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Temperature Dependence of Anderson–Grüneisen Parameter of Ionic Solids*

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A new relation, including the volume-dependent and the cubic-and quartic-term anharmonic contributions, has been derived for the Anderson–Grüneisen parameter δ for ionic solids. This equation has been applied to the KCl crystal to study the temperature dependence of δ, and the role of the volume-dependent and anharmonic contributions has been explained. The wider applicability of the present equation has been discussed.

In an attempt to study the temperature dependence of the bulk modulus of some oxide compounds, Anderson (*1*) derived the relation

$$\frac{dB_S}{dT} = -\delta\gamma(C_p/V), \qquad (1)$$

where C_P is the specific heat at constant pressure, V is the atomic volume, γ is the Grüneisen parameter, and B_S is the adiabatic bulk modulus. The dimensionless parameter δ, which is a fundamental parameter of the solid similar to the Grüneisen γ, is known as the Anderson–Grüneisen parameter. From Eq. (1) δ can be defined as

$$\delta = -\left(\frac{1}{\alpha}\right)\left(\frac{d\ln B_S}{dT}\right) = -\left(\frac{d\ln B_S}{d\ln V}\right), \qquad (2)$$

where α is the volume expansion coefficient.

Since Anderson introduced this parameter in 1966, a number of attempts have been made to study the physical meaning of δ in the case of ionic solids. Chang (*2*), entirely from thermodynamical considerations and using the Grüneisen's equation of state of solids, has shown that the pressure dependence of the bulk modulus at constant temperature is related to δ as

$$\delta = \left(\frac{dB_T}{dP} - 1\right) \simeq \left(\frac{dB_S}{dP} - 1\right), \qquad (3)$$

where B_T is the isothermal bulk modulus. Considering the relation

$$B_T = B_S\left(\frac{C_v}{C_p}\right) \qquad (4)$$

between B_T and B_S, Madan (*3*) derived a more precise relation in place of Eq. (3) as

$$\delta = \left(\frac{dB_T}{dP} - 1\right) - \left(\frac{1}{\alpha}\right)\frac{\partial}{\partial T}(\ln C_p/C_v) \qquad (5)$$

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and on the basis of relation (4)

$$\gamma = \frac{\alpha V B_{\mathrm{T}}}{C_v} = \frac{\alpha V B_{\mathrm{S}}}{C_p} \tag{6}$$

Sharma and Gupta (*5*) simplified Eq. (5) to

$$\delta = \left(\frac{dB_{\mathrm{T}}}{dP} - 1\right) - \frac{B_{\mathrm{T}} V}{C_p \gamma} \frac{\partial}{\partial T} (1 - C_p/C_v). \tag{7}$$

Assuming the quasi-harmonic model and Dugdale and MacDonald's (*6*) and Slater's (*7*) relations between γ and the change of compressibility with volume, Chang (*2*) simplified his Eq. (3), giving the relationships between δ and γ as

$$\delta = 2\gamma \tag{8}$$

and

$$\delta = 2\gamma - 2/3, \tag{9}$$

respectively.

However, a more precise equation using the quasi-harmonic model and on the basis of a central pair potential between the atoms has been derived by Mathur and coworkers (*8*). Using the exponential function due to Born and Mayer for the central pair potential ϕ, as

$$\phi = -\frac{\alpha'(Z'e)^2}{r} + \lambda \exp(-r/\rho), \tag{10}$$

where α' is the Madelung's constant, Z' is the valency, e is the electronic charge, and λ and ρ are the potential parameters, these authors (*8*) have derived the equation for δ as

$$\delta = -\gamma + 2 + \left(\frac{r_0}{3\rho}\right) - \left[\left(\frac{r_0}{3\rho}\right) \Big/ \left(\frac{r_0}{\rho} - 2\right)\right], \tag{11}$$

where r_0 is the equilibrium interionic distance.

Using Eqs. (5)–(9) and Eq. (11) the Anderson–Grüneisen parameter δ of ionic solids has been extensively studied. All these studies have demonstrated that the contribution of the second term on the right-hand side of Eqs. (5) and (7) is substantial and Chang's equation (Eq. (3)) is only an approximation which makes computations simple. Using Eq. (7) Sharma and Gupta (*5*) have also studied the temperature dependence of δ of the NaCl crystal and compared this (δ, T) curve with that obtained from Chang's equations. However, an important aspect of the study—the effect of anharmonicity on δ, particularly at high temperatures—has been overlooked in these studies. It is well known that anharmonicity, through volume dependence and also through the contributions of the cubic and quartic terms of the potential energy function, plays an important role in explaining the temperature dependence of various lattice properties of solids. In the present investigation we have made an attempt to evaluate its effect on the Anderson–Grüneisen parameter, δ. A new equation for δ including these two anharmonic contributions has been derived. The values of δ for the KCl crystal have been computed at various temperatures at high temperature and the results have been compared with those obtained from the equations of other workers. The dependence of δ on γ has also been studied and discussed.

Born and Huang (*4*) have derived a relation for the thermal variation of the isothermal bulk modulus as

$$B_{\mathrm{T}} = B_o + \left\{2 + \frac{V_0 \left(\frac{d^3\phi}{dV^3}\right)_{V=V_0}}{\left(\frac{d^2\phi}{dV^2}\right)_{V=V_0}}\right\} \frac{\gamma E_{\mathrm{vib}}}{V} - \frac{\gamma^2}{V}(TC_v - E_{\mathrm{vib}}), \tag{12}$$

where $(d^2\phi/dV^2)_{V=V_0}$ and $(d^3\phi/dV^3)_{V=V_0}$ are the second- and third-order derivatives of ϕ with respect to V at equilibrium V_0, E_{vib} is the vibrational part of the total energy, and B_0 is the value of the bulk modulus at 0 K. Equation (12) has been derived under the approximation that $(V - V_0)/V_0$ is small so that only the linear term in $(V - V_0)/V_0$ is retained and higher-order terms are dropped, being negligibly small. From the measurements of the lattice parameter of alkali halides at high temperatures by Srivastava and Merchant (*9*) it can be seen that this indeed is the case for these ionic crystals.

Substituting Eqs. (12) and (4) in Eq. (1) and using standard thermodynamical relations, we finally get

$$\begin{aligned}\delta = \delta_0 &- \left(\frac{\delta_0}{B_0}\right)\left[\left(2 + V_0\frac{\phi^{\mathrm{III}}}{\phi^{\mathrm{II}}}\right)\frac{\gamma E_{\mathrm{vib}}}{V_0} - \frac{\gamma^2}{V_0}(TC_v - E_{\mathrm{vib}})\right]\\ &+ \left(\frac{E_{\mathrm{vib}}}{C_v}\right)\left[2\alpha - V_0^2\alpha\left(\frac{\phi^{\mathrm{IV}}}{\phi^{\mathrm{II}}} - \frac{\phi^{\mathrm{III}^2}}{\phi^{\mathrm{II}^2}}\right) + \gamma\left(\gamma\alpha - 2\frac{d\gamma}{dT}\right)\right]\\ &- \left[2 + V_0\frac{\phi^{\mathrm{III}}}{\phi^{\mathrm{II}}} + \gamma T\left(\gamma\alpha - 2\frac{d\gamma}{dT}\right)\right]\\ &+ \gamma T\frac{d}{dT}(\ln C_v) - \left(\frac{1}{\alpha}\right)\frac{d}{dT}(\ln C_p/C_v). \qquad (13)\end{aligned}$$

For a special case for $\gamma = 1$ in the second term on the right-hand side of Eq. (12), a similar equation was derived by us earlier (*10*). In Eq. (13) ϕ^{II}, ϕ^{III}, ϕ^{IV}, . . . , are the second-, third-, and fourth-order derivatives of ϕ with respect to V at $V = V_0$. It can be seen that δ_0—the Anderson–Grüneisen parameter at 0 K—may thus be represented by Chang's Equation (3). Using data listed in Ref. (*11*), δ_0 for KCl has been found to be 2.8.

Equation (13) can be further simplified for high-temperature computations. Enck (*11*) has measured the Grüneisen parameter of the KCl crystal from which it can be seen that the temperature variation of γ is small. As such, we can put $d\gamma/dT = 0$ without much loss of accuracy. At high temperatures, such that $kT \gg h\nu_i$, we have $E_{\mathrm{vib}} = 6\ kT$, where k is Boltzmann's constant. Under these conditions, Eq. (13) for δ reduces to

$$\begin{aligned}\delta = \delta_0 &+ \mu_1 T + \mu_2 T\\ &+ \gamma T\frac{d}{dT}(\ln C_v) + \delta_{\mathrm{CF}}, \qquad (14)\end{aligned}$$

where

$$\mu_1 = \gamma\left[\left(\frac{\gamma\delta_0}{B_0}\right)\left(\frac{12k}{V_0}\right) - \frac{2}{T}\right], \qquad (15)$$

$$\mu_2 = \alpha\left[2 - V_0^2\left(\frac{\phi^{\mathrm{IV}}}{\phi^{\mathrm{II}}} - \frac{\phi^{\mathrm{III}^2}}{\phi^{\mathrm{II}^2}}\right)\right], \qquad (16)$$

and

$$\delta_{\mathrm{CF}} = -\left(\frac{1}{\alpha}\right)\frac{d}{dT}[\ln(C_p/C_v)]. \qquad (17)$$

The values of δ for the KCl crystal from room temperature to near its melting point using Eq. (14) have been calculated on the basis of the Born–Mayer potential energy function and are reported in Table I. For the evaluation of the potential parameters, λ and ρ, of the Born-Mayer potential energy function (Eq. (10)), we have followed the usual procedure (*12*) and the experimental data required for the computations have been taken from Enck (*11*), Srivastava and Merchant (*9*), and Hart (*13*). In Fig. 1 the temperature dependence values of δ obtained from various equations are

TABLE I

VALUES OF THE VARIOUS CONTRIBUTIONS TO THE ANDERSON–GRÜNEISEN PARAMETER AT DIFFERENT TEMPERATURES FOR THE KCl CRYSTAL

T (K)	$\mu_1 T$ (Eq. (5))	$\mu_2 T$ (Eq. (6))	$\gamma T \frac{d}{dT}(\ln C_v)$	δ_{CF} (Eq. (7))	δ (Eq. (4))
573	2.35	0.34	0.039	−2.03	3.50
673	2.06	0.42	0.058	−1.83	3.51
773	1.82	0.45	0.071	−1.45	3.74
873	1.39	0.48	0.081	−1.52	3.23
973	0.82	0.49	0.076	−1.33	2.86

compared and in Fig. 2, δ has been correlated with γ for this crystal.

From Table I we note that the volume dependence and the anharmonic contributions have an opposite effect on the Anderson–Grüneisen δ for the KCl crystal. The anharmonic contribution ($\mu_2 T$) is consistently increasing with temperature while that due to the volume dependence ($\mu_1 T$) is decreasing. The anharmonic contribution is also small compared to the volume-dependent contribution as was expected from the results obtained from the quasi-harmonic approximation (*3*, *8*). The values of δ thus obtained from Eq. (14) are compared with those obtained from other equations for this crystal, in Fig. 1.

The values of δ at different temperatures obtained from various equations show some interesting trends (Fig. 1). The simplest equations for δ derived by Chang (Eqs. (8) and (9)) showed that since δ is dependent only on γ, its temperature dependence is linear. Since the temperature dependence of γ is very small (*11*), δ vs T plots of these equations are almost parallel to the x axis. However, some rapid changes are observed below 773 K. Mathur and coworkers' relation (Eq. (11)) also shows the same trend because it has also been derived under the quasi-harmonic approximation; only the magnitude of δ is different. The δ–T plot of Sharma and Gupta's equation (Eq. (7)) is also nearly a straight line and the magnitude of δ steadily increases with increasing temperature. The δ vs T curves obtained from Eq. (1) and our Eq. (4) are conic but of different nature. In the case of Eq. (1) the value of δ falls considerably up to 773 K and then becomes almost constant

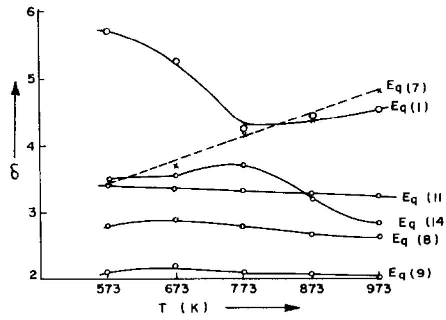

FIG. 1. δ–T curves for the KCl crystal on the basis of various equations.

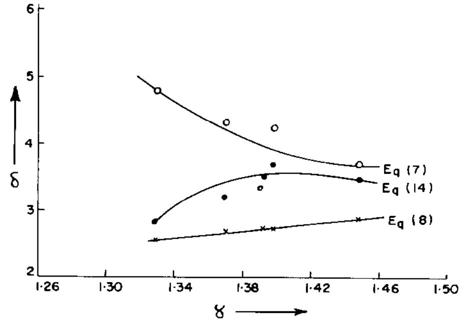

FIG. 2. Correlation of δ with γ at different temperatures for the KCl crystal.

beyond this temperature, while in the case of our equation it increases slightly and then decreases beyond 773 K. The present equation shows that at high temperatures it is the anharmonic cubic- and quartic-term contribution that is predominant while at lower temperatures the volume-dependent contribution seems to predominate.

Sharma and Gupta (*5*) have also made δ vs T plots of Eqs. (1), (7), and (8) for the NaCl crystal and obtained conics of different nature. However, they have computed values only at three temperatures between room temperature and the melting point of NaCl crystal, and as such their graphs cannot be said to be truly representative. This is why they have obtained a conic even for the simpler equation of Chang, whereas in the present study it is conclusively a straight line, as it should be.

The Anderson–Grüneisen parameter δ has been correlated with the Grüneisen parameter γ for the KCl crystal in Fig. 2. As in the case of the NaCl crystal, investigated by Sharma and Gupta (*5*), the correlation done on the basis of the Chang equation (Eq. (3)) for the KCl crystal is a straight line. The (δ–γ) plots obtained on the basis of Eqs. (7) and (14) are again conics, but of different nature, showing therefore that the volume-dependent and other anharmonic contributions to δ and γ vary differently at different temperatures. It is thus clear that these anharmonic contributions are mainly responsible for the deviation of the (δ–γ) plot from the ideal case of a straight line to a conic.

From this investigation we thus conclude that our equation for δ, which has been obtained by removing all the approximations of the earlier workers, has wider applicability. Its application in the case of the KCl crystal presents a clear picture of the temperature dependence of δ, in terms of volume-dependent and other anharmonic contributions, and also shows its dependence on γ in accordance with earlier workers. Other applications of the present equation might be of some interest, especially to molecular crystals, and a study is in progress in this direction.

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