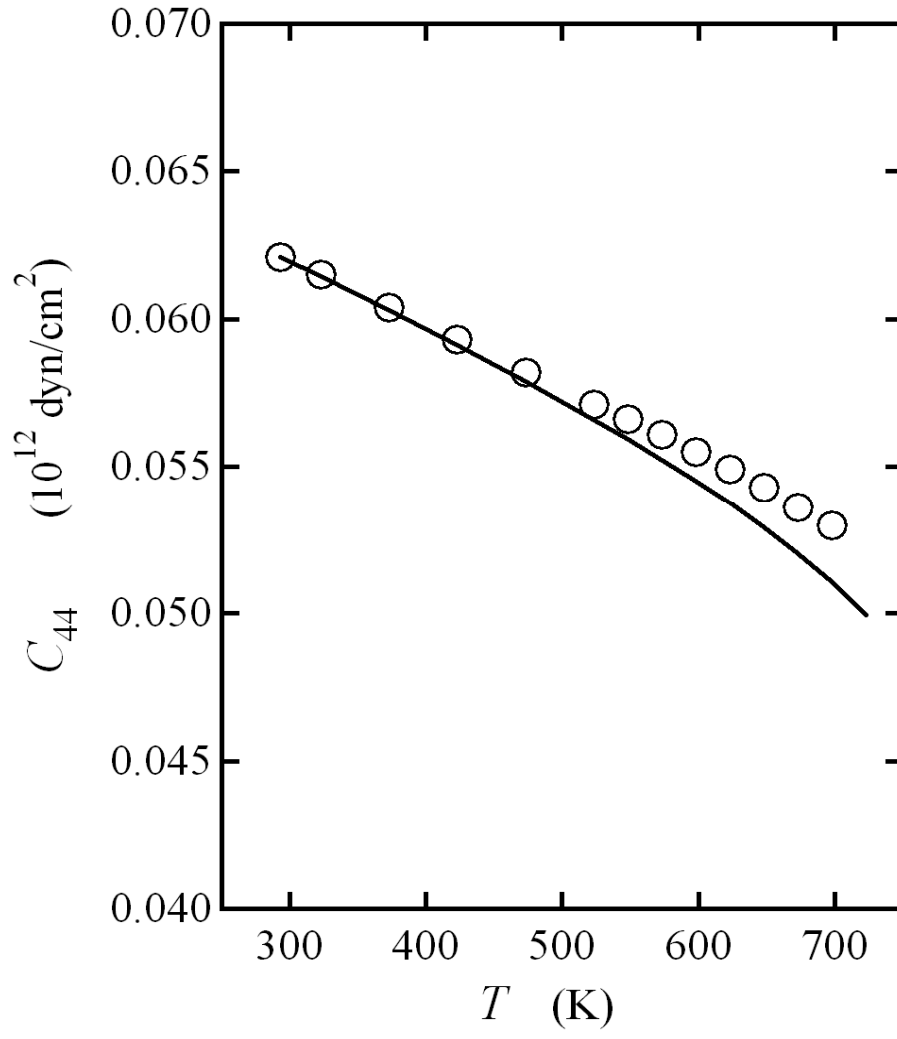
Fig. 1. The temperature dependence of the elastic constant C_{11} of AgCl. The solid line shows the behavior of Eq. (5). The open circles are the experimental data from [14].
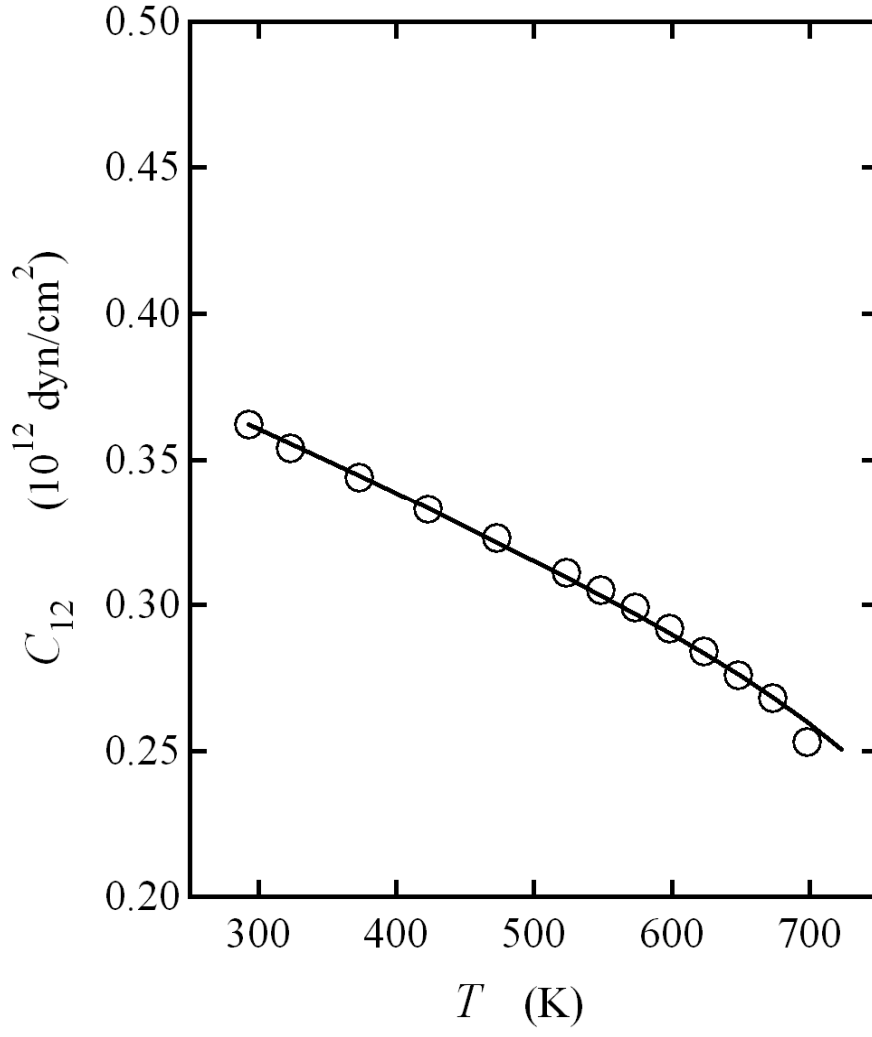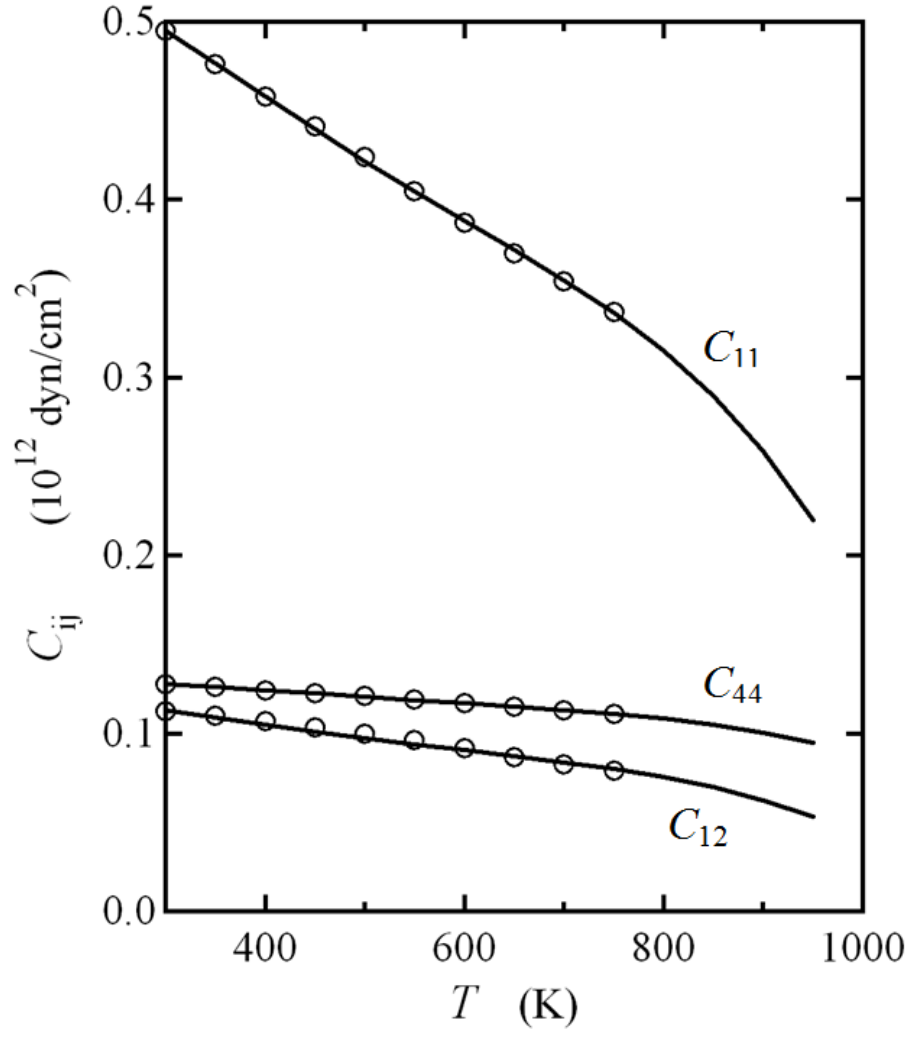
Fig. 2. The temperature dependence of the elastic constant C_{12} of AgCl. The solid line shows the behavior of Eq. (5). The open circles are the experimental data from [14].
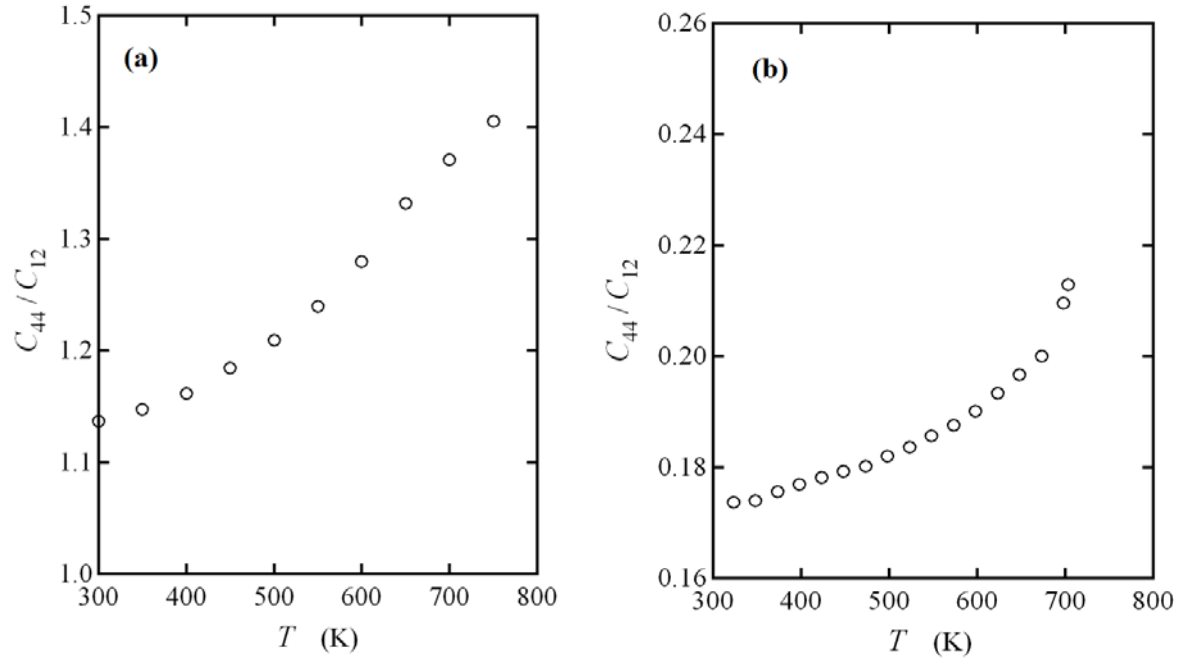
Fig. 3. The temperature dependence of the elastic constant C_{44} of AgCl. The solid line shows the behavior of Eq. (5). The open circles are the experimental data from [14].

Fig. 4. The temperature dependencies of the elastic constants C_{11}, C_{12} and C_{44} of NaCl. The solid lines show the behavior of Eq. (5). The open circles are the experimental data from [4].

Fig. 5. Temperature dependencies of C_{44}/C_{12} in (a) NaCl and (b) AgCl. The experimental data are taken from [4, 14], respectively.