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Moelwyn-Hughes Parameter of Some Diatomic Crystals

By K. P. Thakur

Department of Physics, S. P. College, Dumka-814101, *Bihar, India*

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The Moelwyn-Hughes parameter, $C_1=[\mathrm{d}(1/\beta)/\mathrm{d}P]_T$ and temperature derivative of adiabatic compressibility have been computed for f.c.c. and b.c.c. type ionic crystals with the central-force rigid-ion interaction model, and various methods of calculation. Some applications of the Moelwyn-Hughes parameter are discussed. An empirical relation between adiabatic compressibility and equilibrium internuclear distance of ionic crystals has been developed on the basis of the Moelwyn-Hughes parameter. The validity of this empirical relation has been tested for diatomic alkali halide crystals. The results obtained are encouraging.

Introduction

Anderson (1966) gave a physical interpretation of the constants occurring in the equation of the variation of Young's modulus of elasticity with temperature obtained by Wachtman, Tefft, Lam & Apstein (1961) from experimental observations. He showed that the constant b occurring in the Wachtman equation which can also be written as

$$B_s=B_{00}-bT\exp(-T_0/T) \tag{1}$$

is given by

$$b=3R\gamma\delta/v_0 \tag{2}$$

where γ is the Grüneisen parameter, B_s the adiabatic bulk modulus of elasticity, B_{00} the values of B_s at absolute zero and one atmosphere pressure, v_0 the average specific volume per atom at absolute zero, and δ another physical constant independent of temperature. Following Chang (1967), it is termed the Anderson–Grüneisen parameter and is given by

$$\delta=\frac{\mathrm{d}(\ln\beta_s)/\mathrm{d}T}{\mathrm{d}(\ln v)/\mathrm{d}T} \tag{3}$$

where β_s is the adiabatic compressibility.

Chang (1967) has also derived two simple expressions for δ in terms of γ, on the basis of the two independent relations between γ and the change of compressibility with volume (Slater, 1939; Dugdale & Macdonald, 1953). These expressions can be written:

$$\delta=2\gamma-\tfrac{2}{3} \tag{4}$$

$$\delta=2\gamma\,. \tag{5}$$

Das, Keer & Rao (1963), Rao & Keer (1962), and Rao, Keer & Das (1962, 1963, 1964) have reported values of the Rao–Keer (RK) constant $C_1=[\mathrm{d}(1/\beta)/\mathrm{d}P]_T$, where β is the isothermal compressibility coefficient, P the pressure, and T the absolute temperature, which relates intermolecular energy constants of nonpolar as well as polar liquids to their various physical properties. Keer (1972) has also shown that the same RK constant (C_1) is characteristic of solids. In spite of two characteristic parameters γ and δ of solids, it is still a third parameter. Consequently the calculations of RK constants were repeated by Thakur (1975*a*, 1975*b*) and Thakur & Pandey (1974*a*, 1975).

This RK constant was reported as early as 1951 by Moelwyn-Hughes (1951, 1964). Thus we propose to call C_1 the Moelwyn-Hughes parameter rather than the Rao–Keer constant. This parameter is merely the pressure derivative of the isothermal bulk modulus of elasticity at constant temperature.

From thermodynamic principles (Thakur & Pandey, 1974*a*) C_1 can be related to the potential function $\varphi(r)$

$$C_1=1-\frac{\beta r_0^3}{27v}\left[\varphi'''(r_0)-\frac{6}{r_0}\varphi''(r_0)\right] \tag{6}$$

where r_0 is the equilibrium interionic distance.

Following Chang (1967), the temperature derivative of compressibility may be related to C_1

$$\frac{\mathrm{d}(\ln\beta)}{\mathrm{d}T}=\alpha_v(C_1-1) \tag{7}$$

where α_v is the thermal coefficient of volume expansion.

In the present work the values of C_1 and $[\mathrm{d}(\ln\beta)/\mathrm{d}T]_P$ are reported by an independent method which gives other expressions for C_1 and $[\mathrm{d}(\ln\beta)/\mathrm{d}T]_P$ in terms of the derivatives of the interatomic potential energy functions. Two potential energy functions are used to compute two sets of these values and the results are compared with the values obtained from previous expressions. The utility of these parameters is also discussed.

Theoretical

The potential energy per ion pair of an ionic crystal can be written

$$\varphi(r)=-\frac{\alpha e^2}{r}+f(r) \tag{8}$$

where α is the Madelung constant, r the interionic distance and $f(r)$ includes the overlap repulsive and van der Waals terms.

In terms of volume, equation (8) may be written

$$F(v) = -\frac{\alpha e^2}{v^n} + f(v) \tag{9}$$

where $n = \frac{1}{3}$.

The adiabatic compressibility may be written (Grüneisen, 1912)

$$\beta_s = \beta_{00}(v/v_0)^{[n+2-x(n+1+w)]} \tag{10}$$

where

$$\beta_{00} = -\frac{v_0^{(n+1)} f'(v_0)}{n\alpha e^2[(n+1)f'(v_0) + v_0 f''(v_0)]} \tag{11}$$

$$w = [v_0(\gamma+2)f''(v_0) + v_0^2 f'''(v_0)]/[(\gamma+1)f'(v_0) + v_0 f''(v_0)] \tag{12}$$

and

$$x = [(\gamma+1)f'(v_0) + v_0 f''(v_0)]/[(n+1)f'(v_0) + v_0 f''(v_0)]\,. \tag{13}$$

Hence

$$\frac{\mathrm{d}(\ln\beta)}{\mathrm{d}T} = \alpha_v[n+2-x(n+1+w)] \tag{14}$$

or

$$\frac{\mathrm{d}(\ln\beta)}{\mathrm{d}T} = \alpha_v \times \left[\frac{(\gamma+1)f'(v_0) - v_0(\gamma+1)f''(v_0) - v_0^2 f'''(v_0) + \dfrac{7\alpha e^2(\gamma-n)}{9v_0^{(n+1)}}}{(\gamma+1)f'(v_0) + v_0 f''(v_0) + \alpha e^2(\gamma-n)/3v_0^{(n+1)}}\right] \tag{15}$$

where $f'(v)$, $f''(v)$ and $f'''(v)$ refer to the first, second and third derivatives of $f(v)$, respectively.

In the present investigation, two forms of the interatomic potential energy function have been used to evaluate C_1 and $[\mathrm{d}(\ln\beta)/\mathrm{d}T]_P$ for the f.c.c. and b.c.c. type of ionic crystals from equation (15).

These functions can be expressed in terms of volume as

(*a*) The logarithmic potential (Thakur, 1975*c*):

$$F(v) = -\frac{\alpha e^2}{v^n} - \frac{C}{v^{6n}} - \frac{D}{v^{8n}} + A\log\left[1 + \frac{B}{v^{6n}}\right] \tag{16}$$

(*b*) The Rydberg (1931) potential:

$$F(v) = -\frac{\alpha e^2}{v^n} + \lambda\exp(-bv^n) - \mu v^n \exp(-bv^n) \tag{17}$$

where A, λ, b, B, and μ are the potential parameters and the remaining terms have their usual meanings.

Equation (16) has been successfully used earlier (Thakur, 1973, 1974*a*, 1975*b*, *c*, *d*, *e*; Thakur & Pandey, 1974*b*, 1975). The Rydberg function has also been used (Varshni & Bloore, 1963; Sharma, 1970, 1973; Sharma & Jain, 1973; Mishra & Sharma, 1973).

Method of calculation

Two methods are available for calculating the potential parameters of equations (16) and (17). For a review of both methods, see Pandey (1970) and Kachhava & Saxena (1963). The first method enforces the crystal stability and compressibility conditions to evaluate the potential parameters. This method utilizes experimental compressiblity values at 0 K, which are found by extrapolation and are thus uncertain. The second method (Kachhava & Saxena, 1963) utilizes molecule stability and force constant conditions to evaluate the parameters B and b, and utilizes the crystal stability condition to evaluate A, λ and μ. Here the latter method has been used for the computation of the potential parameters, since it utilizes molecular constants known to a high degree of accuracy.

Values of γ occurring in equation (15) can be computed from

$$\gamma = -\frac{r_0}{6}\,\frac{\varphi'''(r_0)}{\varphi''(r_0)} \tag{18}$$

where $\varphi''(r)$ and $\varphi'''(r)$ are the second and third derivatives of $\varphi(r)$, respectively.

Table 1. *Values of* $[\mathrm{d}(\ln\beta)/\mathrm{d}T]_P$ *for alkali halide crystals* (*in* 10^{-5} deg^{-1})

Alkali halides	From equations (15) and (16)	From equations (15) and (17)	From equations (3), (4) and (16)	From equations (3), (4) and (17)	From equations (3), (5) and (16)	From equations (3), (5) and (17)	Fumi & Tosi (1964)	Huggins (1937)
LiCl	40·39	34·58	45·67	34·98	54·38	43·68	70	70
LiBr	46·03	37·05	52·05	33·45	61·95	43·35	80	80
LiI	46·16	32·49	49·72	33·96	60·42	43·66	50	80
NaCl	28·32	31·32	48·72	30·84	52·64	38·76	62	70
NaBr	39·96	40·02	43·96	31·99	51·99	40·51	41	80
NaI	43·63	38·02	48·82	36·86	58·32	46·37	10	80
KF	34·67	30·56	34·34	31·43	41·47	38·56	10	10
KCl	34·71	24·39	29·64	29·99	47·23	37·57	35	50
KBr	36·00	32·76	40·32	31·92	48·24	39·84	48	60
KI	27·54	34·83	70·61	33·75	79·98	42·66	34	60
RbCl	32·83	29·92	37·04	30·35	44·17	37·48	40	78
RbBr	34·77	31·12	39·10	31·81	46·63	39·33	38	80
RbI	38·44	33·15	42·70	33·54	51·21	41·05	46	80

Table 2. *Values of the Moelwyn-Hughes parameter* (C_1) *(dimensionless)*

Alkali halides	From equations (7), (15) and (16)	From equations (7), (15) and (17)	From equations (3), (4), (7) and (16)	From equations (3), (4), (7) and (17)	From equations (3), (5), (7) and (16)	From equations (3), (5), (7) and (17)	From equations (6) and (16)	From equations (6) and (17)	Mathur & Singh (1968)	Huggins (1937)	Experimental
LiF	4·01	3·92	4·37	1·95	5·03	2·61	7·03	4·61	10·7	13·07	
LiCl	4·06	3·62	4·46	3·65	5·12	4·31	7·12	6·31	6·3	5·81	
LiBr	4·07	3·47	4·47	3·23	5·13	3·89	7·13	5·89	6·1	5·64	
LiI	4·14	3·21	4·45	3·31	5·11	3·97	7·11	5·97	5·3	6·21	
NaF	–	–	–	–	–	–	–	–	8·7	8·29	
NaCl	3·36	3·61	5·06	3·57	5·72	4·23	7·72	6·23	5·3	5·77	6·61[a]
NaBr	4·02	3·77	4·37	3·48	5·03	4·14	7·03	6·14	5·3	5·02	
NaI	3·03	3·64	4·39	3·56	5·05	4·22	7·05	6·22	4·5	5·66	
KF	4·21	3·83	4·18	3·91	4·84	4·57	6·84	6·57	6·3	6·12	
KCl	4·02	3·21	4·45	3·61	5·11	4·27	7·11	6·27	5·4	4·83	
KBr	4·00	3·73	4·36	3·66	5·02	4·32	7·02	6·32	4·8	4·76	
KI	3·04	3·58	6·23	3·50	6·89	4·16	8·89	6·16	4·0	4·30	
RbF	4·50	–	4·49	–	5·15	–	7·15	–	4·6	5·12	
RbCl	4·04	3·77	4·43	3·81	5·09	4·47	7·09	6·47	2·8	4·51	5·48[b]
RbBr	4·05	3·73	4·43	3·79	5·09	4·45	7·09	6·45	2·9	4·41	5·43[b]
RbI	3·98	3·57	4·31	3·60	4·97	4·26	6·97	6·26	2·3	4·50	5·52[b]
CsF	4·15	–	4·65	–	5·31	–	7·31	–	–	–	–
CsCl	4·11	4·05	4·58	4·38	5·24	5·04	7·24	7·04	4·7	5·71	
CsBr	3·72	3·49	3·67	3·84	4·33	4·50	6·33	6·50	–	–	
CsI	2·73	3·68	3·78	3·68	4·42	4·34	6·42	6·34	–	–	

[a]Overton (1962), [b]Chang & Barsch (1971).

The values of r_e, r_0, k_e, $F(v_0)$ and β_0 were taken from Pandey (1970), D_i from Rittner (1951) and α_v from Keer (1972).

Values of $[\mathrm{d}(\ln\beta)/\mathrm{d}T]_P$ and C_1 obtained from the various expressions are reported in Tables 1 and 2, together with values reported by Fumi & Tosi (1964), Huggins (1937), and Mathur & Singh (1968). The most reliable experimental values of C_1 are due to Chang & Barsch (1971) and Overton (1962) whose reported values obtained from the ultrasonic pulse superposition technique are accurate to within ±0·07. Their values for NaCl, RbCl, RbBr and RbI are also listed in Table 2.

Importance of the Moelwyn-Hughes parameter (C_1)

C_1 is of importance in studying the macroscopic behaviour of solids as well as polar and non-polar liquids. It is given by (Moelwyn-Hughes, 1964)

$$C_1=\left[\frac{\mathrm{d}(1/\beta)}{\mathrm{d}P}\right]_T=\left[\frac{\mathrm{d}(1/\beta)}{\mathrm{d}v}\,\frac{\mathrm{d}v}{\mathrm{d}P}\right]_T=-\left[v\beta\frac{\mathrm{d}(1/\beta)}{\mathrm{d}v}\right]_T$$

$$=-\left[\frac{\beta r}{3}\,\frac{\mathrm{d}(1/\beta)}{\mathrm{d}r}\right]_T=\left[\frac{\beta r}{3\beta^2}\,\frac{\mathrm{d}\beta}{\mathrm{d}r}\right]_T=\tfrac{1}{3}\left[\frac{\mathrm{d}(\ln\beta)}{\mathrm{d}(\ln r)}\right]_T \tag{19}$$

where $v=k_1r^3$ and k_1 is the crystal structure constant.

Thus from equation (19) the plot of $\ln\beta$ against $\ln r$ for a particular crystal should be a straight line with slope $3C_1$. No experiment has, as yet, been carried out to find the value of the compressibility for different values of the internuclear distance in a crystal. From equation (19) it is possible to compute the value of the compressibility at any particular value of the internuclear distance r. Integrating equation (19) one gets

$$\ln\beta+\ln K=3C_1\ln r \tag{20}$$

or

$$\beta K=r^{3C_1} \tag{21}$$

where $\ln K$ is the constant of integration which can be computed from the equilibrium conditions *i.e.* at $r=r_0$, $\beta=\beta_0$ and thus $K=r_0^{3C_1}/\beta_0$. For NaCl, $r_0=2{\cdot}82$ Å, $\beta_0=3{\cdot}97\times10^{-12}$ bar^{-1} and $C_1=6{\cdot}614$, thus $K=2{\cdot}1538\times10^{20}$. β has been plotted against r for NaCl in Fig. 1 according to equation (21). Fig. 1 also includes the single experimental point for NaCl. It is seen that β decreases very slowly as r is decreased from the equilibrium internuclear distance (r_0), but increases very quickly with increase of r above r_0. β is nearly zero at $r\leq2{\cdot}2$ Å. The curve predicts that it is possible to reduce the internuclear distance from $r=r_0$ to $r=2{\cdot}2$ Å by compression, a conclusion which will be of interest to experimental workers who wish to investigate these crystals at internuclear distances other than the equilibrium.

We have plotted $\ln\beta_0$ against $\ln r_0$ for the alkali halides in Fig. 2, which shows that all the members of a particular alkali metal fall on a straight line. This regularity is most pronounced for Li, Na, K, and Rb. For Cs one point, CsF, is away from the line, owing to its different crystal structure. It is found that the absolute value of the slope of the curves in Fig. 2 is nearly the same for all the groups. This regularity in the values of ln β_0 gives a ready check for incorrect data and can help to predict the value of β_0 for any member of a group for which data are not available. Moreover, the nature of the curve for any other group may also be predicted. This regularity may help to correct the highly uncertain data of heavy metal halides and alkaline earth chalcides.

Since the plot of ln β_0 against ln r_0 is a straight line for a particular group of alkali halides, we suggest the following equation, similar to equation (19)

$$C'_1=\tfrac{1}{3}\left[\frac{\mathrm{d}(\ln\beta_0)}{\mathrm{d}(\ln r_0)}\right]_T \tag{22}$$

where C'_1 is another constant.

Analogous to equation (21) for one crystal, we get, after integrating equation (22), the following relation between β_0 and r_0 for a group of crystals

$$K'\beta_0=r_0^{3C'_1} \tag{23}$$

where K' is a constant which is different for different groups. Values of C'_1 and K' obtained from Fig. 2 are reported in Table 3, which shows that the values of C'_1 and K' are nearly the same for crystals of f.c.c. structure, while for crystals of b.c.c. structure, K' is slightly greater and C'_1 smaller. Taking the mean of K' and C'_1 from Table 3 for f.c.c. structures we have plotted β_0 against r_0 in Fig. 3 according to equation (23). It is found that all 16 experimental points are close to the theoretical curve. Thus equation (23) may be used for the computation of β_0 for those crystals for which r_0 is known.

Table 3. *Values of K' and C'_1 of alkali halide crystals*

Crystal group	K'	C'_1
f.c.c.		
LiX	8·511	1·107
NaX	10·839	1·159
KX	10·351	1·118
RbX	10·965	1·123
b.c.c.		
CsX	12·162	1·053

As discussed above, two methods are available for calculating the potential parameters of a function $\varphi(r)$. The first method enforces the following crystal stability and compressibility conditions:

$$\varphi'(r_0)=0 \tag{24}$$

$$\varphi''(r_0)=\frac{9k_1r_0}{\beta_0} \tag{25}$$

where $\varphi'(r)$ refers to the first derivative of $\varphi(r)$.

From equations (23) and (25)

$$\varphi''(r_0)=\frac{9k_1K'}{r_0^{(3C'_1-1)}}=\frac{H}{r_0^m} \tag{26}$$

where $H=9k_1K'$ and $m=(3C'_1-1)$, and k_1 is the crystal structure constant; which is 2 for the NaCl and 1·5 for the CsCl structure.

Thus, if reliable compressibility data is lacking, we suggest the use of equations (24) and (26) for the computation of the parameters of the potential energy functions.

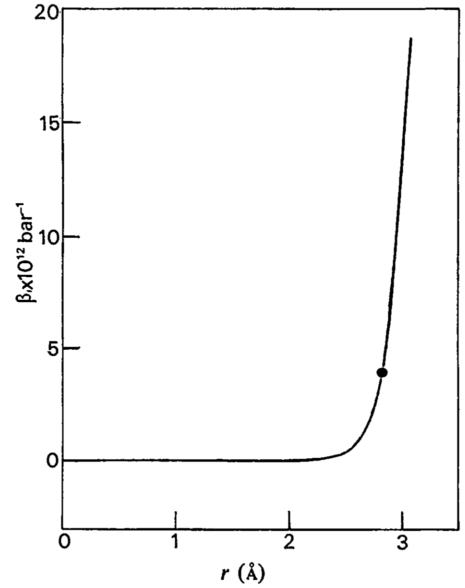

Fig. 1. Variation of compressibility with internuclear distance of NaCl crystal.

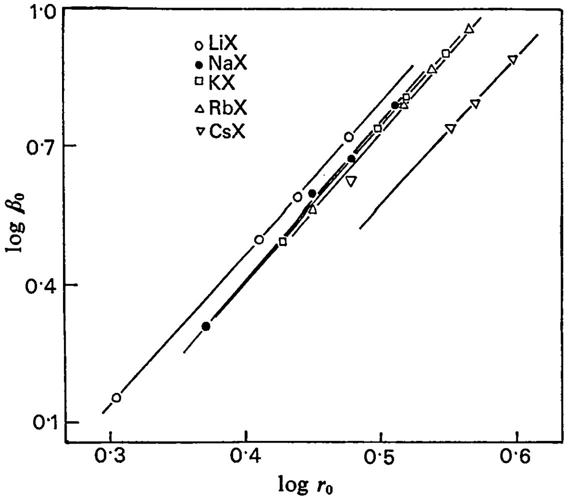

Fig. 2. Plot of log β_0 against log r_0 for alkali halide crystals.

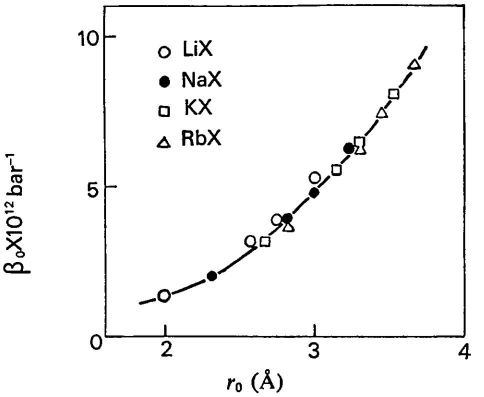

Fig. 3. Variation of compressibility (β_0) with internuclear distance (r_0) according to equation (23) for f.c.c. crystals together with the experimental points.

Following Moelwyn-Hughes (1964) it is also possible to compute the sum of the exponents ($m'+n$) of the Mie (1903) potential, which has been applied to a variety of physicochemical systems, by the relation

$$m'+n=3(C_1-2)\,.$$

References

Anderson, O. L. (1966). *Phys. Rev.* **144**, 553–557.

Chang, Y. A. (1967). *J. Phys. Chem. Solids*, **28**, 697–701.

Chang, Z. P. & Barsch, G. R. (1971). *J. Phys. Chem. Solids*, **32**, 27–40.

Das, C. D., Keer, H. V. & Rao, R. V. G. (1963). *Z. Phys. Chem.* **224**, 377–383.

Dugdale, J. S. & MacDonald, D. K. C. (1953). *Phys. Rev.* **89**, 832–834.

Fumi, F. G. & Tosi, M. P. (1964). *J. Phys. Chem. Solids*, **25**, 31–43.

Grüneisen, E. (1912). *Ann. Phys.* **39**, 257–284.

Huggins, M. L. (1937). *J. Chem. Phys.* **5**, 143–148.

Kachava, C. M. & Saxena, S. C. (1963). *Phil. Mag.* **8**, 1429–1432.

Keer, H. V. (1972). *Z. Phys. Chem.* **251**, 22–26.

Mathur, V. K. & Singh, S. P. (1968). *J. Phys. Chem. Solids*, **29**, 959–962.

Mie, G. (1903). *Ann. Phys.* **11**, 657–675.

Mishra, K. D. & Sharma, M. N. (1973). *Z. Phys. Chem. N. F.* **83**, 188–199.

Moelwyn-Hughes, E. A. (1951). *J. Phys. Chem.* **55**, 1246–1254.

Moelwyn-Hughes, E. A. (1964). *Physical Chemistry*, 2nd revised ed., p. 330. London: Pergamon Press.

Overton, W. C. (1962). *J. Chem. Phys.* **37**, 116–119.

Pandey, J. D. (1970). *Z. Phys. Chem.* **243**, 221–224.

Rao, R. V. G. & Keer, H. V. (1962). *Z. Phys. Chem.* **219**, 321–331.

Rao, R. V. G., Keer, H. V. & Das, C. D. (1962). *Z. Phys. Chem.* **220**, 71–78.

Rao, R. V. G., Keer, H. V. & Das, C. D. (1963). *Indian J. Phys.* **37**, 238–240.

Rao, R. V. G., Keer, H. V. & Das, C. D. (1964). *Indian J. Chem.* **2**, 27–28.

Rittner, E. S. (1951). *J. Chem. Phys.* **19**, 1030–1035.

Rydberg, R. (1931). *Z. Phys.* **73**, 376–394.

Sharma, M. N. (1970). *J. Chem. Phys.* **52**, 3846–3847.

Sharma, M. N. (1973). *Z. Phys. Chem. N. F.* **85**, 86–90.

Sharma, M. N. & Jain, R. (1973). *J. Phys. Soc. Japan*, **35**, 194–198.

Slater, J. C. (1939). *Introduction to Chemical Physics.* New York: McGraw-Hill.

Thakur, K. P. (1973). *Indian J. Pure Appl. Phys.* **11**, 549–551.

Thakur, K. P. (1974*a*). *Indian J. Chem.* **12**, 376–378.

Thakur, K. P. (1974*b*). *J. Inorg. Nucl. Chem.* **36**, 2171–2173.

Thakur, K. P. (1975*a*). *Z. Phys. Chem.* **256**, 529–530.

Thakur, K. P. (1975*b*). *Acta Cryst.* A**31**, 540–542.

Thakur, K. P. (1975*c*). *Austr. J. Phys.* in the press.

Thakur, K. P. (1975*d*). *Curr. Sci. India*, **44**, 45–46.

Thakur, K. P. (1975*e*). *Acta Phys. Polonica*, A**48**, 419–421.

Thakur, K. P. & Pandey, J. D. (1974*a*). *Indian J. Pure Appl. Phys.* **12**, 779–781.

Thakur, K. P. & Pandey, J. D. (1974*b*). *J. Chim. Phys.* **71**, 850–853.

Thakur, K. P. & Pandey, J. D. (1975). *J. Inorg. Nucl. Chem.* **37**, 645–649.

Varshni, Y. P. & Bloore, F. J. (1963). *Phys. Rev.* **129**, 115–121.

Wachtman, J. B. Jr, Tefft, W. E., Lam, D. G. Jr & Apstein, C. S. (1961). *Phys. Rev.* **122**, 1754–1759.