Properties of 2:2 Chalcogenide Crystals with Sodium Chloride Structure

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Abstract

Values of the compressibility, cohesive energy, atomization energy, force constant, i.r. absorption frequency, Debye temperature, Grüneisen parameter, Anderson–Grüneisen parameter and Moelwyn–Hughes parameter for 45 chalcogenide crystals with sodium chloride structure are reported here. These have been obtained using a logarithmic interaction potential energy function. A new method of calculation, derived on the basis of the Moelwyn–Hughes parameter, has been employed for the computation of the potential parameters, since previous methods cannot be applied to these crystals in the absence of compressibility data. The results obtained are encouraging.

Introduction and Theory

In a recent paper (Thakur 1976a) the author has reported the results of calculations of the Moelwyn–Hughes parameter and its various applications to some ionic crystals. The present communication gives the results of an extensive application of the calculated Moelwyn–Hughes parameter to 45 chalcogenide crystals having f.c.c. lattices. Values of the compressibility β_0, force constant f, i.r. absorption frequency ν_0, Debye temperature Θ_D, cohesive energy W, atomization energy E_a, Grüneisen parameter γ, Anderson–Grüneisen parameter δ and Moelwyn–Hughes parameter C_1 of these crystals are derived on the basis of the rigid ion core interaction model. So far, only some of these properties for 15 alkaline earth chalcogenides have been reported (Mayer and Mc. Maltibie 1932; Huggins and Sakamoto 1957; Mathur *et al.* 1965; Gohel and Trivedi 1967; Thakur 1974a; Pandey and Pant 1975; Thakur and Pandey 1975). Because of this lack of compressibility data it is not possible to apply crystal stability and compressibility conditions to an interaction potential energy function in order to compute the various properties of these crystals. However, this difficulty has been removed recently by the introduction of a new method of calculation which does not require these data (Thakur 1976a).

In the past, many interaction potential models have been suggested with repulsive parts that are either inverse power functions or exponential functions. These earlier models have been discredited by Dobbs and Jones (1957) and recently by Thakur (1973). Ree and Holt (1973) have shown that the semi-empirical effective pair potentials of Tosi and Fumi (1964) are too 'soft' and require deeper minima when the elastic constants of the crystals are considered, while the recent perburbation calculation by Brumer and Karplus (1973) has shown that the use of only an exponential form for the overlap repulsion is an inadequate representation. Woodcock (1974) has used a generalized three-term potential corresponding to a simple polarizable ion model, which includes both an inverse power function due to Born and Landé

Table 1. Potential parameters used in calculations

The values of the interionic distance r_0 are taken from Kelly and Groves (1970),
while the present calculated results for the compressibility β_0 are compared
with the available data of Huggins and Sakamoto (1957; HS)

Chalcogenide crystal	r_0 (10^{-1} nm)	β_0 (10^{-12} Pa^{-1}) HS	Present	n index	p (r_0^n units)
Oxides					
BaO	2·910	12·4	15·03	6	0·04964
CaO	2·405	8·6	8·64	5	0·06061
CdO	2·350		8·08	5	0·04120
CoO	2·135		6·11	4	0·16562
FeO	2·147		6·22	4	0·16904
MgO	2·105	6·1	5·87	4	0·15518
MnO	2·225		6·90	4	0·18802
NbO	2·105		5·87	4	0·15492
NiO	2·085		5·71	4	0·14798
SrO	2·580	10·3	10·60	5	0·12134
TaO	2·215		6·81	4	0·19178
TiO	2·090		5·75	4	0·14635
UO	2·460		9·23	5	0·07959
ZrO	2·310		7·68	5	0·02768
Selenides					
BaSe	3·300	20·7	21·71	7	0·01436
CaSe	2·955	15·5	15·90	6	0·06657
CeSe	2·990		16·26	6	0·07552
LaSe	3·030		16·91	6	0·08672
MgSe	2·725	12·0	12·43	5	0·16037
MnSe	2·725		12·43	5	0·16037
PbSe	3·060		17·46	8	0·00744
SnSe	3·010		16·59	6	0·08053
SrSe	3·115	17·8	18·32	6	0·10931
ThSe	2·935		15·42	6	0·05839
USe	2·875		14·52	6	0·04124
Sulphides					
BaS	3·195	18·8	19·72	6	0·13036
CaS	2·845	13·9	14·07	6	0·03196
CeS	2·890		14·74	6	0·04664
LeS	2·920		15·19	6	0·05418
MgS	2·600	10·7	10·84	5	0·12396
MnS	2·225		6·90	4	0·19426
PbS	2·970		15·97	5	0·06043
SrS	3·010	16·1	16·59	6	0·08053
ThS	2·840		14·01	6	0·02997
US	2·740		12·63	5	0·16449
ZrS	2·625		11·15	5	0·13217
Tellurides					
BaTe	3·495	24·6	25·60	7	0·06802
BiTe	3·235		20·45	6	0·14029
CaTe	3·170	18·7	19·27	6	0·12439
CeTe	3·175		19·36	5	0·11569
LaTe	3·205		19·90	6	0·13304
PbTe	3·225		20·28	6	0·13742
SnTe	3·155		19·00	6	0·12044
SrTe	3·235	21·4	20·44	7	0·00149
UTe	3·080		17·73	6	0·09997

(1918) and an exponential function due to Born and Mayer (1932). The repulsive core potential proposed by Woodcock is 'harder' than the inverse power and exponential functions.

In order to remove many of the criticisms levelled at the earlier potential models (Thakur 1973, 1976b), a new logarithmic potential function has recently been suggested. This model is 'harder' than that proposed by Woodcock (1974) and has been found to give reliable values for the observed properties of ionic compounds (Thakur 1973, 1974a, 1974b, 1975a, 1975b, 1975c, 1976a, 1976b; Thakur and Pandey 1974, 1975). In this model the potential energy $\phi(r)$ of an ion pair interacting with each other and with the rest of the lattice is given by (Thakur 1976b)

$$\phi(r) = -AZ_1 Z_2 e^2 r^{-1} + P \operatorname{colog}(1 - pr^{-n}), \qquad (1)$$

where A is the Madelung constant, e is the electronic charge, P and p are potential parameters, Z_1 and Z_2 are the charges on the ions with r the distance between them, and n is the greatest positive integer for which p is positive, i.e. which satisfies

$$n < H/(AZ_1 Z_2 e^2 r_0^{m-3}) + 1. \qquad (2)$$

Here H and m are constants to be discussed in the next section and r_0 is the equilibrium interionic distance. The values of n thus obtained vary between 4 and 8, and are listed in Table 1 for different chalcogenide crystals. Also included in this table are the values of the parameters r_0 (from Kelly and Groves 1970) and β_0 used in the calculations.

Method of Calculation

The following relations (Thakur 1976a) have been suggested to correlate the compressibility β_0 and interionic distance r_0 for a particular group of ionic crystals:

$$C_1' = \tfrac{1}{3}[d(\ln \beta_0)/d(\ln r_0)]_T, \qquad K'\beta_0 = r^{3C_1'}, \qquad (3a,b)$$

where C_1' is the Moelwyn–Hughes parameter for the group and K' is a constant. In order to obtain the values of C_1' and K', log β_0 has been plotted in Fig. 1 against log r_0, from the available data of Huggins and Sakamoto (1957) for 20 crystals. It is found that points for crystals with the same structure tend to fall on a straight line, similar to the result for alkali halides (Thakur 1976a). The values of C_1' and K' obtained from the slope and intercept of this line respectively are, for β_0 in units of 10^{-12} Pa^{-1} and r_0 in 10^{-1} nm:

$$C_1' = 0 \cdot 968, \quad K' = 1 \cdot 4791 \qquad \text{for f.c.c. structure;}$$

$$C_1' = 0 \cdot 85, \quad K' = 1/1 \cdot 4125 \quad \text{for zinc blende structure.}$$

From the general regularity of the curves in Fig. 1 it is assumed that the same values of C_1 and K' hold for all 45 chalcogenide crystals considered here.

From the above results for C_1' and K', values of β_0 were computed for all the crystals from equation (3b) using the known accurate values of r_0 given by Kelly and Groves (1970). The resulting values of β_0 are compared in Table 1 with data of Huggins and Sakamoto (1957), where available.
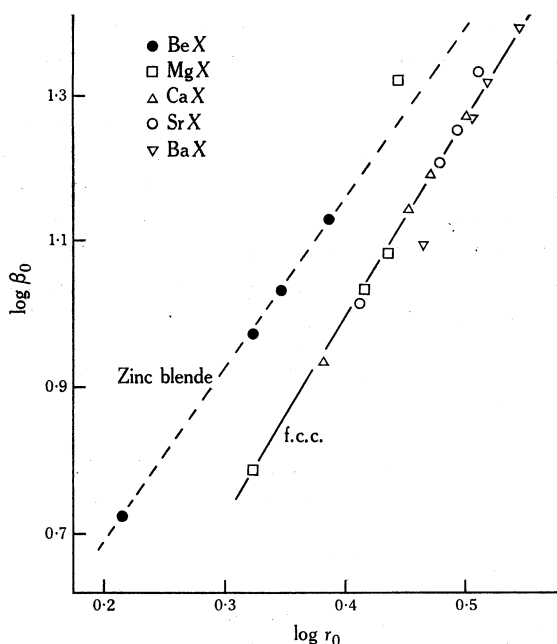
Fig. 1. Plot of $\log \beta_0$ against $\log r_0$ for alkaline earth chalcogenide crystals with f.c.c. and zinc blende structures.

In order to calculate the values of the potential parameters P and p, the following conditions (Thakur 1976a) were imposed on equation (1)

$$\phi'(r_0) = 0, \qquad \phi''(r_0) = Hr_0^{-m}. \tag{4}$$

In these equations the primes denote derivatives with respect to r, $H = 9k_1 K'$ and $m = 3C_1' - 1$, k_1 being the crystal structure constant, which is 2 for f.c.c. lattices. Application of the conditions (4) to equation (1) yields the following expressions for the potential parameters

$$P = \frac{AZ_1 Z_2 e^2}{r_0} \frac{(r_0^n + p)}{np}, \qquad p = \frac{r_0^n \{Hr_0^{3-m} - (n-1)AZ_1 Z_2 e^2\}}{Hr_0^{3-m} + AZ_1 Z_2 e^2}. \tag{5}$$

The values of p thus obtained are listed in Table 1 in units of r_0^n. The physical significance of p has been discussed in an earlier paper (Thakur 1976b).

Thus having defined the potential completely we can now proceed to compute the properties of all 45 chalcogenide crystals.

Results

Force Constant, I. R. Absorption Frequency and Debye Temperature

Following Krishnan and Roy (1951), the force constant f is defined as

$$f = \tfrac{1}{3}\big(\psi''(r_0) + 2r_0^{-1}\psi'(r_0)\big), \tag{6}$$

where $\psi(r)$ is the non-Coulombic part of $\phi(r)$. The i.r. absorption frequency v_0 is given by

$$v_0 = \tfrac{1}{2}\pi^{-1}(f/m)^{\frac{1}{2}}, \tag{7}$$

where m is the reduced mass. Once a value of v_0 is known, it is possible to compute the values of the Debye temperature Θ_D from the relation

$$\Theta_D = hv_0/k, \tag{8}$$

where h is Planck's constant and k Boltzmann's constant. The values of f, v_0 and Θ_D so obtained are reported in Table 2a together with the values derived by Thakur (1974a), Thakur and Pandey (1975) and Huggins and Sakamoto (1957) for comparison.

Crystal Energies

The cohesive energy W per mole is related to the potential function $\phi(r)$ by

$$W = -\left(N\phi(r_0) + \varepsilon\right), \tag{9}$$

where N is Avogadro's number and ε is the zero-point energy. The values obtained for W using equations (1) and (9) are given in Table 2b. Experimental data for these crystals are not available, but the cyclic values compiled by Rossini *et al.* (1952) and Waddington (1959) are included in Table 2b for comparison. The values of the zero-point energy ε used in the calculation of W were obtained from the Debye temperature data of Table 2a by the relation

$$\varepsilon = \tfrac{9}{8}k\Theta_D. \tag{10}$$

The atomization energy E_a of ionic crystals is of much interest, since it gives a better idea of the stability of the crystals than the cohesive energy. Only a few theoretical and experimental attempts have been made to estimate E_a for some of these crystals (Sanderson 1967; Sinha and Thakur 1974; Thakur 1974a; Thakur and Pandey 1975). Values of E_a for a particular ionic crystal AB may also be computed from the interaction potential energy functions by the relation

$$E_a = W - E - I, \tag{11}$$

where E is the electron affinity for forming B^{2-} ions and I is the ionization energy to produce A^{2+} ions. In the present calculations the values of I have been taken from Massey (1972) and those of E from Ladd and Lee (1963, 1965); the values of E in kJ mol^{-1} are: $O^{2-} = 715 \cdot 5$, $S^{2-} = 418$, $Se^{2-} = 490$ and $Te^{2-} = 406$.

The computed values of E_a from equation (11) are listed in Table 2b together with the available data of Sanderson (1967) and Thakur and Pandey (1975).

Grüneisen, Anderson–Grüneisen and Moelwyn–Hughes Parameters

The Gruneisen parameter γ is related to $\phi(r)$ by

$$\gamma = -\tfrac{1}{6}r_0\,\phi'''(r_0)/\phi''(r_0), \tag{12}$$

and the present computed values of γ from equations (1) and (12) are given in Table 2b. The Anderson–Grüneisen parameter δ was calculated using Chang's (1967) expression connecting γ and δ, which was derived on the basis of Dugdale and Macdonald's (1953) formula relating γ to the change of compressibility with volume. The results are also given in Table 2b.

Table 2. Calculated properties of chalcogenide crystals

(a) *Force Constant* f, *I.R. Absorption Frequency* v_0 *and Debye Temperature* Θ_D

Chalcogenide crystal	f (10^4 N m^{-1})		v_0 (10^{12} Hz)			Θ_D (K)	
	Present	Calc.[A]	Present	Calc.[A]	Est.[B]	Present	Calc.[A]
Oxides							
BaO	11·6	12·0	12·5	11·6	7	599	555
CaO	16·7	16·5	14·9	14·9	12	716	713
CdO	17·5		13·8			662	
CoO	21·0		16·1			775	
FeO	20·7		15·9			765	
MgO	21·5	21·4	18·4	18·4	16	886	882
MnO	19·3		15·4			741	
NbO	21·5		15·6			746	
NiO	21·9		15·6			751	
SrO	14·6	18·7	12·8	14·5	9	616	696
TaO	19·5		14·7			707	
TiO	21·8		16·7			800	
UO	16·0		12·8			612	
ZrO	18·1		14·2			683	
Selenides							
BaSe	9·1	6·8	5·3	4·6	4	253	219
CaSe	11·2	8·1	8·0	6·8	7	385	327
CeSe	11·0		5·8			277	
LaSe	11·0		5·7			274	
MgSe	13·2	18·4	10·4	12·3	10	499	590
MnSe	13·2		7·9			378	
PbSe	10·5		5·3			254	
SnSe	10·9		5·1			246	
SrSe	10·2	7·5	6·1	5·2	5	294	252
ThSe	11·4		5·4			261	
USe	11·9		5·5			265	
Sulphides							
BaS	9·7	6·6	7·4	6·2	5	355	299
CaS	12·1	15·7	6·4	11·6	8	309	556
CeS	11·8		8·3			398	
LaS	11·5		8·2			394	
MgS	14·4	19·0	12·6	14·5	13	605	696
MnS	19·3		12·1			579	
PbS	11·2		6·8			327	
SrS	10·9	14·1	8·4	9·6	7	404	459
ThS	12·2		8·1			390	
US	13·0		8·4			402	
ZrS	14·1		9·5			457	
Tellurides							
BaTe	8·2	6·4	4·4	4·8	4	209	184
BiTe	9·5		4·3			205	
CaTe	9·9	9·9	6·3	6·3	6	301	303
CeTe	9·8		4·7			227	
LaTe	9·7		4·7			226	
PbTe	9·5		4·3			206	
SnTe	10·0		5·0		6·3	4	239	209
SrTe	9·5	6·4	5·3	6·3	4	253	209
UTe	10·4		4·4			210	

[A] Calculated results from Thakur (1974a) for the oxides and from Thakur and Pandey (1975) for the other compounds.
[B] Estimated values from Huggins and Sakamoto (1957).

Table 2 (*Continued*)

(*b*) *Cohesive Energy* W, *Atomization Energy* E_a, *Grüneisen Parameter* γ, *Anderson–Grüneisen parameter* δ *and Moelwyn–Hughes parameter* C_1

Chalcogenide crystal	W (kJ mol^{-1}) Present	W (kJ mol^{-1}) Cyclic[c]	E_a (kJ mol^{-1}) Present	E_a (kJ mol^{-1}) Exp.[D]	γ Present work	δ Present work	C_1 Present work
Oxides							
BaO	3160		976	979[c]	1·78	3·56	4·56
CaO	3360		907	1060[c]	1·62	3·24	4·24
CdO	3420	3780[a]	210		1·58	3·16	4·16
CoO	3610	3990[a]	495		1·63	3·26	4·26
FeO	3600	3920[a]	560		1·64	3·28	4·28
MgO	3660		753	996[c]	1·61	3·22	4·22
MnO	3490	3810[a]	545	912[c]	1·68	3·36	4·36
NbO	3660		896		1·61	3·22	4·22
NiO	3690	4080[a]	483		1·60	3·20	4·20
SrO	3160		831	1000[c]	1·76	3·52	4·52
TaO	3500		464		1·69	3·38	4·38
TiO	3670	3880[a]	995		1·59	3·18	4·18
UO	3290				1·66	3·32	4·32
ZrO	3480		837		1·55	3·10	4·10
Selenides							
BaSe	2630	2760[b]	668	690[c]	1·87	3·74	4·74
CaSe	2860	3030[b]	636		1·82	3·64	4·64
CeSe	2830		524		1·85	3·70	4·70
LaSe	2800		662		1·87	3·74	4·74
MgSe	3010	3340[b]	334	552[c]	1·85	3·70	4·70
MnSe	3010	3300[a]	297		1·85	3·70	4·70
PbSe	2880		224		2·02	4·04	5·04
SnSe	2810		202		1·86	3·72	4·72
SrSe	2730	2900[b]	625	644[d]	1·93	3·86	4·86
ThSe	3170				1·80	3·60	4·60
USe	2930				1·76	3·52	4·52
Sulphides							
BaS	2670		782	714[d]	1·99	3·98	4·98
CaS	2950		802	895	1·74	3·48	4·48
CeS	2910		662		1·77	3·54	4·54
LaS	2890		825		1·79	3·58	4·58
MgS	3140		531	715[d]	1·76	3·52	4·52
MnS	3390	3350[a]	746	761[c]	1·69	3·40	4·40
PbS	2740	3090[a]	153		1·62	3·24	4·24
SrS	2810		780	837[d]	1·86	3·72	4·72
ThS	2960				1·73	3·46	4·46
US	3000				1·86	3·72	4·72
ZrS	3110		770		1·78	3·56	4·56
Tellurides							
BaTe	2500		622	554[d]	2·02	4·04	5·04
BiTe	2640				2·02	4·04	5·04
CaTe	2690		547	664[d]	1·98	3·96	4·96
CeTe	2580		364		1·74	3·48	4·48
LaTe	2660		610		2·00	3·99	4·99
PbTe	2650		79		2·01	4·02	5·02
SnTe	2700		173		1·96	3·92	4·92
SrTe	2670		653	621[d]	1·84	3·68	4·68
UTe	2760				1·94	3·82	4·82

[c] Cyclic results from (a) Wadington (1959) and (b) Rossini *et al.* (1952).
[D] Experimental results from (c) Sanderson (1967) and (d) Thakur and Pandey (1975).

The values of the Moelwyn–Hughes parameter C_1 have been calculated for the potential (1) using the relation (Thakur 1975d)

$$C_1 = 1 - (r_0^3 \beta_0/27 V)\phi'''(r_0).\tag{13}$$

(It should be noted that the Moelwyn–Hughes parameter C_1 was previously referred to as the Rao–Keer constant.)

Unfortunately there are no experimental data for γ, δ or C_1 available in the literature with which the results in Table 2b can be compared.

Discussion

The presently available information on chalcogenide crystals is far from complete, but this paper adds a little to the physics of these crystals by predicting the values of the parameters $\beta_0, f, \nu_0, \Theta_D, W, E_a, \gamma, \delta$ and C_1. Where comparisons can be made, the computed values are found to be in fair agreement with the previous data.

Many previous workers have made attempts to obtain values of β_0 both theoretically and experimentally, but their results are conflicting (Huggins and Sakamoto 1957) and, moreover, are only available for some of the alkaline earth chalcogenides. The present computed values of β_0 are in satisfactory agreement with the few results of Huggins and Sakamoto (1957) and it is expected that the remaining values should be a reliable guide in the absence of further data.

Since experimental values of f, ν_0 and Θ_D are not available, the present results have been compared here with the theoretical values of Thakur (1974a) and Thakur and Pandey (1975) and the estimated values of Huggins and Sakamoto (1957). The overall agreement is reasonable. Because the frequency spectrum and consequently the Debye temperature of a solid is dependent upon the relative masses of the vibrating ions, the Θ_D values for these crystals have been plotted against their reduced masses in Fig. 2. The compounds have been grouped on the basis of their anions. The nature of the plot is similar to that for the alkali metal halides (Thakur and Thakur 1976). It is found that all members of a group tend to fall on a straight line, this regularity being most pronounced for the telluride group; the crystal groups in order of regularity are ATe, AO, ASe and AS. It is seen that the effect of the reduced mass on the Θ_D value is more pronounced for the lighter chalcogenide ions (O^{2-}, S^{2-}) as the mass of the cation increases, and thus the absolute value of the slope decreases as we pass from oxide to telluride group. These curves may be useful for checking Θ_D data where other information is not available.

The computed values of W listed in Table 2b are about 10% smaller than the cyclic values of Waddington (1959) and Rossini $et\ al.$ (1952), except for MnS. This probably indicates that van der Waals terms should be included in equation (1). It is found that the cohesive energy of a particular cation A varies in general as AO > AS > ASe > ATe. There is only one exception to this: the value of W for PbSe is greater than that for PbS.

The present values of E_a compare satisfactorily with the experimental data although, except for BaS, BaTe and SrTe, the calculated results are smaller. This further suggests that inclusion of van der Waals terms in equation (1) would improve the agreement. Indeed the van der Waals energy is important for heavier crystals, but because of the lack of data for the relevant constants it was not possible to include them in the present calculations. However, a rough estimate of the van der Waals

energy can probably be made from the differences between the cyclic and calculated values of W in Table 2b or from the differences between the experimental and calculated values of E_a. These differences suggest that the contribution of the van der Waals energy could be about 10% of the total value of W.
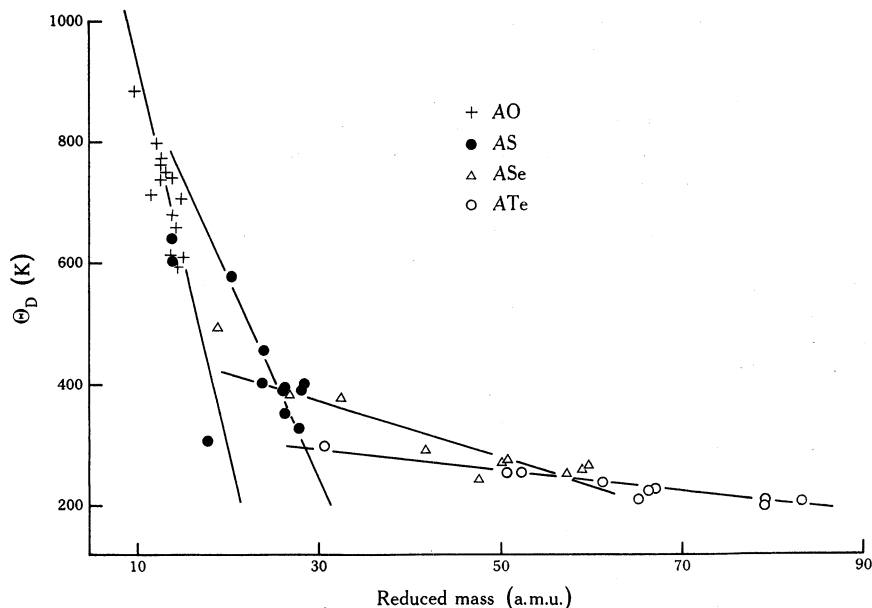

Fig. 2. Plot of the Debye temperature Θ_D against reduced mass for the chalcogenide crystals considered.

The calculated values of the Grüneisen parameter in Table 2b are seen to lie in a narrow band about $\gamma = 1.7$. There are no experimental data with which to draw comparison, but the present results indicate that γ depends upon the specific volume since the values tend to increase as we move from oxides to tellurides.

To summarize, the well-tested logarithmic potential energy model, when used with a method of calculation based on the Moelwyn–Hughes parameter, has been shown to yield encouraging results for chalcogenide crystals. Since previous methods cannot be applied in the absence of compressibility data, this model is expected to be useful for calculating the properties of a large number of such crystals.

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