

## Statistical Approach to Anderson-Grüneisen Parameter $\delta^*$

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A simple and general relation has been developed for the Anderson-Grüneisen parameter  $\delta$  in terms of the Grüneisen parameter  $\gamma$ , employing a statistical approach for ionic crystals. The relation can be expressed as  $\delta = a\gamma^b$ , where  $a$  and  $b$  are some arbitrary constants. It has been concluded that the developed relation is a general form of Chang's relation ( $\delta = 2\gamma$ ).

### Introduction

Analogous to Grüneisen parameter  $\gamma$  (1), the Anderson-Grüneisen parameter  $\delta$  is also an important parameter in describing the macroscopic properties of solids. It was first introduced by Anderson (2) during his studies on the temperature variation of bulk modulus of MgO. To date, several formulas have been put forward relating it to various microscopic lattice properties (3-10). Recently Sharma and Tripathi (7, 8) obtained a general expression for  $\delta$  that can be applied directly to any form of potential energy function. In the present work, this expression has been used to compute the theoretical values of  $\delta$  for some cubic crystals employing two forms of potential energy functions, i.e., the well-known Lennard-Jones (12:6) and the Wasastjerna potential models. Moreover, an empirical relation has been developed between  $\delta$  and  $\gamma$  employing the statistical method of least squares.

### Theory

Following Anderson, Sharma and Tripathi (7, 8) have successfully derived a general expression for ionic crystals relating  $\delta$  with  $\gamma$

through the potential parameters. It can be expressed as

$$\delta = \frac{(1 + \gamma)f'(V_0) - (1 + \gamma)V_0f''(V_0) - V_0^2f'''(V_0) + (7\alpha e^2/(9V_0^{4/3}))(\gamma - (1/3))}{(1 + \gamma)f'(V_0) + V_0f''(V_0) + (\alpha e^2/(3V_0^{4/3}))(\gamma - (1/3))} \quad (1)$$

where  $\gamma$  is the Grüneisen parameter,  $\alpha$  is the Madelung constant, and  $e$  is the electronic charge.  $f'(V_0)$ ,  $f''(V_0)$ , and  $f'''(V_0)$  are respectively the first, second, and third derivatives of potential energy function  $f(v)$  at  $V = V_0$ .

To compute  $f'(V_0)$ ,  $f''(V_0)$ , and  $f'''(V_0)$  for evaluating  $\delta$  from Eq. (1), two potential models have been chosen, as stated in the preceding section. The Wasastjerna potential energy function has been extensively used to evaluate the lattice energies and other crystal properties for several alkali halide and hydride crystals (11, 12). The well-known Lennard-Jones (12:6) model has been successfully used earlier to explain the various lattice properties for alkali and metal halides (13-15).

The Wasastjerna and Lennard-Jones potential energy functions can be expressed in terms of specific volume as:

$$F(v) = -\frac{\alpha e^2}{v^n} + \mu v^{7n} \exp(-\beta v^n) - \frac{C}{v^{6n}} - \frac{D}{v^{8n}} \quad (2)$$

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and

$$F(v) = -\frac{\alpha e^2}{v^n} + \frac{\lambda}{v^{12n}} - \frac{C}{v^{6n}} - \frac{D}{v^{8n}} \quad (3)$$

where  $v = r^3$  and  $n = \frac{1}{3}$ .  $r$  is the interionic distance,  $\mu$ ,  $\beta$ , and  $\lambda$  are the parameters of potential energy functions, and  $C$  and  $D$  are the van der Waals constants.

The potential parameters  $\mu$  and  $\beta$  in Eq. (2) and (3) have been evaluated by applying the following lattice conditions:

$$\psi(r)|_{r=r_0} = -E \quad (4)$$

$$\left. \frac{d\psi(r)}{dr} \right|_{r=r_0} = 0 \quad (5)$$

where  $E$  is the lattice energy of the crystal. For the Lennard-Jones (12:6) model the sole potential parameter  $\lambda$  has been evaluated from the lattice condition expressed by Eq. (5).

Once the potential parameters are evaluated,

the first, second, and third derivatives of  $f(v)$ , i.e.,  $f'(V_0)$ ,  $f''(V_0)$ , and  $f'''(V_0)$  can be computed for the respective potential models, simply by feeding the necessary experimental data (19-22).

Recently Sharma and Jain (10) and Misra and Sharma (16) have suggested a general expression for the Grüneisen parameter  $\gamma$  in terms of the derivatives of the potential energy function, which can be expressed as:

$$\gamma = \frac{-r_0}{6} [\psi'''(r_0)] [\psi''(r_0)]^{-1} \quad (6)$$

where  $\psi''(r_0)$  and  $\psi'''(r_0)$  are, respectively, the second and third derivatives of the potential energy function  $\psi(r)$  at  $r = r_0$ .

The theoretical values of  $\gamma$  are computed from Eq. (6) using Wasastjerna as well as Lennard-Jones potential functions. These values have been presented in Table I (Cols. 2 and 3, respectively).

TABLE I

THE VALUES OF GRÜNEISEN PARAMETER  $\gamma$  AND ANDERSON-GRÜNEISEN PARAMETER  $\delta$

Crystals	$\gamma_1$	$\gamma_2$	$\gamma_3$	$\delta_A$	$\delta_B$	$\delta_C$	$\delta_{11}$	$\delta_{12}$	$\delta_{21}$	$\delta_{22}$	$\delta_{31}$	$\delta_{32}$
LiF	2.6628	0.6064	1.7611	—	4.12	3.5222	3.7479	5.8085	—	1.6133	4.6565	2.2396
LiCl	2.7392	0.8218	1.7853	—	4.63	3.5706	3.5827	5.5069	0.7804	2.6742	4.5212	1.7179
LiBr	2.7450	1.5364	2.0282	—	4.68	4.0564	3.6092	4.5174	1.3017	2.4462	4.3222	1.9720
LiI	2.7708	2.2782	2.2325	—	5.17	4.4650	3.7524	4.2495	2.5890	3.0518	4.2944	3.0939
NaF	2.7128	0.9241	1.8059	—	4.19	3.6118	3.1294	5.6716	0.8955	2.0103	4.8209	1.0707
NaCl	2.7451	1.3792	1.7454	3.5448	4.25	3.4908	3.7225	5.1003	1.3605	2.3123	4.7318	2.0189
NaBr	2.6807	1.3327	1.7857	—	—	3.5714	4.5396	5.8756	0.6836	2.4837	5.4439	1.9579
NaI	2.7611	1.8770	1.8967	3.2684	4.48	3.7934	3.9061	4.4865	2.0179	2.8993	4.5726	2.8794
KF	2.7515	2.0537	1.7398	—	—	3.4796	3.7535	4.4500	2.3174	2.7739	4.7654	3.3090
KCl	2.6306	1.3338	1.6069	—	4.31	3.2138	3.8956	3.9336	1.0600	2.3559	4.9224	2.0829
KBr	2.7667	1.5955	1.5841	—	4.38	3.1682	3.9106	4.9473	0.4638	1.4313	4.9614	1.4395
KI	2.7830	1.9139	1.7262	3.8539	4.09	3.4524	4.4106	5.0071	1.9364	2.8056	5.4641	2.9882
RbF	2.7600	—	1.4217	—	—	2.8434	3.7602	—	—	—	5.0989	—
RbCl	2.7970	1.6361	1.5353	4.6220	4.35	3.0706	3.7757	4.9394	1.4798	2.6467	5.0404	2.7416
RbBr	2.7752	1.8146	1.5080	4.4787	4.30	3.0160	3.5405	4.4937	1.6256	2.8675	4.8088	3.1608
RbI	2.7467	3.2735	1.7430	4.4119	4.40	3.4860	4.1932	3.7126	5.1382	4.6481	5.2040	6.1673
CsF	2.8008	—	2.7555	—	—	5.5110	3.6099	—	—	—	3.7472	—
CsCl	2.7817	2.0041	1.9700 <sup>a</sup>	4.0098	4.78	3.9400	4.0075	4.7761	3.1124	3.9084	4.9298	3.9297
CsBr	2.8694	1.7846	1.9300 <sup>a</sup>	4.5498	4.81	3.8600	3.3711	4.4085	1.2113	1.9240	5.3373	1.8205
CsI	3.0252	2.7720	2.0000 <sup>a</sup>	4.3053	3.76	4.0000	3.5928	3.8344	3.5269	3.7780	4.5997	4.5403

First subscript denotes values of  $\gamma$  used. Second subscript (1) denotes Lennard-Jones model. Second subscript (2) denotes Wasastjerna model.

<sup>a</sup> Ref. (20).

TABLE II  
THE VALUES OF PARAMETERS  $a$  AND  $b$

Parameters <sup>a</sup>	Halides					Alkali fluorides	Alkali chlorides	Alkali bromides	Alkali iodides
	Li	Na	K	Rb	Cs				
$a_{11}$	1.00	0.33	0.34	0.69	0.75	1.89	-1.51	2.37	27.56
$b_{11}$	1.00	0.75	0.77	-0.25	-0.42	-30.50	4.77	-4.07	-60.00
$a_{21}$	0.63	0.76	0.57	0.71	0.77	0.72	0.70	0.85	2.45
$b_{21}$	0.25	0.33	0.36	-0.23	-0.40	-0.18	-1.41	-0.84	-0.49
$a_{31}$	-1.58	0.79	0.64	0.67	0.94	0.78	0.99	1.04	0.93
$b_{31}$	-0.32	-0.39	0.28	0.15	-0.83	-0.44	-0.13	-0.14	-0.89
$a_{12}$	-6.02	-10.36	-1.40	5.54	-10.87	0.68	5.92	2.27	15.61
$b_{12}$	14.06	23.83	3.41	-11.71	24.41	-12.00	13.20	-40.50	35.40
$a_{22}$	0.35	0.29	0.09	0.24	0.08	0.35	0.31	0.38	0.85
$b_{22}$	0.36	0.71	1.25	0.85	1.23	0.71	0.94	-0.22	-0.87
$a_{32}$	0.49	1.14	0.19	-0.40	-14.59	-0.16	0.53	0.48	0.85
$b_{32}$	-0.52	-31.15	0.78	4.86	51.50	2.12	-0.63	0.73	-0.98

<sup>a</sup> The first and second subscripts have the same meanings as in Table 1.

Experimental values of  $\gamma$  have also been obtained using following general equation which defines macroscopic Grüneisen parameter as:

$$\gamma = B_T v \alpha_v / C_v \quad (7)$$

where  $B_T$  is the isothermal bulk modulus,  $v$  is the specific volume,  $\alpha_v$  is the coefficient of volume thermal expansion, and  $C_v$  is the specific heat at constant volume. In Eq. (7),  $C_v$  can be expressed by the well-known thermodynamic relation as:

$$C_v = C_p - B_T v \alpha_v^2 T \quad (8)$$

where  $C_p$  is the specific heat at constant pressure. Making use of Eq. (7) in conjunction with (8) and using the recent experimental input data (19-22) the experimental values of  $r$  have been obtained. These values of  $r$  are tabulated in Table I (Col. 4). In this way we have obtained three different values of  $r$ . Two theoretical values of  $r$  obtained from Lennard-Jones and Wasastjerna potentials are denoted by  $r_1$  and  $r_2$ , respectively, and the experimental  $r$  is expressed as  $r_3$  in Table I.

The values of  $r_1$ ,  $r_2$ , and  $r_3$  have been used in conjunction with Eq. (1) for both the potential energy functions and thus we get six

values of  $\delta$ . The seventh value of  $\delta$  ( $\delta_c$ ) has been obtained using Chang's relation (3) ( $\delta = 2r$ ) in conjunction with Eq. (7). These values of  $\delta$  have been presented in Table I. The theoretical and experimental values of  $\delta$  thus obtained have been plotted against the corresponding values of  $r$ . The statistical approach of the least-squares method has been applied and the best-fit equation for the curves has been derived, it may be expressed as:

$$\delta = ar^b \quad (9)$$

where  $a$  and  $b$  are two arbitrary constants that depend on the potential parameters. The calculated values of  $a$  and  $b$  have been reported in Table II.

## Discussion

Experimental and theoretical values of  $\delta$  have been presented in Table I. The recent experimental values of  $\delta$  ( $\delta_A$  and  $\delta_B$ ) have been taken from Sharma et al. (17). The theoretical values of  $\delta$ , computed with the help of potential energy functions, i.e., the well-known Lennard-Jones (12:6) and the Wasastjerna model, compare satisfactorily with the experimental ones ( $\delta_A$  and  $\delta_B$ ).

Note that compared to other microscopic or macroscopic properties  $\delta$  varies in an irregular fashion for almost all the ionic crystals studied. The minimum value of  $\delta$  is 0.46 for KBr and the maximum value is 6.16 for RbI.

Recently, Chang (3) suggested two simple and direct relations between  $\delta$  and  $\gamma$ . Since Chang was not definite about the correctness of his relations, it was thought desirable to develop a simple relation between  $\delta$  and  $\gamma$

to remove this uncertainty. The curves plotted during present investigations may be put under two categories: (1) for  $\text{LiX}$ ,  $\text{NaX}$ , etc., where  $X = \text{F}$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$  for both the potential energy functions, and (2) for  $\text{RX}$ ,  $\text{RCl}$ , etc., where  $R = \text{Li}$ ,  $\text{Na}$ ,  $\text{K}$ ,  $\text{Rb}$ ,  $\text{Cs}$  for both potential models. For want of space it is not possible to reproduce all the curves; therefore, only two curves are reported. Other curves are similar in nature to these

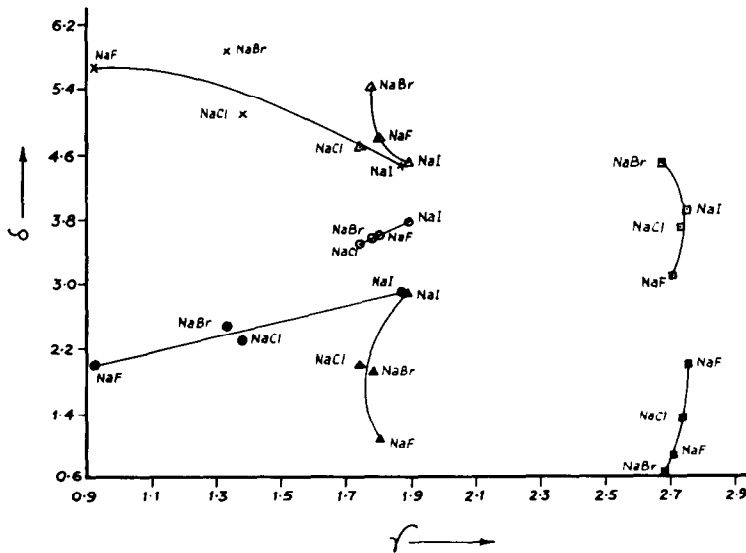


FIG. 1.  $\delta$ - $\gamma$  curves for  $\text{NaX}$  crystals.  $\circ$ , Chang's relation ( $\delta = 2\gamma$ );  $\square$ ,  $\times$ ,  $\Delta$ ,  $\delta$ - $\gamma$  curves for Lennard-Jones potential function using  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$ , respectively;  $\blacksquare$ ,  $\bullet$ ,  $\blacktriangle$ ,  $\delta$ - $\gamma$  curves for Wasastjerna potential function using  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$ , respectively.

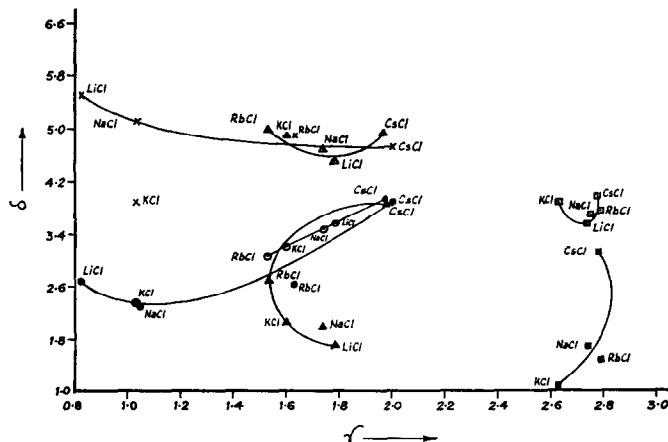


FIG. 2.  $\delta$ - $\gamma$  curves for  $\text{RCl}$  crystals. Symbols have the same meanings as in Fig. 1.

curves. Fig. 1 represents  $\text{NaX}$  curves and Fig. 2 represents  $\text{RCl}$  curves for both potential models. It is important to mention that these values of constants  $a$  and  $b$  exist only for a set of crystals, i.e., for LiF, LiCl, LiBr, and LiI, etc., and cannot be evaluated individually for each crystal. The computed values of  $a$  and  $b$  differ considerably from one group of crystals to another, and hence, it is rather difficult to work out a relation between  $a$  and  $b$ . Thus, we can infer that the constants  $a$  and  $b$  vary with the  $\gamma$  values and depend on the particular potential model used. Hence, it can be concluded that the relationship between  $\delta$  and  $\gamma$  is not very simple and straightforward, as was expected by Chang. Eq. (9) refers to a more general form of the  $\delta$ - $\gamma$  relationship and the Chang's relation ( $\delta = 2\gamma$ ) may be treated as a special case of this equation where  $a = 2$  and  $b = 1$ . Furthermore, Eq. (9) seems to be a concise form of Eq. (1) (derived earlier by Sharma and Tripathi (7)). A similar conclusion has been inferred by Sharma et al. (17, 18).

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