

The analysis of thermal and elastic behaviour of mixed alkali halide systems using Rydberg potential

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Abstract: The thermal and elastic behaviour of mixed alkali halide systems of NaBr-NaCl, KBr-KCl and KI-KBr have been studied employing the Rydberg potential extending upto next nearest neighbours and including the van der Waals interactions. The isothermal bulk modulus (B_T), the first and second order pressure derivatives (dB_T/dP and d^2B/dP^2) of isothermal bulk modulus of these systems have been calculated. Computations have further been extended to predict the Gruneisen parameter (γ) and mode Gruneisen parameter (q) using Slater, Dugdale and McDonald and Free Volume theories. The results are discussed with the available interpolation of experimental data.

Keywords: Mixed alkali halides, Rydberg potential, pressure derivatives of bulk modulus, Gruneisen parameter, mode Gruneisen parameter.

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1. Introduction

Mixed crystals or solid solutions owe their scientific and technological importance because of the fact that most of the physical properties they exhibit differ significantly from their parent crystals (Kamiyoshi and Nigara 1971, Subbarao and Haribabu 1980). The fact that the microhardness of mixed alkali halide crystals is much greater than that for the pure or component crystals, makes them very suitable materials for use in laser windows. One of the striking behaviours of mixed crystals of alkali halides is the appearance of a first order Raman spectrum which remains totally absent in the component pure crystals. A considerable amount of work regarding the physical properties of mixed crystals has been done during last few decades. An up-to-date survey on the physical properties of mixed crystals of alkali halides has recently been presented by Sirdeshmukh and Shrinivas (1986). There have been several attempts (Kamiyoshi and Nigara 1971, Ferraro *et al* 1970 and Varotsos 1980) to study the physical properties of mixed

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crystals through experiments but theoretical approach based on inter-ionic potential has been quite scanty. The inter-ionic potential model adopted by Fancher and Barsch (1969) is very simple as it considers only the overlap repulsion between nearest neighbours and completely ignores the van der Waals interactions. Such a crude model does not yield with high precision the values of cohesive energy even for pure alkali halide crystals (Tosi 1964, Shanker *et al* 1980 and Jain 1983). Several potential functions for short range overlap repulsion have been proposed to explain the various thermodynamic and lattice dynamical properties of the ionic crystals (Tosi 1964, Catlow *et al* 1977, Sangster and Atwood 1978, Shanker and Kumar 1987) in addition to the classical rigid ion approach (Born and Huang 1954).

Rydberg (1931) proposed a short range potential function of the form

$$\phi(r) = \lambda \exp(-r/\rho) - \mu r \exp(-r/\rho) \quad (1)$$

where, r is the inter-ionic separation at no external pressure, λ and μ are the constants and ρ representing the softness parameter for a given diatomic crystal, in order to explain the cohesive energy of metals. Rydberg potential which remained ignored for a pretty long time differs from all other conventional forms in the sense that it not only assumes the repulsive interaction due to the overlap of orbital electrons when compressed but also accounts for the attractive interaction arising from the mutual interaction of the nucleus of one ion with the orbital electrons of the other ion as pointed out by Dick and Overhauser (1958). Gupta and Agrawal (1982) have recently, reviewed Rydberg potential to explain a few properties of alkali halides, constraining the potential only upto nearest neighbour contribution and omitting the contribution of van der Waals interaction. Gupta and Sipani (1990a) extended this potential upto next nearest neighbour contributions taking into account the three-body interactions and van der Waals dipole-dipole and dipole-quadrupole interaction to study the various thermal and elastic properties of pure alkali halide crystals. The method of evaluation and the values of the constants λ , μ and ρ appearing in eq. (1) are given in detail in our earlier work (Gupta and Sipani 1990a) and therefore, need not be repeated. Sipani and Gupta (1990b) in their recent communication, have extended the applicability of Rydberg potential to study the volume dependence of dielectric constant of alkali halide crystals.

In the present work, we have examined the applicability of Rydberg potential to predict the various thermal and elastic properties of the alkali halide mixed crystals extending it upto next nearest neighbours and including the van der Waals contributions. The mathematical details of the theory are given in Section 2 and the results are discussed in Section 3 of the paper.

2. Theory

The pseudo unit cell model (Chang and Mitra 1968) for mixed crystals assumes complete randomization of ions and treats all unit cells in the mixed crystal identical. For a mixed crystal of AB and AC mixed in the molar proportions of x and $(1-x)$ respectively, the pseudo unit cell model, maintains its symmetry and contains two atoms, one of A and the other of a complex hypothetical atom $x\text{B}+(1-x)\text{C}$. X-ray diffraction measurements on mixed crystals do indeed confirm unique unit cell dimensions throughout the composition range (Ferraro *et al* 1971 and Shrinivas and Sirdeshmukh 1986). The expression of lattice energy of the pseudo unit cell as a mixed crystal can be written as

$$\psi(r) = -\frac{\alpha_M Z^2 e^8}{r} + \phi_M(r) - \frac{x C_{AB} + (1-x) C_{AC}}{r^6} - \frac{S_{--} \sqrt{x(1-x)} C_{BC}}{r^6} - \frac{x D_{AB} + (1-x) D_{AC}}{r^6} - \frac{T_{--} \sqrt{x(1-x)} D_{BC}}{r^6} \quad (2)$$

where, the first term on the right hand side of eq. (2) represents the Madelung energy, the fourth and sixth terms represent the van der Waals dipole-dipole and dipole-quadrupole interactions between the two different anions B and C respectively. C_{BC} and D_{BC} can be taken as the geometric mean of C_{BB} and C_{CC} and D_{BB} and D_{CC} . S_{--} and T_{--} represent the appropriate lattice sums in NaCl structure and are given in Tosi (1964). C_{AB} , C_{AC} and D_{AB} , D_{AC} are the dipole-dipole and dipole-quadrupole van der Waals coefficients for the component crystals respectively. r is the nearest neighbour (cation-anion) distance of the mixed crystal calculated from Vegard's law (Vegard 1921)

$$r = x r_1 + (1-x) r_2. \quad (3)$$

Zen (1956) pointed out that if the difference between r_1 and r_2 is very small, eq. (3) is indistinguishable from Retger's rule. We have however, calculated the values of r from eq. (3) ignoring the Retger's rule as the later applies strictly to an ideal crystal where the volumes are assumed to be additive. $\phi_M(r)$, representing the short-range potential function for a mixed system can be written as

$$\phi_M(r) = x \phi_{AB}(r) + (1-x) \phi_{AC}(r) \quad (4)$$

where, $\phi_{AB}(r)$ and $\phi_{AC}(r)$ are the repulsive potential function for pure or component crystals A^+B^- and A^+C^- respectively.

Rydberg's short-range repulsive interaction for a pure alkali halide crystal extended upto second neighbours can be written as

$$\begin{aligned} \phi(r) = n_1 \left[\lambda \exp \left(\frac{r_+ + r_- - r}{\rho} \right) - \mu r \exp \left(\frac{r_+ + r_- - r}{\rho} \right) \right] \\ + \frac{n_2}{2} \left[\lambda \exp \left(\frac{2r_+ - r'}{\rho_+} \right) - \mu r' \exp \left(\frac{2r_+ - r'}{\rho_+} \right) \right] \\ + \frac{n_2}{2} \left[\lambda \exp \left(\frac{2r_- - r'}{\rho_-} \right) - \mu r' \exp \left(\frac{2r_- - r'}{\rho_-} \right) \right] \quad (5) \end{aligned}$$

where n_1 and n_2 are the coordination numbers being $n_1=6$ and $n_2=12$ for NaCl structure, r is the inter-ionic separation and r' is the next nearest neighbour distance. The values of r_+ and r_- , the cation and anion radii respectively, have been taken from Sysio (1969), λ and μ are constants. The parameters λ , μ and ρ can be evaluated by the method given in Gupta and Agrawal (1982). The values of the softness parameter ρ obey the additivity rule (Shanker and Kumar 1987)

$$\rho = \rho_+ + \rho_- \tag{6}$$

Following Born and Huang (1954), the short-range force constant A can be written as

$$A = \frac{1}{8} \left[\phi''(r) + \frac{2}{r} \phi'(r) \right] = 3krB_x \tag{7}$$

where $k=2$ for NaCl structure.

Definition of the isothermal bulk modulus provides

$$B_x = -VP' \tag{8}$$

which on differentiation with respect to P yields

$$\frac{dB_x}{dP} = -1 - V \frac{P''}{P'} \tag{9}$$

subsequent differentiation of eq. (9) with respect to P renders

$$\frac{d^2B_x}{dP^2} = -\frac{P''}{(P')^2} - \frac{VP'''}{(P')^2} + \frac{V(P'')^2}{(P')^3} \tag{10}$$

where, $P = -\frac{d\psi}{dV}$ and, P' , P'' and P''' represent the first, second and third order derivatives of P , with respect to volume at constant temperature.

Gruneisen parameter $\gamma \left(= \frac{\beta V B_x}{C_v} \right)$ describing the thermodynamic behaviour of the crystals was first evaluated by Slater (1939) from the theory of elasticity. His expressions for the vibrational velocities are valid only when the solid is under zero external pressure. Dugdale and McDonald (1953) derived a more general expression for γ by including the effect of pressure. Unfortunately, these theories do not take into account the variation of Poisson's ratio with volume (Pastine 1965). Vaschenko and Zubarev (1963) developed a formulation for γ using the free volume theory. Recently Migault and Romain (1977) have proposed a unification of these theories taking into account the variation of Poisson's ratio with the volume and evaluated a common formula for γ giving

$$\gamma = -\frac{(4-3s)}{6} - \frac{V}{2} \frac{d^2(PV^s)/dV^2}{d(PV^s)/dV} \tag{11}$$

where P is the pressure at volume V , at absolute zero of temperature and s is the parameter which takes for all solids the value zero in Slater's theory, $\frac{2}{3}$ in DM theory and $\frac{4}{3}$ in the free volume theory.

The mode Gruneisen parameter q at zero external pressure can be expressed as

$$q = \frac{d \ln \gamma}{d \ln V}$$

$$q = \frac{1}{2\gamma} \left[s(1+s) - \frac{(1-s)VP''}{P'} - V^s \left\{ \frac{P'''}{P'} - \left(\frac{P''}{P'} \right)^2 \right\} \right] \quad (12)$$

3. Results and discussion

The potential parameters (λ and μ) and softness parameter (ρ_+ and ρ_-) for parent crystals under consideration are presented in Table 1. We have used the values of van der Waals coefficients from Shanker and Rajoria (1982). The calculated

Table 1. Calculated values of softness parameters (ρ_+ and ρ_-) along with the Rydberg potential parameters λ and μ (appearing in eq. (5)) for parent crystals.

Crystals	ρ_+ Å	ρ_- Å	λ (10^{-12})	μ (10^{-4})
NaCl	0.0413	0.394	1.075	0.258
NaBr	0.0413	0.422	1.090	0.234
KCl	0.0385	0.394	1.003	0.196
KBr	0.0385	0.422	0.985	0.182
KI	0.0385	0.449	0.838	0.133

values of nearest neighbour distance (r), isothermal bulk modulus (B_T), first and second order pressure, derivatives of isothermal bulk modulus (dB_T/dP and d^2B_T/dP^2), Gruneisen parameter (γ) and mode Gruneisen parameter (q) for $(\text{NaBr})_x(\text{NaCl})_{(1-x)}$, $(\text{KBr})_x(\text{KCl})_{(1-x)}$ and $(\text{KI})_x(\text{KBr})_{(1-x)}$ mixed crystals are presented in Tables 2–7. The composition dependence of bulk modulus for $(\text{KBr})_x(\text{KCl})_{(1-x)}$ mixed system has been studied by Varotsos (1980a, b). The values predicted using his formulation for rest of the systems considered, are found in good agreement with our calculated values of bulk modulus.

Pastine (1965) for an isotropic solid has considered in the classical range of temperature, the Slater's theory to be a valid approximation to the Gruneisen parameter provided that the Poisson's ratio is assumed invariable. However, this assumption is hardly justifiable for any real solid under hydrostatic stress. Dugdale and McDonald (1953) attributed the inexactness of Slater's formula for γ to the neglect of the theory of finite strain. According to the theory of finite

strain, the Slater formula is valid for an isotropic solid, provided Poisson's ratio is considered as independent of volume. Dugdale and McDonald (1953)

Table 2. Calculated values of nearest neighbour distance (r), isothermal bulk modulus (B_T) and first and second order pressure derivatives of isothermal bulk modulus ($\frac{dB_T}{dP}$ and $\frac{d^2B_T}{dP^2}$) alongwith the interpolated experimental data for $(\text{NaBr})_x(\text{NaCl})_{(1-x)}$ mixed crystals.

Molar concentration of NaBr (%)	r Å Cal (a)	B_T (10^{10}Nm^{-2})		$\frac{dB_T}{dP}$		$-\frac{d^2B_T}{dP^2}$ (10^{-11}pa^{-1})
		Cal (eq. 8)	Expt (b)	Cal (eq. 9)	Expt (c)	Cal (eq. 10)
0	2.82	0.259	0.237	4.48	5.38	20.3
10	2.837	0.224	0.233	4.59		25.8
17	2.849	0.216	0.230	4.62		27.3
26	2.864	0.208	0.226	4.65		27.8
36	2.881	0.201	0.222	4.68		30.5
46	2.898	0.197	0.218	4.70		31.3
55	2.913	0.195	0.214	4.70		31.7
70	2.938	0.196	0.207	4.69		30.8
83	2.961	0.199	0.202	4.67		29.5
100	2.989	0.218	0.195	4.58	5.44	26.6

- (a) Interpolated using eq. (2) from experimental values for parent crystals, taken from Tosi (1964).
- (b) Calculated using Varotsos (1980 a, b) formula, the experimental data for parent crystals given in Smith and Cain (1975).
- (c) Roberts and Smith (1970).

Table 3. Values of Gruneisen parameter (γ) and mode Gruneisen parameter (q) calculated from eqs. (11) and (12) respectively for $(\text{NaBr})_x(\text{NaCl})_{(1-x)}$ mixed crystal using Slater, Dugdale and McDonald (DM) and Free Volume (FV) theories alongwith the available experimental data for parent crystals.

Molar concentration of NaBr (%)	γ				q			
	Slater	DM	FV	Expt* (a)	Slater	DM	FV	Expt* (a)
0	2.08	1.77	1.44	1.61	1.17	0.78	0.37	1.14
10	2.13	1.80	1.46		1.36	0.88	0.49	
17	2.15	1.81	1.48		1.38	0.90	0.51	
26	2.16	1.82	1.49		1.40	0.92	0.54	
36	2.17	1.84	1.51		1.41	0.94	0.56	
46	2.18	1.85	1.51		1.41	0.94	0.56	
55	2.18	1.85	1.57		1.42	0.95	0.56	
70	2.18	1.85	1.51		1.39	0.92	0.52	
83	2.17	1.83	1.50		1.36	0.88	0.48	
100	2.13	1.80	1.48	1.64	1.43	0.98	0.54	1.46

(a) Shanker and Singh (1982).

*The values of γ and q have been calculated from the thermoelastic data.

therefore, introduced some corrections to Slater formula providing a better approximation for γ . Considering the above facts Pastine (1965) presented a

Table 4. Calculated values of nearest neighbour distance (r), isothermal bulk modulus (B_T) and first and second order pressure derivatives of isothermal bulk modulus (dB_T/dP and d^2B_T/dP^2) alongwith the interpolated experimental data for $(KBr)_x(KCl)_{(1-x)}$ mixed crystal.

Molar concentration of KBr (%)	r Å (a)	B_T (10^{10}Nm^2)		dB_T/dP		$-d^2B_T/dP^2$ (10^{-11}pa^{-1}) Cal (eq. 10)
		Cal (eq. 8)	Expt (b)	Cal (eq. 9)	Expt (c)	
0	3.147	0.178	0.174	4.50	5.46	31.2
6	3.156	0.171	0.172	4.54		34.2
13	3.167	0.165	0.170	4.56		35.8
38	3.204	0.154	0.163	4.60		39.5
54	3.216	0.151	0.159	4.60		40.2
61	3.239	0.149	0.157	4.60		40.5
71	3.254	0.148	0.154	4.60		40.5
85	3.275	0.148	0.150	4.58		39.7
100	3.298	0.148	0.146	4.64	5.47	41.8

(a) Interpolated using eq. (2) from experimental values for parent crystals taken from Tosi (1964).

(b) Calculated using Varotsos (1980a, b) formula, the experimental data for parent crystals given in Smith and Cain (1975).

(c) Roberts and Smith (1970).

formulation for γ for cubic crystals under hydrostatic pressure taking into account the effect of variation of Poisson's ratio with volume. In addition, Pastine's

Table 5. Values of Gruneisen parameter (γ) and mode Gruneisen parameter (q) calculated from eqs. (11) and (12), respectively for $(KBr)_x(KCl)_{(1-x)}$ using Slater, Dugdale and McDonald (DM) and Free Volume (FV) theories alongwith the available experimental data for parent crystals.

Molar concentration of KBr (%)	γ				q			
	Slater	DM	FV	Expt* (a)	Slater	DM	FV	Expt.* (a)
0	2.08	1.75	1.42	1.49	1.35	0.88	0.50	1.53
6	2.10	1.77	1.44		1.39	0.92	0.54	
13	2.11	1.78	1.45		1.40	0.94	0.56	
38	2.13	1.80	1.47		1.43	0.96	0.59	
54	2.14	1.80	1.47		1.42	0.95	0.58	
61	2.13	1.80	1.47		1.42	0.95	0.57	
71	2.13	1.80	1.47		1.41	0.94	0.56	
85	2.12	1.79	1.45		1.38	0.91	0.53	
100	2.15	1.82	1.49	1.50	1.44	0.97	0.60	1.14

(a) Shanker and Singh (1982).

*The values of γ and q have been calculated from the thermoelastic data.

Table 6. Calculated values of neighbour distance (r), isothermal bulk modulus (B_T) and first and second order derivatives of isothermal bulk modulus (dB_T/dP and d^2B_T/dP^2) alongwith the interpolated experimental data for $(Kl)_x(KBr)_{(1-x)}$ mixed crystals.

Molar concentration of Kl (%)	r \AA Cal (a)	B_T (10^{10}Nm^{-2})		dB_T/dP		$-d^2B_T/dP^2$ (10^{-11}pa^{-1})	
		Cal (eq. 8)	Expt (b)	Cal (eq. 9)	Expt (c)	Cal (eq. 10)	Expt (d)
		0	3.298	0.153	0.146	4.64	5.47
10	3.322	0.136	0.143	4.63		44.5	
15	3.333	0.132	0.142	4.66		46.7	
22	3.350	0.128	0.140	4.68		48.8	
29	3.366	0.124	0.138	4.70		50.5	
40	3.392	0.120	0.134	4.73		52.7	
48	3.411	0.118	0.132	4.74		53.7	
60	3.439	0.116	0.128	4.81		58.5	
80	3.486	0.115	0.122	4.72		51.5	
90	3.510	0.116	0.119	4.70		49.6	
100	3.533	0.121	0.116	4.64	5.56	44.8	53 ± 15

(a) Interpolated using eq. (2) from experimental values for parent crystals, taken from Tosi (1964).

(b) Calculated using Varotsos (1980a, b) formula, the experimental data for parent crystals given in Smith and Cain (1975).

(c) Roberts and Smith (1970).

(d) Barsch and Schull (1971).

Table 7. Values of Gruneisen parameter (γ) and mode Gruneisen parameter (q) calculated from eqs. (11) and (12) respectively, for $(Kl)_x(KBr)_{(1-x)}$ using Slater, Dugdale and McDonald (DM) and Free Volume (FV) theories alongwith the available experimental data for parent crystals.

Molar concentration of Kl (%)	γ				q			
	Slater	DM	FV	Expt* (a)	Slater	DM	FV	Expt* (a)
0	2.15	1.82	1.49	1.50	1.44	0.97	0.60	1.14
10	2.15	1.82	1.48		1.41	0.94	0.59	
15	2.16	1.83	1.49		1.42	0.95	0.57	
22	2.17	1.84	1.51		1.43	0.96	0.58	
29	2.18	1.85	1.52		1.44	0.97	0.59	
40	2.20	1.87	1.53		1.44	0.97	0.59	
48	2.21	1.87	1.54		1.44	0.97	0.59	
60	2.24	1.90	1.57		1.52	1.06	0.69	
80	2.19	1.86	1.53		1.35	0.87	0.47	
90	2.18	1.85	1.51		1.32	0.83	0.42	
100	2.15	1.82	1.49	1.53	1.26	0.76	0.341	0.99

(a) Shanker and Singh (1982).

*The values of γ and q have been calculated from the thermoelastic data.

formulation for γ was constructed solely from the knowledge of the energy of an atom as a function of the lattice parameter at absolute zero i.e. ignoring the vibrational energies. It is observed from Tables 3, 5 and 7 that the values of Gruneisen parameter γ calculated from free volume (FV) theory are comparatively in better agreement with experiment for pure crystals as it considers the variation of the Poisson's ratio with volume. The values of mode Gruneisen parameter (q) calculated from DM and FV theory are in general, lower while those calculated from Slater's theory are comparatively closer to the corresponding thermodynamic values. The similar type of conclusions have been reached by Sipani and Gupta (1989) while discussing the properties of mixed alkali halide crystals and by Gupta and Sipani (1990b) while discussing the similar properties of alkali halide pure crystals within the framework of compressible ion theory. We therefore, conclude that Rydberg potential is quite suitable to predict the elastic and thermodynamic behaviour of mixed alkali halide crystals.

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References

- Barsch G R and Schull H E 1971 *Phys. Stat. Sol. (b)* **43** 637
 Born M and Huang K 1954 *Dynamical Theory of Crystal Lattices* (Oxford : Clarandon Press)
 Catlow C R A, Diller K M and Norgett M J 1977 *J. Phys.* **C10** 1395
 Chang I F and Mitra S S 1968 *Phys. Rev.* **172** 924
 Dick B G and Overhauser A W 1958 *Phys. Rev.* **112** 40
 Dugdale J S and McDonald D K C 1953 *Phys. Rev.* **89** 832
 Fancher D L and Barsch G R 1969 *J. Phys. Chem. Solids* **30** 2503
 Ferraro J R, Postmus C, Mitra S S and Hoskins C J 1970 *Appl. Optics* **9** 5
 Ferraro J R, Mitra S S and Quattrochi A 1971 *J. Appl. Phys.* **42** 3677
 Gupta V P and Agrawal C P 1982 *Phys. Stat. Sol. (b)* **114** 265
 Gupta V P and Sipani S K 1990a *Phys. Stat. Sol. (b)* **161** 131
 —1990b *J. Phys. Chem. Solids.* **51** 141
 Jain G D 1983 *Ph. D. Thesis* (Agra University, India)
 Kamiyoshi K and Nigara Y 1971 *Phys. Stat. Sol. (a)* **6** 223
 Migault A and Romain J P 1977 *J. Phys. Chem. Solids* **38** 555
 Pastine D J 1965 *Phys. Rev.* **138A** 767
 Roberts R W and Smith C S 1970 *J. Phys. Chem. Solids* **31** 619, 2397
 Rydberg R 1931 *Z. Phys.* **73** 376
 Sangster M J L and Atwood R M 1978 *J. Phys.* **C11** 1541
 Shanker J, Jain V C and Sharma L P 1980 *Indian J. Pure Appl. Phys.* **18** 314

- Shanker J and Kumar M 1987 *Phys. Stat. Sol. (b)* **142** 325
Shanker J and Rajoria A K 1982 *Indian J. Pure Appl. Phys.* **20** 169
Shanker J and Singh K 1982 *Phys. Stat. Sol. (b)* **112** 615
Shrinivas K and Sirdeshmukh D B 1986 *Cryst. Res. Techno.* **21** 1, 157
Sipani S K and Gupta V P 1989 *J. Phys. Chem. Solids* (Communicated)
— 1990 *J. Phys. Chem. Solids* (accepted)
Sirdeshmukh D B and Shrinivas K 1986 *J. Mater. Sci.* **21** 4117
Slater J C 1939 *Introduction to Chemical Physics* (New York : McGraw Hill)
Smith C S and Cain L S 1975 *J. Phys. Chem. Solids* **36** 205
Subbarao U V and Haribabu V 1980 *Indian J. Phys.* **54A** 147
Sysio P A 1969 *Acta Cryst.* **B25** 2374
Tosi M P 1964 *Solid State Physics* **16** 1 (New York : Academic)
Vaschenko V Ya and Zubarev V N 1963 *Soviet Phys. Solid State* **5** 653
Varotsos P 1980a *Phys. Stat. Sol. (b)* **100** K133
— 1980b *ibid* **99** K93
Vegard L 1921 *Z. Phys.* **5** 17
Zen E-AN 1956 *Amer. Min.* **41** 523