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The Anderson–Grüneisen Parameter for Cubic Crystals*

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A new, simple relation for δ the Anderson-Grüneisen parameter, developed by Sharma and Tripathi (M. N. Sharma and S. R. Tripathi, *Phys. Status Solidi* (*b*) **59**, K1 (1973)), which involves fewer approximations than other complex, cumbersome equations available in literature, has been used to compute values of δ employing three different potentials viz the Varshni–Shukla, the Logarithmic, and the Rydberg's function. The comparison of these values with experimental ones indicates the suitability of Varshni–Shukla and Logarithmic potential functions for the study of the property δ.

I. Introduction

The Anderson–Grüneisen parameter (*1*) δ is an important parameter in that it provides knowledge of the macroscopic behaviour of thermal properties of solids for which the experimental data are not known with much precision. The basic formula for its computation has been shown by Anderson (*2*), proceeding on the basis of Grüneisen's theory, to be

$$\delta = -\frac{1}{\alpha_v}\left[\frac{d(\ln B_S)}{dT}\right] = \frac{d(\ln \beta_S)|dT}{d(\ln v)|dT}, \qquad (1)$$

where α_v is the coefficient of volume thermal expansion, B_S is the Bulk modulus, β_S the adiabatic compressibility and v the average volume per atom at temperature T. But, unfortunately, the use of this relation is limited due to the lack of precise data for $(\partial\beta_S/\partial v)$.

Chang (*1*), on the basis of thermodynamic calculations, has given two relations for δ; one from Slater's theory is

$$\delta = 2\gamma, \qquad (2)$$

and the other, from Dugdale and Macdonald's theory, is

$$\delta = 2\gamma - 2/3. \qquad (3)$$

But these relations are basically approximate since, in the derivation of these equations, Chang has assumed that the ratio (C_v/C_p) remains constant for all temperatures, which is true only at high temperatures. It is interesting to mention here that Chang himself was not sure about the correctness of any one of these two relations.

Mathur and Singh (*3*) followed Anderson (*2*) to compute the values of δ employing a Born–Mayer potential energy function. Later on, Mathur et al. (*4*) gave an expression for δ in terms of γ and the potential parameters, assuming repulsive interaction energy of the form $[Bf(v)]$, and calculated the values of δ for a few alkali halides employing a Born–Mayer potential energy function. Recently Sharma and Tripathi (*5*), generalized this equation by excluding the parameter B and thus developed a new general expression for δ applicable to any form of potential energy function. Later, this general expression was shaped into a simple and concise form (*6*).

A very simple theory, involving the fewest approximations, has been developed by Sharma and Tripathi (*7*) to give a new simple and general equation for δ. In the present communication we have used this relation to calculate the δ values for some alkali halides,

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employing three different types of potential energy functions.

II. Theory

For practically all ionic crystals, the adiabatic compressibility closely approximates the isothermal compressibility, the difference being, at the most 5% (*8*, *9*); thus, as pointed out by Madan (*10*), the differences between values of ($d \log \beta_T / d \log v$) and ($d \log \beta_S / d \log v$) are practically insignificant. Therefore, β_S in Eq. (1) can be expressed in terms of potential energy function as (*11*)

$$\beta = (qkr/\psi''(r))\, F_{T,P} \qquad (4)$$

where k is the structure constant, r is the interatomic separation, $\psi''(r)$ is the second derivative of $\psi(r)$, the potential energy function with respect to r, and $F_{T,P}$ is a correction term.

Solving for δ we get (*7*)

$$\delta = 1/3[1 - (r_0\psi'''(r_0)/\psi''(r_0))] \qquad (5)$$

where $\psi''(r_0)$ and $\psi'''(r_0)$ refer to the second and third derivatives of $\psi(r)$ at $r = r_0$, the equilibrium separation between the two ions.

The authors use this equation to compute δ employing three different forms of potential energy function $\psi(r)$ viz (1) a suitably modified Varshni–Shukla model, earlier used by Patel et al. (*12*), (2) a suitably modified logarithmic potential used earlier by Prakash and Behari (*13*), Pande et al. (*14*) and Misra et al. (*15*) for the computation of some lattice properties of ionic crystals, and (3) the Rydberg potential (*16*), successfully applied in the studies of

TABLE I

THE ANDERSON–GRÜNEISEN PARAMETER δ

Crystals	δ^a	δ^b	δ^c	δ^d	δ^e	δ^f	δ^g
LiF	4.12	3.42	4.36	1.94	2.17	9.06	2.68
LiCl	4.63	4.02	4.45	3.64	5.74	4.95	3.75
LiBr	4.68	4.66	4.46	3.22	5.71	4.71	—
LiI	5.17	4.51	4.44	3.30	2.99	3.80	—
NaF	4.19	4.08	4.93	3.51	2.04	7.37	—
NaCl	4.25	4.14	5.05	3.56	5.64	4.04	3.77
NaBr	—	4.28	4.36	3.47	3.44	3.98	3.75
NaI	4.48	4.42	4.38	3.55	7.41	3.22	3.75
KF	—	3.47	4.17	3.90	1.00	5.10	3.48
KCl	4.31	3.89	4.44	3.60	3.46	4.23	4.15
KBr	4.38	4.12	4.34	3.65	4.36	3.59	3.86
KI	4.09	4.22	5.21	3.49	2.72	2.74	3.42
RbF	—	4.39	4.48	3.88	2.10	3.36	—
RbCl	4.35	4.13	4.42	3.80	4.06	1.66	4.25
RbBr	4.30	4.30	4.42	3.78	3.65	1.73	4.23
RbI	4.40	4.45	4.30	3.58	3.87	1.21	3.65
CsCl	—	4.08	4.57	4.37	—	—	—
CsBr	—	4.08	3.66	3.87	—	—	—
CsI	—	3.74	3.74	3.67	—	—	—

[a] See Ref. (*22*).
[b] Using Eqs. (5) and (6).
[c] Using Eqs. (5) and (7).
[d] Using Eqs. (5) and (8).
[e] See Ref. (*3*); Eq. (3).
[f] See Ref. (*3*); Eq. (7).
[g] See Ref. (*23*).

metals (*17*) and some ionic crystals (*18–20*). These potentials may be mathematically expressed as

$$\psi(r) = -\alpha e^2/r + \lambda \exp(-br^{3/2}) - (C/r^6) - (D/r^8) \quad (6)$$

(suitably modified Varshni–Shukla model);

$$\psi(r) = (-\alpha e^2/r) + A \log\ (1 + B/r^9) - (C/r^6) - (D/r^8) \quad (7)$$

(suitably modified Logarithmic model);

$$\psi(r) = (-\alpha e^2/r) + \mu \exp(-\sigma r) + \nu r \exp(-\sigma)r \quad (8)$$

(Rydberg potential model);
where λ, b, A, B, μ, σ, and ν are the potential parameters and C and D are the van der Waals constants. These potential parameters have been evaluated employing the method given by Sharma and Jain (*21*).

The three different values of δ, thus computed for some alkali halides using the above-mentioned potential models are presented in Table I along with the experimental (*22*) and other theoretical values calculated by earlier workers (*3*, *23*).

III. Discussion

It may be noted that the theoretical values of δ calculated using Eqs. (5) and (6) are in good agreement with the experimental values presented in column II of Table I. The values of δ calculated using Eqs. (5) and (7) also show a notable accordance with the experimental ones. The only values systematically smaller than the experimental ones are those calculated from Eqs. (5) and (6).

The above behaviour of δ values has implications for the suitability of several models. One may directly infer that the suitably modified Varshni–Shukla and suitably modified logarithmic potential gives satisfactory results for δ in case of ionic crystals, while the Rydberg potential yields values lower than the experimental ones and hence may not be considered suitable for the study of the property δ with ionic crystals.

It may also be pointed out that our results (columns III and IV) are in better agreement with experimental values than are those of Mathur and Singh (columns VI and VII). Probably the choice of unsuitable values of derivatives of β_S with pressure and temperature led to their erroneous results. The values calculated by Sastry and Mulimani (*23*) (column VIII) also show a poor agreement with the experimental ones.

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