

Effect of pressure on F-band energies in alkali halides

NAWAB SINGH and A W JOSHI

Department of Physics, Institute of Advanced Studies, Meerut University,
Meerut 250 001

MS received 8 September 1977

Abstract. Variation of peak F-band absorption energy and lattice distortion with pressure has been calculated for lithium halides employing extended ion model and using values of local compressibility in the neighbourhood of the F-centres which include the effect of vacancy and pressure. The calculated results are in very good agreement with experimental results.

Keywords. Pressure effect on F-band energies; F-band absorption energies; F-centres in alkali halides.

1. Introduction

Variation of peak F-band absorption energy ϵ_m with pressure in alkali halides has been experimentally studied by a number of investigators (Mollwo 1931; Ivey 1947; Jacobs 1954; Maisch and Drickamer 1958; Eppler and Drickamer 1960; Knof and Maisch 1963; Brother and Lynch 1967; Buchenauer and Fitchen 1968, etc.). Mollwo (1931), Ivey (1947), Smakula (1961) and Singh and Joshi (1976) have also proposed empirical relations to explain the pressure dependence of ϵ_m . However, on the theoretical side only a few workers (Bartram and Stoneham 1968 and Drickamer *et al* 1972) have studied this effect. The theoretically calculated pressure dependence of ϵ_m is found to be two to three times lower than the experimental values. Brother and Lynch (1967) have remarked that this might be due to the limitation of the theories to explain such second order effects. Jacobs (1954) and Bertram and Stoneham (1968), on the other hand, have pointed out that this stronger pressure dependence of ϵ_m might be due to the change of compressibility in the neighbourhood of the F-centre because of vacancy. Recently, Singh and Joshi (1976) have modified the empirical Mollwo-Ivey relation to account for the stronger pressure dependence of ϵ_m taking into consideration the effect of vacancy and pressure on the compressibility in the neighbourhood of the F-centre, and have obtained very satisfactory results. In the present paper, we have theoretically investigated the pressure dependence of ϵ_m for lithium halides employing the extended ion model (Wood and Korringa 1961; Wood 1965) for the calculation of energies and using values of compressibility in the neighbourhood of the F-centres which include the effect of vacancy and pressure as in Singh and Joshi (1976). Following Jacobs (1954), we have assumed that the main pressure dependence of ϵ_m is due to the variation of interionic distances. The effect of optical lattice vibrations has thus been neglected in the present calculations. We have considered the distortion of the first neighbour ions of the F-centre only for simpli-

city. The ground state distortion of the first neighbours of the F-centre has also been calculated for various pressures for all the lithium halides.

2. Theory

2.1. Energy calculation

F-electron Hamiltonian (in Hartree atomic units) can be written as

$$H = -(\nabla^2/2) - \sum_{i \neq 0}^M (\pm)_i |\mathbf{r} - \mathbf{R}_i|^{-1}, \quad (1)$$

where \mathbf{R}_i is the distance of the i th ion from the centre of the vacancy (i.e. of the F-centre), $(\pm)_i = 1$ or -1 according as the charge on the i th ion is positive or negative. Summation over i includes all the ions of the lattice.

The ground and the excited state energies of the F-centre have been calculated by variational method using extended ion model (Wood and Korringa 1961; Wood 1965).

Following Wood and Joy (1964), we have used vacancy centred trial wave functions

$$\psi_{2s} = N_s r \exp(-\beta r), \quad (2)$$

and

$$\psi_{3p} = N_p r^2 \cos \theta \exp(-\eta r), \quad (3)$$

for the ground and the excited states respectively, where N_s and N_p are normalization constants, β and η are variational parameters. Since these functions have been found to be the most appropriate ground and excited state wave functions for lithium halides, we have not tested other functions. Though ψ_{2s} violates the boundary condition at $r=0$ and causes corresponding error in the energy, it is a very satisfactory trial wave function as other more accurate nodeless functions involve very complex calculations without much gain in accuracy.

The ground and the excited state energies ϵ_{2s} and ϵ_{3p} are then given by

$$\begin{aligned} \epsilon_{2s} = \langle \psi_{2s} | H | \psi_{2s} \rangle = & \beta^2/6 - a_M/R_1 + \sum_{i \neq 0}^M (\pm)_i (3\beta/2 + 1/R_i \\ & + \beta^2 R_i + \beta^3 R_i^3/3) \exp(-2\beta R_i), \end{aligned} \quad (4)$$

and

$$\begin{aligned} \epsilon_{3p} = \langle \psi_{3p} | H | \psi_{3p} \rangle = & 7\eta^3/30 - a_M/R_1 + \sum_{i \neq 0}^M (\pm)_i (5\eta/3 + 1/R_i \\ & + 4\eta^2 R_i/3 + 2\eta^3 R_i^2/3 + 2\eta^4 R_i^3/9 + 2\eta^5 R_i^4/45) \exp(-2\eta R_i), \end{aligned} \quad (5)$$

where a_M is the Madelung constant and R_1 is the distance of the first neighbours from the centre of the vacancy for a perfect lattice.

2.2. *Orthogonalization of wave functions to ion core orbitals*

The wave functions have been orthogonalized to the core orbitals $\phi_\nu^{1s}(\mathbf{r}-\mathbf{R}_\nu)$ ($1 \leq \nu \leq 6$) of the six first neighbour lithium ions. The effect of other neighbours, being very small (Wood and Joy 1964), has been neglected. The orthogonalized wave functions ψ_{2s}^0 and ψ_{3p}^0 are given by

$$\psi_{2s}^0 = G_{2s} \{ \psi_{2s}(\mathbf{r}) + \sum_{\nu=1}^6 C_{2s, \nu} \phi_\nu^{1s}(\mathbf{r}-\mathbf{R}_\nu) \}, \quad (6)$$

and

$$\psi_{3p}^0 = G_{3p} \{ \psi_{3p}(\mathbf{r}) + \sum_{\nu=1}^2 C_{3p, \nu} \phi_\nu^{1s}(\mathbf{r}-\mathbf{R}_\nu) \}, \quad (7)$$

where the coefficients $C_{j, \nu}$ ($j = 2s$ or $3p$) are given by

$$C_{j, \nu} = - \langle \psi_j(\mathbf{r}) | \phi_\nu^{1s}(\mathbf{r}-\mathbf{R}_\nu) \rangle, \quad (8)$$

$$G_{2s} = (1 - 6 C_{2s, \nu}^2)^{-1/2}, \quad (9)$$

$$G_{3p} = (1 - 2 C_{3p, 1}^2)^{-1/2}. \quad (10)$$

The excited state wave functions are orthogonal to the core orbitals of four of the first neighbour ions (for example, those lying in the xy plane in the case of the p_z function of the F-centre) owing to symmetry. It is found that $|C_{2s, \nu}|$ has the same value for all ν and $|C_{3p, 1}| = |C_{3p, 2}|$. The ground state energy ϵ_{2s}^0 of the F-electron with orthogonalized wave function (eq. (6)) is given by

$$\epsilon_{2s}^0 = G_{2s}^2 \epsilon_{2s} + 2 G_{2s} \sum_{\nu=1}^6 G_{2s, \nu} \epsilon_{2s, \nu} + \sum_{\nu=1}^6 G_{2s, \nu}^2 \epsilon_{\nu\nu}^{2s}, \quad (11)$$

where

$$G_{2s, \nu} = G_{2s} C_{2s, \nu}, \quad (12)$$

and $\epsilon_{\nu\nu}^{2s}$ ($\nu \neq \nu'$) has been neglected, being very small compared to $\epsilon_{\nu\nu}^{2s} \cdot \epsilon_{2s, \nu}$ and $\epsilon_{\nu\nu}^{2s}$ which have been determined by using the exact potential for the ion under consideration are given by

$$\begin{aligned} \epsilon_{2s, \nu} &= (E^{1s} + a_M/R_1) \langle \psi_{2s}(\mathbf{r}) | \phi_\nu^{1s}(\mathbf{r}-\mathbf{R}_\nu) \rangle \\ &\quad - \langle \psi_{2s}(\mathbf{r}) | (1/r) | \phi_\nu^{1s}(\mathbf{r}-\mathbf{R}_\nu) \rangle, \end{aligned} \quad (13)$$

and

$$\epsilon_{\nu\nu}^{2s} = E^{1s} + (a_M - 1)/R_1 \quad (14)$$

where E^{1s} is the ionization energy of the core electron. For excited state we similarly get

$$\epsilon_{3p}^0 = G_{3p}^2 \epsilon_{3p} + 2G_{3p} \sum_{\nu=1}^2 G_{3p, \nu} \epsilon_{3p, \nu} + \sum_{\nu=1}^2 G_{3p, \nu}^2 \epsilon_{\nu\nu}^{3p}, \quad (15)$$

where

$$G_{3p, \nu} = G_{3p} C_{3p, \nu}. \quad (16)$$

$\epsilon_{3p, \nu}$ is identical to $\epsilon_{2s, \nu}$ and is obtained by replacing ψ_{2s} by ψ_{3p} in eq. (13) and $\epsilon_{\nu\nu}^{3p}$ is same as $\epsilon_{\nu\nu}^{2s}$. The two centre integrals have been evaluated by using spheroidal coordinate system (Kotany *et al* 1955).

2.3. Lattice distortion

When an F-centre is introduced in a perfect lattice, it causes displacement of the neighbouring ions. For simplicity, we have considered the displacement of the first neighbour ions only. In fact the displacement of the other neighbours will be very small at least for the ground state with which we are concerned here. The distortion of the first neighbours when F-electron is in the ground state has been calculated by minimizing the total energy of the lattice as a function of the displacement of the first neighbour ions.

The total energy E_t of the crystal can be written as

$$E_t = E_l + E_e, \quad (17)$$

where E_l is the energy of a fictitious crystal from which a complete halide ion has been removed without permitting any rearrangement of the valence or core electrons other than those of displaced first neighbour ions. E_e is the energy of the F-electron in this fictitious crystal, E_l has been calculated by classical ionic crystal theory and is given by

$$E_l = E_c + E_r - E_c^h - E_r^h, \quad (18)$$

where E_c is the coulomb energy of the complete but distorted lattice, E_r is the energy of the repulsive interaction between the ionic core of the lattice and E_c^h and E_r^h are the terms in E_c and E_r corresponding to the removed halide ion. It has also been assumed that only nearest neighbour ions experience core interaction, which to a good approximation, following Wood and Korringa (1961), can be taken as

$$V(r) = CR^{-\sigma}, \quad (19)$$

where values of the constants C and σ have been taken from Seitz (1940). The quantities on the right hand side of eq. (18) have been expanded in Taylor series in the atomic displacement neglecting third and higher powers.

Now, let the first neighbour ions be displaced by a distance ΔR_1 in the inward direction such that $\Delta R_1 = R_1 \delta$ with $0 < \delta < 1$. This distortion will cause changes in the values of E_c , E_r , E_c^h and E_r^h which are given by

$$\Delta E_c = (3 + 18\sqrt{2}) \delta^2/4R_1, \quad (20)$$

$$\Delta E_c^h = -6(1 + \delta) \delta/R_1, \quad (21)$$

$$\Delta E_r = a_M(\sigma - 1) \delta^2/R_1, \quad (22)$$

$$\Delta E_r^h = a_M \{1 + (1 + \sigma) \delta/2\} \delta/R_1. \quad (23)$$

The ground state energy of the F-electron for the distorted lattice will now be given by

$$\epsilon_{2s}^{0'} = G_{2s}^{\prime 2} \epsilon_{2s}' + 2G_{2s}' \sum_{\nu=1}^6 G_{2s, \nu}' \epsilon_{2s, \nu}' + \sum_{\nu=1}^6 G_{2s, \nu}^{\prime 2} \epsilon_{\nu\nu}^{2s'}, \quad (24)$$

where

$$\begin{aligned} \epsilon_{2s}' = & \epsilon_{2s} - 6(1 + \delta) \delta/R_1 + 6 \{3\beta/2 + 1/(1 - \delta) R_1 \\ & + \beta^2(1 - \delta) R_1 + \beta^3(1 - \delta)^2 R_1^2/3\} \exp \{-2\beta R_1(1 - \delta)\} \\ & - 6(3\beta/2 + 1/R_1 + \beta^2 R_1 + \beta^3 R_1^2/3) \exp(-2\beta R_1), \end{aligned} \quad (25)$$

$$\begin{aligned} \epsilon_{2s, \nu}' = & [E^{1s} + a_M/R_1 - \{(2 + 8\sqrt{2})\delta + (3 + 14\sqrt{2})\delta^2\}/8R_1] \\ & \langle \psi_{2s}(\mathbf{r}) | \phi_{\nu}^{1s}(\mathbf{r} - \mathbf{R}_{\nu}) \rangle' - \langle \psi_{2s}(\mathbf{r}) | (1/r) | \phi_{\nu}^{1s}(\mathbf{r} - \mathbf{R}_{\nu}) \rangle', \end{aligned} \quad (26)$$

$$\epsilon_{\nu\nu}^{2s'} = E^{1s} + a_M/R_1 - \{8 + (10 + 8\sqrt{2})\delta + (11 + 14\sqrt{2})\delta^2\}/8R_1, \quad (27)$$

(For distorted lattice $\sum_{i \neq 0}^M (\pm)_i (1/R_i) \neq a_M/R_1$) where the primed quantities refer to the distorted lattice and these should be calculated by taking the first neighbour ions in their new distorted positions. $\epsilon_{2s}^{0'}$ can be further expressed in the form

$$\epsilon_{2s}^{0'} = \epsilon_{2s}^0 + a\delta + b\delta^2, \quad (28)$$

where the coefficients a and b are determined graphically. The change in the ground state energy of the F-electron is then given by

$$\Delta E_e = \Delta \epsilon_{2s}^{0'} = a\delta + b\delta^2, \quad (29)$$

and the change in the total energy of the lattice by

$$\begin{aligned} \Delta E_t = & [a + (6 - a_M)/R_1] \delta + [b + \{27 + 18\sqrt{2} \\ & + 2(\sigma - 3) a_M\}/4R_1] \delta^2. \end{aligned} \quad (30)$$

The value of δ is obtained by minimizing ΔE_t . Substituting this value of δ , the ground state energy of the F-electron is determined from eq. (28).

As the Franck-Condon principle applies here we can take, for the purpose of calculation of absorption energies, the distortion of the first neighbour ions when F-electron is in the excited state to be the same as the ground state distortion δ . The excited state F-electron energy for the distorted lattice is given by

$$\epsilon_{3p}^{0'} = G_{3p}^{\prime 2} \epsilon_{3p}' + 2G_{3p}' \sum_{\nu=1}^2 G_{3p, \nu}' \epsilon_{3p, \nu}' + \sum_{\nu=1}^2 G_{3p, \nu}^{\prime 2} \epsilon_{\nu\nu}^{3p'}, \quad (31)$$

where

$$\begin{aligned} \epsilon_{3p}' = & \epsilon_{3p} - 6(1 + \delta)\delta/R_1 + 6\{5\eta/3 + 1/(1 - \delta)R_1 \\ & + 4\eta^2(1 - \delta)R_1/3 + 2\eta^3(1 - \delta)^2 R_1^2/3 + 2\eta^4(1 - \delta)^3 R_1^3/9 \\ & + 2\eta^5(1 - \delta)^4 R_1^4/45\} \exp\{-2\eta(1 - \delta)R_1\} \\ & - 6(5\eta/3 + 1/R_1 + 4\eta^2 R_1/3 + 2\eta^3 R_1^2/3 + 2\eta^4 R_1^3/9 \\ & + 2\eta^5 R_1^4/45) \exp(-2\eta R_1), \end{aligned} \quad (32)$$

and primed quantities again correspond to distorted lattice. $\epsilon_{3p, \nu}'$ is identical to $\epsilon_{2s, \nu}'$ and is obtained by replacing ψ_{2s} by ψ_{3p} in eq. (26); $\epsilon_{\nu\nu}^{3p'}$ is the same as $\epsilon_{\nu\nu}^{2s'}$. The peak F-band absorption energy $\epsilon_m = \epsilon_{3p}^{0'} - \epsilon_{2s}^{0'}$ can now be easily obtained.

2.4. Effect of pressure on the nearest neighbour distance of the ions

When an external pressure is applied to a crystal, it changes the nearest neighbour distance of the ions. The nearest neighbour distance R at any pressure p is given by $R = R_0 - \Delta R_0$, where R_0 is the value of R at normal atmospheric pressure and ΔR_0 is the change in it due to the applied pressure. But in the neighbourhood of the F-centre, the value of the compressibility (known as local compressibility) is different from (say λ_p times) the bulk compressibility of the lattice because of the effect of vacancy and pressure (Singh and Joshi 1976). The nearest neighbour distance R , in the neighbourhood of the F-centre, is then given by

$$R = R_0 - \lambda_p \Delta R_0. \quad (33)$$

The local compressibility λ_p is also pressure dependent and following Singh and Joshi (1976) can be written as

$$\lambda_p = \bar{\alpha} - \bar{\beta} \Delta R_0/R_0, \quad (34)$$

where $\bar{\alpha}$ and $\bar{\beta}$ are parameters depending on the type of the halide and alkali ions. The distance R_1 of the first neighbours of the F-electron from the centre of the vacancy can be obtained from eq. (33) replacing R by R_1 .

Since the vacancy mainly affects the repulsive interaction of its first neighbour ions, λ_p will be different from unity only for these ions and for others it will be very nearly equal to unity. Moreover, since the dominant dependence of ϵ_m is on the distance of these first neighbour ions from the vacancy, there will not be much error if we take $\lambda_p = 1$ for all other ions.

3. Calculations, results and discussion

The ground and the excited state energies ϵ_{2s}^0 and ϵ_{3p}^0 have been calculated for various values of β and η using eqs (11) and (15) respectively, and values of β and η which give minimum ϵ_{2s}^0 and ϵ_{3p}^0 have been found. As the distortion does not cause much change in the values of β and η , the same values have also been used for distorted lattice. Values of lattice constant R_0 have been taken from Tosi (1964) and those of C and σ from Seitz (1940). We have taken $\sigma = 6.0, 7.0, 7.5$ and 8.5 for LiF, LiCl, LiBr and LiI, respectively, and the same values have been used at all pressures. C is taken to be given by $C = a_M R_0^{\sigma-1} / 6\sigma$. For λ_p we have used $\bar{\alpha} = 2.5$ and $\bar{\beta} = 6.0$ which are somewhat different from those of Singh and Joshi (1976) but give a better agreement with the experimental results. This difference is obviously because of the fact that we have used here a more sophisticated method for calculation of ϵ_m .

The lattice distortion δ has been calculated for the ground state of all the lithium halides at various pressures and its values are shown in figure 1. No experimental measurement of the pressure variation of δ has been made so far, therefore, the comparison of the present results with experimental values is not possible. Pressure dependence of ϵ_m has been calculated and the results have been shown in figure 2 where $\log(\nu/\nu_0)$ (which is the same as $\log(\epsilon_m/\epsilon_0)$) has been plotted against $\log(\rho/\rho_0)$; ν and ν_0 are wave numbers corresponding to ϵ_m and ϵ_0 , ρ is the density of

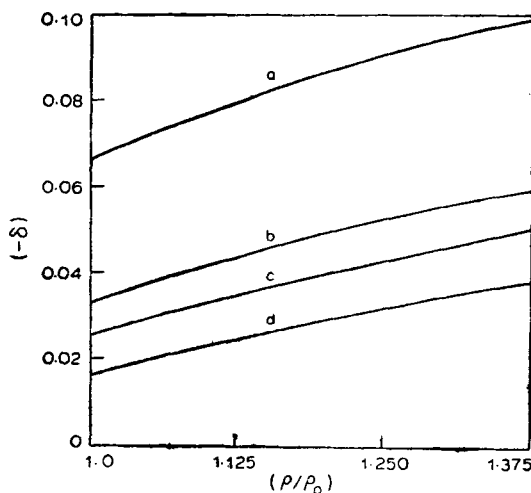


Figure 1. Lattice distortion δ vs ρ/ρ_0 for lithium halides a: LiF; b: LiCl; c: LiBr; d: LiI.

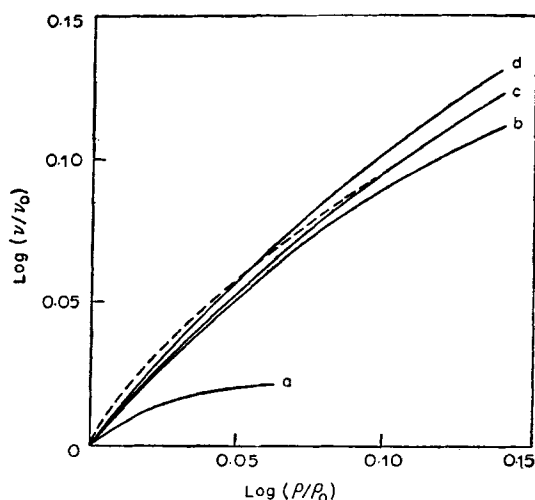


Figure 2. $\text{Log} (\nu/\nu_0)$ vs $\text{log} (\rho/\rho_0)$ for lithium halides. Dashed curve: Experimental data of Eppler and Drickamer (1960) for LiCl; a, b, c and d: Present calculations for LiF, LiCl, LiBr and LiI, respectively.

Table 1. Values of $\partial \log (\nu/\nu_0)/\partial \log (\rho/\rho_0)$ for lithium halides.

Lithium halides	$\partial \log (\nu/\nu_0)/\partial \log (\rho/\rho_0)$	
	Present calculations	Experimental* values
LiF	0.75	1.20
LiCl	1.12	1.15
LiBr	1.15	1.00
LiI	1.20	—

*Buchenaer and Fitchen (1968).

Table 2. Wave number ν_0 corresponding to peak F -band absorption energy ϵ_0 at normal atmospheric pressure for lithium halides.

Lithium halides	Wave number ν_0 (per cm)	
	Present calculations	Experimental values*
LiF	30282	39279
LiCl	23260	25235
LiBr	21066	22124
LiI	18652	18832

*Gourary and Adrian (1960)

the crystal at the applied pressure and ϵ_0 and ρ_0 are the values of ϵ_m and ρ , respectively, at the normal atmospheric pressure. It is clear from figure 2 that the present results are very close to the experimental results in case of LiCl. For LiF, LiBr and LiI such experimental results for high pressure region are not available and hence no such comparison could be made. Table 1 shows the comparison of the slope $\partial \log (\nu/\nu_0)/\partial \log (\rho/\rho_0)$ of the present curves with the experimental values of Buchenaer and Fitchen (1968) in the low pressure region. Agreement in case of LiCl and

LiBr is very good. For LiI the experimental value is not available. In the case of LiF, however, the calculated value is much lower than the experimental value.

In order to check the accuracy of our results we have compared in table 2 the values of peak F-band absorption frequencies at normal atmospheric pressure ν_0 , with the experimental results of Gourary and Adrian (1960). It is clear from this table that the calculated values are nearly 8%, 5% and 1% lower than the experimental values in case of LiCl, LiBr and LiI, respectively, and very low (23%) in case of LiF. Thus, we see that the accuracy of our method for energy calculations is very satisfactory in case of LiCl, LiBr and LiI. The method appears to be unsuitable for LiF due to the fact that we have not considered the effect of polarization which is not negligible in this case.

We, therefore, conclude that the pressure variation of peak-F-band absorption energy ϵ_m in lithium halides can be satisfactorily explained by taking into consideration the effect of vacancy and pressure on the local compressibility in the neighbourhood of the F-centre and using $2s$ and $3p$ wave functions for the ground and the excited states of the F-electron respectively for the calculation of energies by extended ion model. In case of LiF, however, the effect of polarization should be considered to get satisfactory results.

Acknowledgements

We wish to thank Prof. S P Khare for providing necessary facilities and Shri D K Jain and Dr B L Jhanwar for their help in computation. One of us (NS) is grateful to the Principal, J V College, Baraut, for sanctioning leave, and the University Grants Commission, India, for the award of a Teacher Fellowship and for providing financial assistance to meet computer expenses vide Code No. 6012 of January 1976 and No. 7041 of January 1977 which enabled him to pursue this work.

References

- Bartram R H and Stoneham A M 1968 *Phys. Rev.* **176** 1014
 Brother A D and Lynch D W 1967 *Phys. Rev.* **164** 1124
 Buchenauer C J and Fitchen D B 1968 *Phys. Rev.* **167** 846
 Drickamer H G, Frank C W and Slichter C P 1972 *Proc. Natl. Acad. Sci. USA* **69** 933
 Epler R A and Drickamer H G 1960 *J. Chem. Phys.* **32** 1418
 Gourary B S and Adrian F J 1960 *Solid State Phys.* **10** 127
 Ivey H F 1947 *Phys. Rev.* **72** 341
 Jacobs I S 1954 *Phys. Rev.* **93** 993
 Knof H and Maisch W G 1963 *J. Phys. Chem. Solids* **24** 1625
 Kotany M, Ameniya A, Ishiguro E and Kinura T 1955 *Table of Molecular Integrals* (Tokyo: Maruzen Co.)
 Maisch W G and Drickamer H G 1958 *J. Phys. Chem. Solids* **5** 328
 Mollwo E 1931 *Nachr. Ges. Wiss. Göttingen Math. Phys.* **K1** 97
 Seitz F 1940 *The Modern Theory of Solids* (New York: Book Co.) p. 80
 Singh N and Joshi A W 1976 *Phys. Stat. Solidi(b)* **76** K39
 Smakula A 1961 *Proc. Int. Conf. Phys. Semicond.* (Czechoslovak Academy of Sci., Prague) p. 729
 Tosi M P 1964 *Solid State Phys.* **16** 1
 Wood R F 1965 *J. Phys. Chem. Solids* **26** 615
 Wood R F and Joy H W 1964 *Phys. Rev.* **136** A451
 Wood R F and Korringa J 1961 *Phys. Rev.* **123** 1138