

# APPLICATION OF MORSE POTENTIAL TO METALS IN THE MOLECULAR-METALLIC-FRAMEWORK

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Morse potential function has been applied to explain a number of metallic properties by exploiting the hypothesis of identical atomic behaviour in the molecular and crystal states, as first propounded by Kumar and Kachhava (1970). The properties considered are cohesive energy, thermal expansion, Grüneisen parameter, elastic constants and equation of state. The proposed hypothesis derives excellent support from alkali metals, but leads to appreciable discrepancies for Cu and Pb. On the whole, the reported calculations justify the usefulness of the proposed simple approach.

## INTRODUCTION

APPLICABILITY of Morse potential function for the description of metallic properties has been emphasized by Slater (1939) and also by Torrens (1972). Girifalco and Weizer (1959) applied this function to cubic metals by fitting the three unknown parameters to the experimental values of the energy of vapourization, lattice constant and compressibility; they claimed a good match for the equation of state and elastic constants with the experimental data. Recently Roy *et al.* (1972, 1974) have extended the use of Morse function to alloys, which has aroused new interests in this potential function. Thus, any calculation for the metals on the basis of Morse potential would require three types of experimental data for the determination of its parameters. Hence computation of the relevant properties is not automatic. It is, therefore, useful and instructive to suggest other means of fixing the parameters. The present authors intend to achieve the objective by proposing the correlation between solid state and molecular properties by assuming the identity of qualitative behaviour of metals in the two states. This hypothesis permits the invariance of the fundamental potential parameter  $\alpha$  in the two states for the metals. This type of approach has been successfully employed earlier by Kumar & Kachhava (1970) for alkali halides and by Dass and Kachhava (1977) for alkali hydrides.

## THEORY

The Morse potential function, which represents the energy of interaction of two atoms at a distance  $r$ , is of the form

$$\phi(r) = D[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}], \quad \dots(1)$$

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where  $\alpha$  is a sensitive parameter of the potential,  $r_0$  is the equilibrium separation of two atoms and  $D = -\phi(r_0)$  represents the dissociation energy.

The generalization of eqn. (1) for a crystal containing  $N$  atoms can be achieved by summing up the energy of interaction of an atom (assumed to be situated at the origin) with all the other atoms in the crystal and multiply the result so obtained by  $N/2$ . Thus, the total energy of the crystal in the following form is obtained:

$$\Phi = \frac{1}{2} ND \sum_j' [e^{-2\alpha(r_j-r_0)} - 2e^{-\alpha(r_j-r_0)}] \quad \dots(2)$$

where the prime over sigma excludes  $j = 0$  from the summation,  $r_0$  and  $D$  now become parameters satisfying certain crystal conditions in the metal and  $r_j$  represents the distance of the  $j$ th atom from the origin and is given by

$$r_j = \left[ m_j^2 + n_j^2 + l_j^2 \right]^{\frac{1}{2}} a \equiv M_j a, \quad \dots(3)$$

where  $m_j$ ,  $n_j$  and  $l_j$  are the position coordinates of the  $j$ th atom in the lattice under consideration. For convenience, the authors define the following quantities:

$$L = \frac{1}{2} ND \quad \dots(4)$$

and

$$\beta = e^{\alpha r_0} \quad \dots(5)$$

and then write eqn. (2) in the form

$$\Phi(a) = L \beta \left[ \beta \sum_j' e^{-2\alpha a M_j} - 2 \sum_j' e^{-\alpha a M_j} \right] \quad \dots(6)$$

The first three derivatives of eqn. (6) with respect to  $a$  would be needed for the calculations of various properties and are as follows:

$$\frac{d\Phi}{da} = -2\alpha L \beta \left[ \sum_j' M_j e^{-2\alpha a M_j} - \sum_j' M_j e^{-\alpha a M_j} \right], \quad \dots(7)$$

$$\frac{d^2\Phi}{da^2} = 2\alpha^2 L \beta \left[ 2\beta \sum_j' M_j^2 e^{-2\alpha a M_j} - \sum_j' M_j^2 e^{-\alpha a M_j} \right] \quad \dots(8)$$

and

$$\frac{d^3\Phi}{da^3} = -2\alpha^3 L \beta \left[ 4\beta \sum_j' M_j^3 e^{-2\alpha a M_j} - \sum_j' M_j^3 e^{-\alpha a M_j} \right]. \quad \dots(9)$$

Morse (1929) is used here to ascertain  $\alpha$  by using the classical frequency data of small vibrations ( $w_e$ ) of a diatomic molecule. The relevant expression is

$$\alpha = 2\pi w_e \sqrt{\frac{\mu}{2D_e}}, \quad \dots(10)$$

where  $\mu$  is the reduced mass of the molecule and  $D_e$  represents its Dissociation energy. To evaluate  $\beta$ , the authors assert that the equilibrium condition of the crystal requires

$$\left( \frac{d\Phi}{da} \right)_{a=r_0} = 0 \quad \dots(11)$$

which gives

$$\beta = \frac{\sum_j M_j e^{-\alpha a_0 M_j}}{\sum_j M_j e^{-2\alpha a_0 M_j}}, \quad \dots(12)$$

where  $a_0$  is the equilibrium value of  $a$ . Parameter  $r_0$  is then readily obtained from

$$r_0 = \frac{1}{\alpha} \ln(\beta) \quad \dots(13)$$

The remaining parameter  $D$  is obtained by making the Morse function reproduce the experimental compressibility ( $K_{00}$ )

$$\frac{1}{K_{00}} = V_0 \left( \frac{d^2\Phi}{dV^2} \right)_{a=a_0}, \quad \dots(14)$$

where  $V_0$  is the equilibrium value of the crystal volume  $V$ . Using the relation

$$V = Nc a^3, \quad \dots(15)$$

with  $c$  having a value '4' for body centred and '2' for face centred crystals, eqn. (14) yields

$$\frac{1}{K_{00}} = \frac{1}{9Nca_0} \left( \frac{d^2\Phi}{da^2} \right)_{a=a_0}, \quad \dots(16)$$

which will assume the following explicit form:

$$\frac{1}{K_{00}} = \frac{2\alpha^2 L\beta}{9Nca_0} [2\beta \sum_j M_j^2 e^{-2\alpha a_0 M_j} - \sum_j M_j^2 e^{-\alpha a_0 M_j}]. \quad \dots(17)$$

Having determined the potential parameters cohesive energy  $U_0$  is easily obtained through

$$U_0 = -\Phi(a_0) = -L\beta [\beta \sum_j e^{-2\alpha a_0 M_j} - 2 \sum_j e^{-\alpha a_0 M_j}] \quad \dots(18)$$

Following Kachhava and Saxena (1965), the coefficient of thermal expansion ( $\alpha'$ ) is given by

$$\alpha' = -\frac{C_v}{2a_0} \times \frac{\left[ \frac{d^3\Phi}{da^3} \right]_{a=a_0}}{\left[ \frac{d^2\Phi}{da^2} \right]_{a=a_0}^2}, \quad \dots(19)$$

where  $C_v$  is the specific heat at constant volume. Another property of interest is the Grüneisen parameter ( $\gamma$ ), which may be evaluated by making use of the relation (Kachhava & Saxena, 1966).

$$\gamma = -\frac{a_0}{6} \times \frac{\left[ \frac{d^3\Phi}{da^3} \right]_{a=a_0}}{\left[ \frac{d^2\Phi}{da^2} \right]_{a=a_0}} \quad \dots(20)$$

Next the equation of state could be obtained on the lines of Girifalco and Weizer (1959) and is found to have the corrected form:

$$P = -\frac{1}{3Nc a^2} \frac{d\Phi}{da} + \frac{3\gamma N k T}{V} \mathcal{D}(\theta/T), \quad \dots(21)$$

where  $\theta$  is the Debye temperature,  $T$  is absolute temperature,  $\mathcal{D}(\theta/T)$  represents the Debye function and  $k$  is the Boltzmann's constant. Eqn. (21) could be expressed as a direct relationship between the applied pressure  $P$  and the fractional change in

volume,  $\left(\frac{\Delta V}{V_0}\right)$ , by using eqn. (15) and the relation

$$a = a_0 \left(1 + \frac{\Delta V}{V_0}\right)^{1/3}. \quad \dots(22)$$

The expressions for elastic constants  $c_{11}$  and  $c_{12} = c_{44}$ , as illustrated by Girifalco & Weizer (1959), have the following form:

$$\begin{aligned} c_{11} = \frac{D\alpha^2\beta}{ca_0} & \left[ 2\beta \sum_j \frac{m_j^4 e^{-2\alpha a_0 M_j}}{M_j^2} - \sum_j \frac{m_j^4 e^{-\alpha a_0 M_j}}{M_j^2} \right] \\ & + \frac{D\alpha\beta}{ca_0^2} \left[ \beta \sum_j \frac{m_j^4 e^{-2\alpha a_0 M_j}}{M_j^3} - \sum_j \frac{m_j^4 e^{-\alpha a_0 M_j}}{M_j^3} \right] \end{aligned} \quad \dots(23)$$

and

$$\begin{aligned} c_{12} = c_{44} = \frac{D\alpha^2\beta}{ca_0} & \left[ 2\beta \sum_j \frac{m_j^2 n_j^2 e^{-2\alpha a_0 M_j}}{M_j^2} - \sum_j \frac{m_j^2 n_j^2 e^{-\alpha a_0 M_j}}{M_j^2} \right] \\ & + \frac{D\alpha\beta}{ca_0^2} \left[ \beta \sum_j \frac{m_j^2 n_j^2 e^{-2\alpha a_0 M_j}}{M_j^3} - \sum_j \frac{m_j^2 n_j^2 e^{-\alpha a_0 M_j}}{M_j^3} \right]. \end{aligned} \quad \dots(24)$$

#### RESULTS AND DISCUSSION

The values of the potential parameters determined on the basis of molecular framework are assembled in Table I. The required spectroscopic data have been taken from Herzberg (1959) and Gaydon (1968). For other physical data, Seitz & Turnbull (1964) and Kittel (1976) were consulted. The values of Debye function as given in Weiss (1963) have been used.

TABLE I  
Potential parameters in molecular metallic framework

Metal	$\alpha_0$ ( $-\text{\AA}^{-1}$ )	$r_0$ ( $\text{\AA}$ )	$D$ ( $10^{-1}\text{eV}$ )	$\beta$
Li	0.8362	3.9821	0.6086	27.9292
Na	0.8416	4.3743	0.5732	39.6988
K	0.7735	5.1658	0.4679	54.3760
Rb	0.7262	5.5143	0.5518	54.8404
Cs	0.6905	5.9164	0.4416	59.4692
Cu	0.8341	3.7017	4.1801	21.9238
Pb	3.9199	3.4938	0.3223	88.6648

TABLE II

Values of cohesive energy  $-U_0$  (in eV/at), thermal expansion  $\alpha'$  (in  $10^{-6}$  per  $^{\circ}\text{C}$ ), Grüneisen parameter  $\gamma$ , and elastic constants (in  $10^{12}$  dynes/cm $^2$ ), determined in molecular-metallic framework

Metal	$-U_0$		$\alpha'$		$\gamma$		$c_{11}$		$c_{12}=c_{44}$	$c_{12}$	$c_{44}$
	Calcu- lated	Exptl.	Calcu- lated	Exptl.	Calcu- lated	Exptl.	Calcu- lated	Exptl.	Calcu- lated	Exptl.	Exptl.
Li	0.89	1.63	74.6	45	1.47	1.18	0.130	0.177	0.109	0.132	0.108
Na	0.654	1.113	95.7	70.6	1.71	1.31	0.074	0.073	0.065	0.062	0.042
K	0.461	0.934	123.8	83	1.89	1.37	0.0335	0.0416	0.0312	0.0341	0.0286
Rb	0.542	0.852	105.7	88.1	1.90	1.67	0.0325	0.0317	0.0303	0.0266	0.0198
Cs	0.420	0.804	139.0	97	1.95	1.44	0.0252	0.0245	0.0180	0.0208	0.0159
Cu	8.169	3.49	10.5	16.7	1.28	2.00	1.585	1.762	1.262	1.249	0.818
Pb	0.194	2.03	73.1	29.0	6.85	2.62	0.643	0.555	0.324	0.454	0.194

The calculated values of cohesive energy, thermal expansion, Grüneisen parameter and elastic constants are compared with the experimental data in Table II. It may be observed that the elastic constants of alkali-metals have been successfully reproduced as compared with the experimental data of Beg & Nielsen (1976) for Li at 110  $^{\circ}\text{K}$ , from Kittel (1971) for Na at 300  $^{\circ}\text{K}$  and for K at 0  $^{\circ}\text{K}$ , of Gutman *et al.* (1967) for Rb at 78  $^{\circ}\text{K}$ . For Cs experimental data are not available. Therefore, we view our values against the results of Martin Baily as given in Seitz & Turnbull (1958), which show a good agreement. A satisfactory accord is also obtained for elastic constants of Cu and Pb when compared with the experimental values at 0  $^{\circ}\text{K}$ , given in Kittel (1971).

TABLE III

*Potential parameters for Cu and Pb on fitting  $\alpha$  to cohesive energy*

Metal	$\alpha$ ( $\text{\AA}^{-1}$ )	$r_0$ ( $\text{\AA}$ )	$D$ ( $10^{-1}\text{eV}$ )	$\beta$
Cu	1.3550	2.8669	0.3364	48.6474
Pb	1.1815	3.7376	0.2337	82.7587

TABLE IV

*Values of thermal expansion  $\alpha'$  (in  $10^{-6}$  per  $^{\circ}\text{C}$ ), Grüneisen parameter  $\gamma$ , and elastic constants (in  $10^{12}$  dynes/cm $^2$ ) of Cu & Pb using the fitted parameters*

Metal	$\alpha'$		$\gamma$		$c_{11}$		$c_{12} = c_{44}$	$c_{12}$	$c_{44}$
	Calcu- lated	Exptl.	Calcu- lated	Exptl.	Calcu- lated	Exptl.	Calcu- lated	Exptl.	Exptl.
Cu	15.0	16.7	1.82	2.00	1.038	1.762	0.798	1.249	0.818
Pb	22.8	29.0	2.14	2.62	0.553	0.555	0.368	0.454	0.194

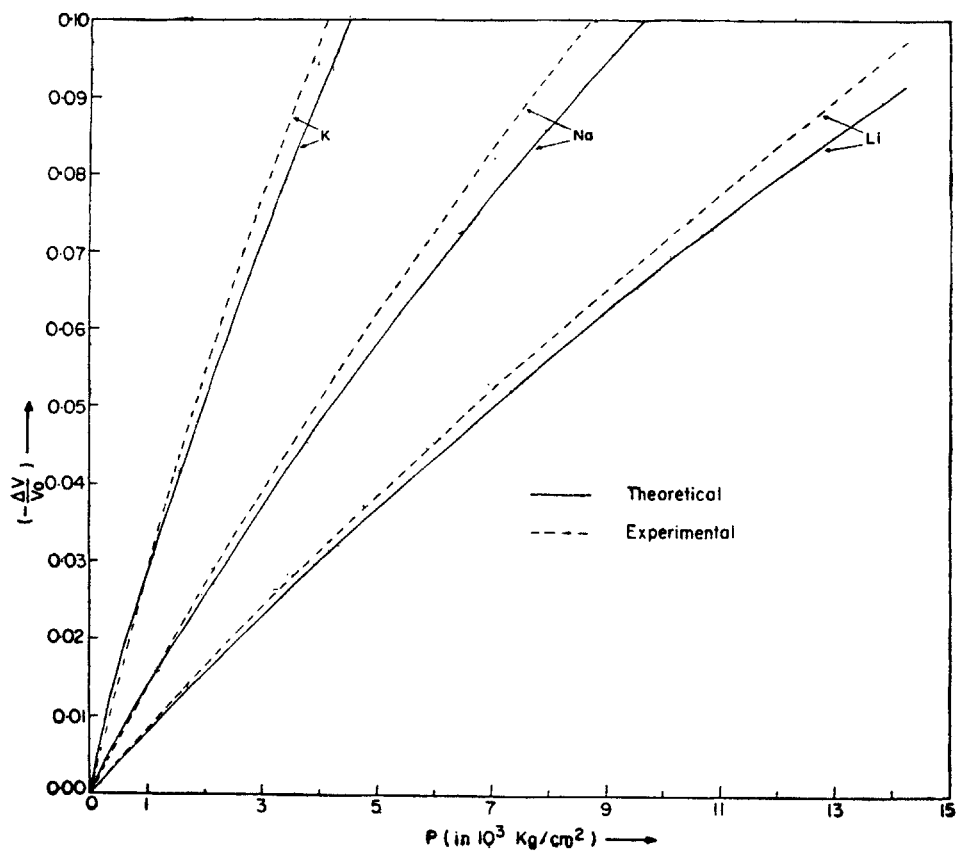


FIG. 1. Equation of state curves for Li, Na &amp; K.

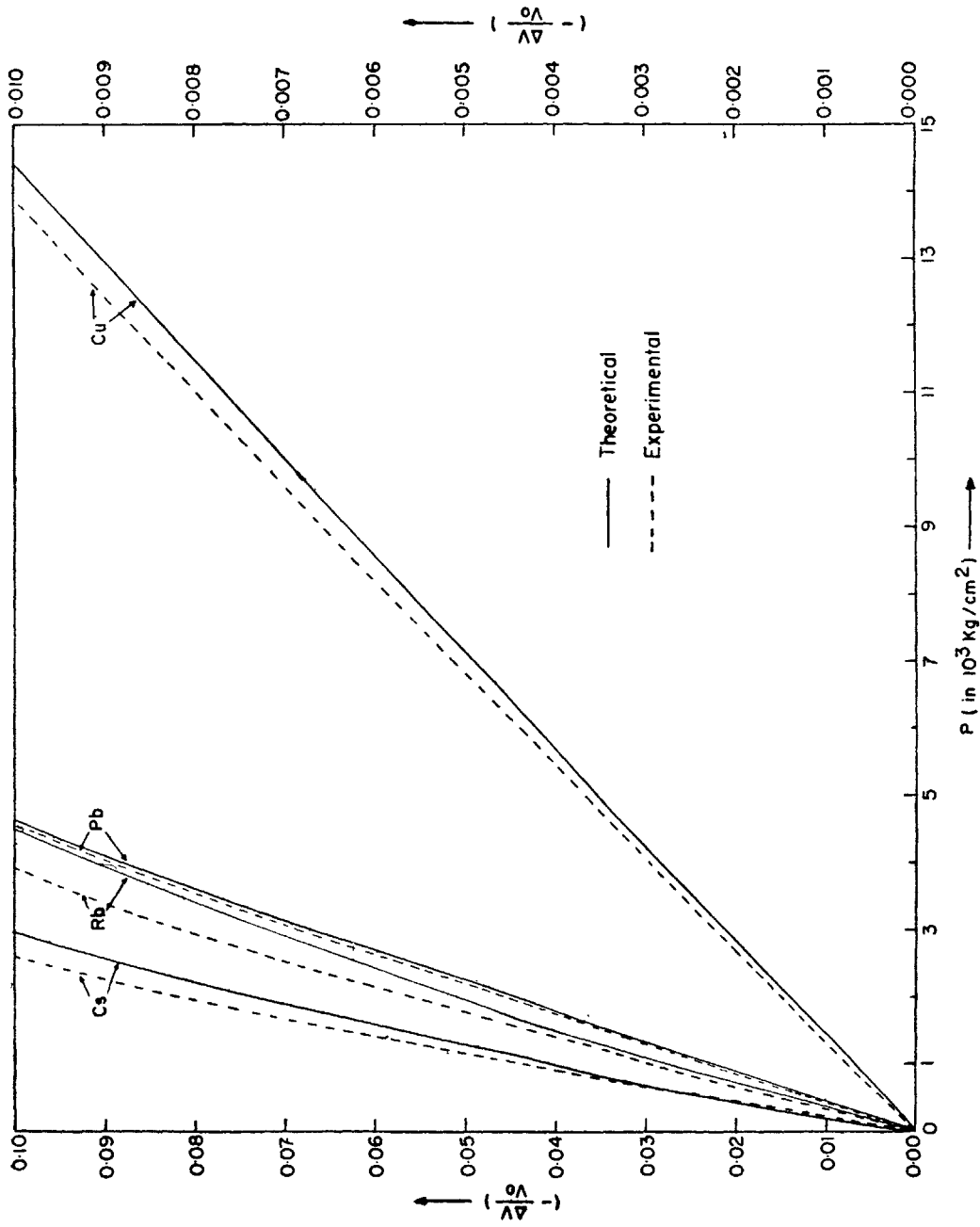


Fig. 2. Equation of state curves for Rb, Cs, Cu & Pb.  
Scale : left side—Rb and Cs right side—Cu and Pb

A comparison with the experimental data for thermal expansion and Grüneisen parameter, as given in Seitz & Turnbull (1964), shows that the values of these quantities have been fairly successfully reproduced for alkali metals, but the reproduction is less satisfactory for Cu and that for Pb may be termed poor. This feature is further confirmed when we compare the cohesive energy values to the experimental data given in Kittel (1976). The observed deviations in cohesive energy values for alkali metals show that the use of  $\alpha_{\text{molecular}}$  is quite satisfactory for the explanation of elastic and thermal properties of these metals but less convincing for the description of cohesion, which is more sensitively dependent on  $\alpha$ .

In view of the failure on the part of the hypothesis of identical behaviour in the molecular and solid state for Cu and Pb, it is proposed to improve the overall situation for these two metals by adopting an alternative approach in which  $\alpha$  is fitted from cohesive energy values. The corresponding values of the potential parameters are, displayed in Table III. These parameters then lead to the results of Table IV, which reveals a reasonable accord between theory and experiment.

The present approach is extended for the prediction of equation of state. The relevant results are graphed in Figs. 1 and 2, wherein we have employed the cohesive energy approach for Cu and Pb. It is gratifying to observe the closeness between the theoretical and experimental curves, whose data are reproduced from Seitz & Turnbull (1964).

#### CONCLUSION

The results reported in this paper may be regarded as convincingly satisfactory in view of the heavy machinery of calculations required when one uses the sophisticated theories, e.g., pseudopotential theory (Harrison, 1966). The reasonable success of the philosophy of correlation between the molecular and crystal states not only justifies the determination of potential parameters but also points to the fact that the nature of forces in simple monovalent metals is almost identical to their molecular counter parts and that in the case of multivalent and complex metals there are appreciable discrepancies between the two owing to the existence of large number of valence electrons, band effects, *s-d* hybridization etc.

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#### REFERENCES

- Beg, M. M., and Nielsen, M. (1976). Temperature dependence of lattice dynamics of Li<sup>7</sup>. *Phys. Rev.*, **B14**, 4266.
- Dass, L., and Kachhava, C. M. (1977). Bulk Properties of Alkali Hydride Crystals on the Molecular Behaviour. *Proc. Indian natn. sci. Acad.* **43**, 110.
- Gaydon, A. G. (1968). *Dissociation Energies*. Chapman & Hall London, III edn.
- Girifalco, L. A., and Weizer, V. G. (1959). Application of Morse potential function to cubic metals. *Phys. Rev.*, **114**, 687.



- Gutman, E. J., and Trivisonno, J. (1967). Temperature dependence of the elastic constants of Rubidium. *J. phys. Chem. Solids*, **28**, 805.
- Harrison, W. A. (1966). *Pseudopotentials in the Theory of Metals*. W. A. Benjamin Inc., Massachusetts.
- Herzberg, G. (1959). *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*, D. van Nostrand Company Inc., New York.
- Kachhava, C. M., and Saxena, S. C. (1965). A simple method of calculating thermal expansion of ionic crystals. *Indian J. Phys.*, **39**, 145.
- (1966). Thermal expansion and Grüneisen constants of crystals: alkali halides. *Indian J. Phys.*, **40**, 273.
- Kittel, C. (1971). *Introduction to Solid State Physics*. John Wiley & Sons Inc., New York, IV edn.; (1976) V edn.
- Kumar, V., and Kachhava, C. M. (1970). Simple properties of ionic crystals on the molecular behaviour. *Proc. Indian natn. Sci. Acad.*, **36**, 170.
- Morse, P. M. (1929). Diatomic molecules according to the wave mechanics. II. Vibrational levels. *Phys. Rev.*, **34**, 57.
- Roy, D., Manna, A., and Sen Gupta, S. P. (1972). The application of Morse potential function in ordered Cu<sub>3</sub> Au and Au<sub>3</sub> Cu alloys. *I. J. Phys. F.: Metal Phys.*, **2**, 1092.
- (1974). The application of Morse potential function in ordered Cu<sub>3</sub> Au alloys. II. Thermal expansion and equation of state. *J. Phys. F.: Metal Phys.*, **4**, 2145.
- Seitz, F., and Turnbull, D. (1958). *Solid State Physics*, **7**. Academic Press, New York; (1964). **16**.
- Slater, J. C. (1939). *Introduction to Chemical Physics*. McGraw Hill Book Company Inc., New York.
- Torrens, I. M. (1972). *Interatomic Potentials*. Academic Press, New York.
- Weiss, J. W. (1963). *Solid State Physics for Metallurgists*. Pergamon, Oxford, pp. 381–383.