PHYSICAL REVIEW B VOLUME 18, NUMBER 6 15 SEPTEMBER 1978

Lattice anharmonicity of alkali metals

P. C. Trivedi, H. O. Sharma, and L. S. Kothari
Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India

(Received 5 November 1976)

Frequencies and eigenvectors are obtained for alkali metals by using the force constants calculated by Shyu and Gaspari. These are used to calculate the cubic and quartic anharmonic contributions to the specific heat in the high-temperature limit with nearest-neighbor central-force interaction, in which the effect of thermal expansion is included. Calculated values of the anharmonic coefficient A, defined by $C_v/3Nk = 1 + AT$, are in good agreement with the experimental results. The values of A are positive for alkali metals. Calculated dispersion curves lie higher than the experimental ones. The sum $\Sigma_{i=1}^{3}\omega_i^2(\vec{k})$ is independent of $\vec{k}$ for sodium, potassium, and rubidium, but not for lithium. It is concluded that a potential which may be adequate in estimating the effects of anharmonicity may not be essentially suitable to describe the harmonic properties.

I. INTRODUCTION

In recent years several authors[1,2] have derived the theoretical expressions for the cubic (F_3) and quartic (F_4) terms of the Helmholtz free energy of an anharmonic crystal. Maradudin *et al.*[3] and Flinn and Maradudin[4] made the first detailed calculations of F_3 in the high-[3] and low[4]-temperature limits for a specified central-force model involving nearest neighbors in a monatomic face-centered-cubic lattice. Similar calculations have also been reported recently for monatomic,[5,6] body-centered-cubic, and diatomic[7] face-centered-cubic lattices.

The increase in specific heat with temperature is due to effects of anharmonicity, to premelting induced by impurities, or to the thermal creation of imperfections in the lattices. In fact in a correct analysis these latter effects should also be taken into account. Unfortunately such an analysis has not been reported for alkali metals but Martin[8] has estimated the anharmonic coefficients A, defined by $C_v/3Nk = 1 + AT$, from entropy considerations.

The harmonic properties of alkali metals have been studied in detail.[9] Recently, Shyu and Gaspari[10] have calculated the force constants for alkali metals by using the pseudopotential form factors as evaluated by Animalu,[11] based on the model potential of Heine *et al.*[12] and a modified Hartree dielectric function.[13,14] Heine and coworkers[12,15] used this model potential for band-structure calculations and obtained very good results for the energy bands and Fermi surfaces. The model potential has also provided reasonable phonon dispersion curves[16] and band-structure energies.[17]

The force constants calculated by Shyu and Gaspari[10] for the alkali metals are used in the present work. The anharmonic coefficients A are calculated. The entropy and specific heat at constant volume are also calculated in the harmonic approximation. Dispersion curves are studied. It is tested if the sum $\sum_{i=1}^{3}\omega_i^2(\vec{k})$ is independent of $\vec{k}$ for the alkali metals.

In Sec. II we give the relevant expressions used in the calculations. The method of calculations is described in Sec. III. Results and discussions are given in Sec. IV. Finally, Sec. V contains some conclusions.

In the present work we follow closely the notation of Ref. 5.

II. EXPRESSION FOR THE SPECIFIC HEAT

The Helmholtz free energy $F(T)$ of an anharmonic crystal can be written

$$F(T) = F_0(T) + F_3(T) + F_4(T) + \cdots , \tag{1}$$

where F_0, F_3, F_4 are the corresponding quadratic, cubic, and quartic term, respectively. In the following only the leading terms are retained in the potential, and the evaluation of the F_3 and F_4 terms is restricted to nearest neighbors only. In the high-temperature limit Eq. (1) can be written[5]

$$F(T) = 3N \left\{ kT \ln\left[0.6505 \frac{\hbar}{kT} \left(\frac{8\varphi''(r_1)}{M}\right)^{1/2}\right] + (kT)^2 \left(c_4 \frac{f'^2}{M^2} \varphi^{\mathrm{IV}}(r_1) - c_3 f_3 \frac{[\varphi'''(r_1)]^2}{[\varphi''(r_1)]^3} \right) + c_4' \frac{\hbar^2}{M^2} f' \varphi^{\mathrm{IV}}(r_1) + \frac{\hbar^2}{6MkT} \varphi''(r_1) + \cdots \right\} , \tag{2}$$

where

$$c_4=\tfrac{8}{27}\,,\quad c_3=\tfrac{1}{31104}\,,\quad c_4'=\tfrac{4}{81}\,,$$

$$f'=\sum_{\vec{k}j}\frac{[e_x(\vec{k}j)+e_y(\vec{k}j)+e_z(\vec{k}j)]^2}{\omega^2(\vec{k}j)}\sin^2\pi a\,(k_x+k_y+k_z)\,,$$

and

$$f_3=\sum_{\vec{n},\vec{n}_1,\vec{n}_2}\Bigg(\sum_{\vec{k}j}\frac{[\vec{n}_1\cdot\vec{e}(\vec{k}j)][\vec{n}_2\cdot\vec{e}(\vec{k}j)]}{\lambda^2_j(\vec{k})}[\cos 2\pi a\vec{k}\cdot\vec{n}-\cos 2\pi a\vec{k}\cdot(\vec{n}-\vec{n}_1)$$
$$-\cos 2\pi a\,\vec{k}\cdot(\vec{n}+\vec{n}_2)+\cos 2\pi a\vec{k}\cdot(\vec{n}-\vec{n}_1+\vec{n}_2)]\Bigg)^3\,, \tag{3}$$

$$\omega^2(\vec{k}j)=[2\varphi''(r_1)/M]\,\lambda_j^2(\vec{k})\,;$$

$2a$ is the lattice constant and r_1 is the nearest-neighbor equilibrium separation; $\omega(\vec{k}j)$ is the frequency of the normal mode described by the wave vector $\vec{k}$ and polarization index j; $\vec{e}(\vec{k}j)$ is the polarization vector for the mode $(\vec{k}j)$; $\varphi(r)$ is the interatomic potential, N is the number of unit cells in the crystal.

Using Eq. (2) the specific heat at constant volume can be expressed[5] in the high-temperature limit as

$$\frac{C_v}{3Nk}=1-kT\left(\frac{c_4}{2}f_4\frac{\varphi^{\mathrm{IV}}(r_1)}{[\varphi''(r_1)]^2}-(2c_3f_3+\tfrac{1}{4})\frac{[\varphi'''(r_1)]^2}{[\varphi''(r_1)]^3}\right)$$
$$-\frac{\hbar^2}{3M}\frac{\varphi''(r_1)}{(kT)^2}\,, \tag{4}$$

where

$$f_4=[2\varphi''(r_1)f'/M]^2.$$

The fourth term on the right-hand side of Eq. (4) is a consequence of the effect of the thermal expansion. Equation (4) will be used to calculate the anharmonic coefficients A for the alkali metals.

III. NUMERICAL CALCULATIONS

The various harmonic properties, and the sums occurring in f_3 and f_4 have been calculated by the following sampling technique. The irreducible sector of the Brillouin zone ($\frac{1}{48}$ portion) is defined by the set of equations

$$k_x+k_y\leq 1,\quad k_y+k_z\leq 1,\quad k_z+k_x\leq 1\,,$$
$$k_x\leq 1,\quad k_y\leq 1,\quad k_z\leq 1\,. \tag{5}$$

Dividing the k_x, k_y, and k_z axes into Z equal intervals and writing

$$k_x=p_x/Z\,,\quad k_y=p_y/Z\,,\quad k_z=p_z/Z\,,$$

Eq. (5) becomes

$$p_x+p_y\leq Z\,,\quad p_y+p_z\leq Z\,,\quad p_z+p_x\leq Z\,,$$
$$p_x\leq Z\,,\quad p_y\leq Z\,,\quad p_z\leq Z\,, \tag{6}$$

where Z is mesh size and p_x, p_y, p_z are integers such that $p_x+p_y+p_z$ is even. This choice generates a face-centered-cubic net in the reciprocal space.

Each point is weighted according to the number of points equivalent to it by symmetry. Care has to be taken in giving the proper weights lying on the surface, edges, and corners of the Brillouin zone. The total number of points in the whole zone is thus Z^3.

A set of wave vectors for a mesh size is generated by the technique described above and the corresponding eigenvalues and eigenvectors are obtained by solving the secular equation

$$|D(\vec{q})-\omega^2 I|=0\,, \tag{7}$$

where $D(\vec{q})$ is the dynamical matrix, $\vec{q}$ is the propagation vector, ω is the angular frequency, and I is the 3×3 unit matrix. The elements of the dynamical matrix $D(\vec{q})$, for the nth-neighbor tensor force model, are given by Squires,[18] where we have used the force constants of Shyu and Gaspari.[10]

IV. RESULTS AND DISCUSSION

To calculate the anharmonic coefficients A the wave vectors for mesh size 10 are generated by using the technique given in Sec. III. Frequencies and eigenvectors are calculated for this set of wave vectors lying in $\frac{1}{48}$th of the Brillouin zone by diagonalizing the dynamical matrix $D(\vec{q})$ by the Jacobi method. The details of calculation of f_3 and f_4 are similar to those given elsewhere.[5,6] Values of f_3 for various neighbors $(\vec{n})$ are given in Table I. It may be observed that the only large contribution to f_3 comes from two sets of $\vec{n}$, namely, (0, 0, 0) and (1, 1, 1).

Using these values of f_3 and f_4, the anharmonic coefficients A, and A' which are the values of A in which the effect of the thermal-expansion coefficient is not included, are calculated. The results thus obtained for A and A' are given in Table II along with the exper-

TABLE I. Values of f_3 (in units of N^3) for the alkali metals. In each row are also given the contributions to f_3 arising from the indicated lattice shells in $\vec{n}$ space. $Z=10$.

	f_3 $\vec{n}$											
	(0,0,0)	(1,1,1)	(2,0,0)	(2,2,0)	(3,1,1)	(2,2,2)	(4,0,0)	(3,3,1)	(4,2,0)	(4,2,2)	(3,3,3)	Total
Li	4760.844	5208.011	458.135	100.54	−11.79	−392.51	0.39	−130.198	−2.801	−12.676	0.637	9978.582
Na	770.1606	779.1684	−0.698	−1.313	0.479	−15.758	−0.008	−1.131	−0.001	0.017	−1.640	1529.276
K	995.9194	1006.5976	−4.542	−1.699	1.167	−19.214	−0.052	−1.617	0.013	0.051	−2.147	1974.477
Rb	1130.399	1141.747	−7.703	−1.973	1.743	−21.497	−0.082	−1.974	0.026	0.082	−2.409	2238.359
Cs	1169.436	1181.328	−9.003	−2.105	2.026	−22.739	−0.092	−2.138	0.032	0.094	−2.457	2314.382

TABLE II. Values of A (in units of $10^{-4}\ K^{-1}$), defined by $C_v/3NK = 1 + AT$, are given for the alkali metals. A' is that value of A which is calculated without including the effect of thermal expansion. $Z=10$.

	A		A'
	Present calculations	Experiments (Ref. 7)	Present calculations
Li	2.180	2.0 ± 0.02	1.396
Na	1.138	1.5 ± 0.1	−0.225
K	1.313	2.2 ± 0.15	0.349
Rb	1.577	1.8 ± 0.1	0.720
Cs	1.701	2.3 ± 0.1	1.039

imental values[8] of A. It may be noted that the calculated values of A are in excellent agreement with the experimental ones obtained by Martin.[8] The values of A' are much smaller than the experimental results, showing that the effect of thermal expansion in anharmonicity calculations for alkali metals is important. The values of A given in Table II are positive, which shows that the net effect of the anharmonic contributions to the specific heat is to increase it as the temperature increases. These results are in sharp disagreement with the general conclusions of Keller and Wallace[19] who predict negative values of the anharmonic coefficients A for the face-centered-cubic and body-centered-cubic crystals.

The specific heat and entropy are also calculated, in the harmonic approximation, by using the following expressions:

$$C_v = k \sum_{\vec{k}j} \frac{[\hbar\omega(\vec{k}j)/2kT]^2}{\sinh^2[\hbar\omega(\vec{k}j)/2kT]}, \tag{8}$$

$$S = k \sum_{\vec{k}j} \left([\hbar\omega(\vec{k}j)/2kT]\coth[\hbar\omega(\vec{k}j)/2kT] - \ln\{2\sinh[\hbar\omega(\vec{k}j)/2kT]\}\right). \tag{9}$$

Wave vectors are generated for a size-20 mesh, and frequencies are calculated by diagonalizing the matrix $D(\vec{q})$.

The specific heat at constant pressure C_p is measured experimentally. The specific heat at constant volume C_v is calculated by using the relation

$$C_p/C_v = 1 + A_1 C_p T, \tag{10}$$

where A_1 is a constant which has been calculated for the alkali metals by Sharma and Singh.[20] Experimental values of C_p are taken from Refs. 21–24.

Calculated values of C_v, obtained by using Eq. (8), are shown in Fig. 1 along with the experimental results. It may be noted that there is a large discrepancy between the calculated and experimental values. For lower temperatures this

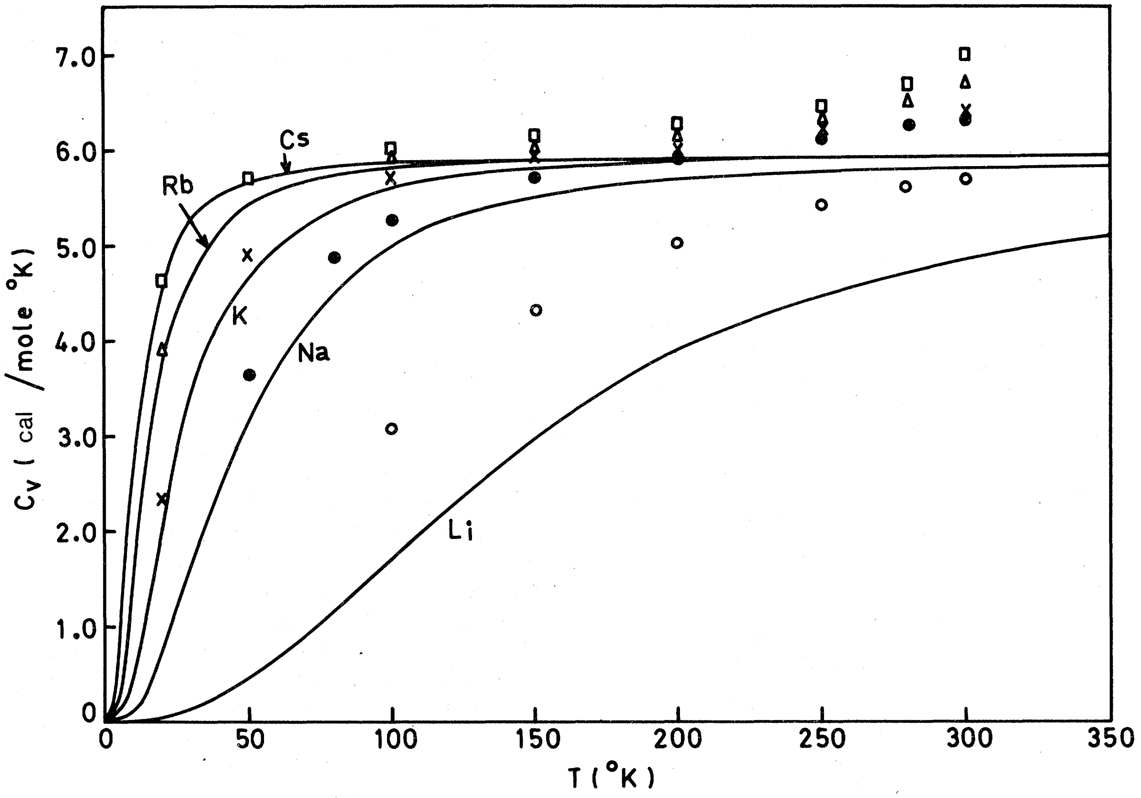

FIG. 1. Values of specific heat at constant volume, calculated in the harmonic approximation, are shown as a function of temperature for the alkali metals. Experimental values are also shown. Experiments: ○ lithium (Ref. 21), ● sodium (Ref. 22), X potassium (Ref. 23), △ rubidium (Ref. 24), □ cesium (Ref. 25). There is a large discrepancy between the calculated and experimental values. For lower temperatures this discrepancy is largest in the case of lithium and smallest in the case of cesium, and it decreases consistently as we go from lithium to cesium in the series. The experimental values keep on increasing consistently for temperatures which are greater than one-half the Debye temperatures, whereas the theoretical values tend to $3R$. This consistent increase indicates the importance of anharmonicity considerations in the specific-heat calculations.

discrepancy is largest in the case of lithium and smallest in the case of cesium, and it decreases consistently as we go from lithium to cesium, that is, from lighter to heavier elements in the series. The experimental values of C_v for all these metals are larger than the theoretical ones. It was mentioned before that the increase in C_p with temperature is due to effects of anharmonicity, to premelting induced by impurities, or to the thermal creation of imperfections in the lattices. Some of these contributions may be included in the experimental values of C_v obtained from Eq. (10), whereas the theoretical values obtained from Eq. (8) represent purely harmonic contribution. Effects of anharmonicity become predominant at higher temperatures. Temperatures greater than one-half the Debye temperature Θ_D can be considered rather high. Debye temperatures for the alkali metals are low.[25] It may be noted from Fig. 1 that the experimental values keep on increasing consistently for temperatures which are higher than one-half the Debye temperatures, whereas the theoretical ones naturally tend to $3R$. This consistent increase indicates the importance of anharmonicity considerations in the specific-heat calculations.

Calculated values of entropy, obtained by using Eq. (9) are shown in Fig. 2 along with experimental results.[8] It may be noted that there is some discrepancy between the theoretical and experimental results, which is largest in the case of lithium and smallest in the case of cesium, and it decreases consistently as we go from lithium to cesium in the series.

A comparison of Figs. 1 and 2 shows that the magnitude of the discrepancy between the theoretical and experimental results for the various alkali metals is larger in the specific heat at constant volume than in the entropy. Thus, it may be concluded that the specific heat at constant

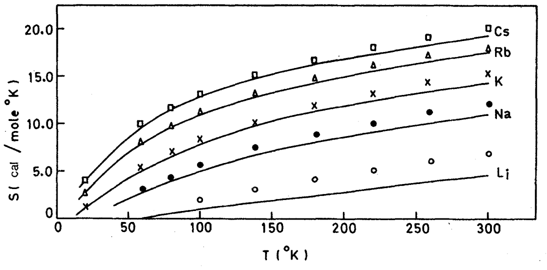

FIG. 2. Values of entropy, calculated in the harmonic approximation, are shown as a function of temperature for the alkali metals. Experimental values (Ref. 8) are also shown. Experiments: ○ lithium, ● sodium, X potassium, △ rubidium, □ cesium. It may be noted that there is some discrepancy between the theoretical and experimental results, which is largest in the case of lithium and smallest in the case of cesium, and which decreases consistently as we go from lithium to cesium in the series.

volume is more sensitive to the effects of anharmonicity than the entropy.

The behavior[26] of the sum $\sum_{i=1}^{3}\omega_i^2(\vec{k})$ as a function of $\vec{k}$ is studied along the three principal symmetry directions [111], [100], and [110]. From Figs. 3 and 4 it can be noted that the sum $\sum_{i=1}^{3}\omega_i^2(\vec{k})$ is independent of $\vec{k}$ for sodium,[27] potassium,[28] and rubidium[29] but not for lithium.[30] Experimental values of frequencies for cesium are not available.

Dispersion curves are drawn, but not shown here, along the three principal symmetry directions [111], [110], and [100] for the alkali metals. It is observed that the calculated dispersion curves lie higher than the experimental ones. The discrepancy is rather large.

It may be remarked that excellent results were obtained in the calculations of the anharmonic coefficients A for the alkali metals. The study of harmonic properties such as entropy, specific heat, and dispersion curves, as we have seen, gave poor results. Thus, it may be concluded that the potential which may be adequate in the anharmonicity calculations may not be essentially suitable to describe the harmonic properties. That is, good harmonic forces are not essential in estimating the effects of anharmonicity.

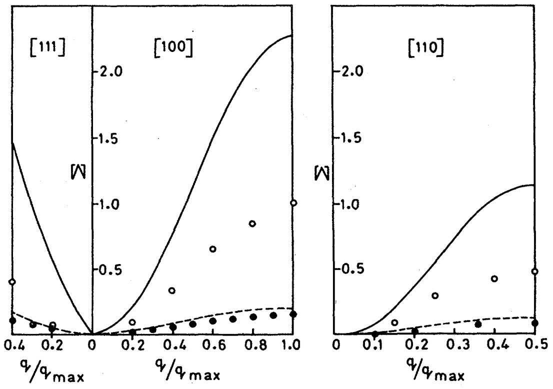

FIG. 3. The sum $\Sigma = \sum_{i=1}^{3} 10^{-28}\omega_i^2(\vec{k})$ is drawn in the figure along the [111], [100], and [110] symmetry directions for lithium and sodium. —— lithium, ------ sodium, experimental points [○ lithium (Ref. 30), ● sodium (Ref. 27)]. Σ is independent of $\vec{k}$ for sodium, but not for lithium.

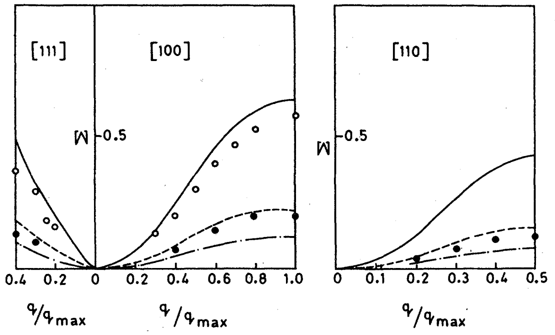

FIG. 4. The sum $\Sigma = \sum_{i=1}^{3} 10^{-27}\omega_i^2(\vec{k})$, is drawn in the figure along the [111], [100], and [110] symmetry directions for potassium, rubidium, and cesium. —— potassium, ------ rubidium, —•— cesium, experimental points [○ potassium (Ref. 28), ● rubidium (Ref. 29)]. Σ is independent of $\vec{k}$ for potassium and rubidium. Experimental points for cesium are not available.

V. CONCLUSIONS

Frequencies and eigenvectors are obtained for alkali metals by using the force constants calculated by Shyu and Gaspari. These are used to calculate the cubic and quartic anharmonic contributions to the specific heat in the high-temperature limit, with nearest-neighbor central force interactions, in which the effect of thermal expansion is included. Calculated values of anharmonic coefficient A, defined by $C_v/3Nk = 1 + AT$, are in good agreement with the experimental ones. The net effect of the anharmonic contributions to the specific heat of alkali metals is to increase it as the temperature increases. Values of the entropy and specific heat at constant volume, calculated in the harmonic approximation, are in poor agreement with the experimental results. Calculated dispersion curves lie higher than the experimental ones. The sum $\sum_{i=1}^{3}\omega_i^2(\vec{k})$ is independent of $\vec{k}$ for sodium, potassium, and rubidium but not for lithium.

It is concluded that a potential which may be adequate in estimating the effects of anharmonicity may not be essentially suitable to describe the harmonic properties. The form factors are available[11] for other elements also. Work is in progress to utilize these in anharmonicity studies.

ACKNOWLEDGMENTS

The authors would like to thank Professor F. C. Auluck and Dr. D. P. Goyal for their interest in this work. The financial support of a NSF Grant No. 0IP72-02844 A01 is gratefully acknowledged. The cooperation of the staff of the computing center at the Delhi University is greatly appreciated.

---

[1] W. Ludwig, J. Phys. Chem. Solids 4, 283 (1958).

[2] A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (N.Y.) 15, 337 (1961).

[3] A. A. Maradudin, P. A. Flinn, and R. A. Coldwell-Horsfall, Ann. Phys. (N.Y.) 15, 360 (1961).

[4] P. A. Flinn and A. A. Maradudin, Ann. Phys. (N.Y.) 22, 223 (1963).

[5] P. C. Trivedi, J. Phys. F 1, 262 (1971).

[6] P. C. Trivedi, in *A Short Course in Solid State Physics*, edited by F. C. Auluck (Thomson, New Delhi, 1972), Vol. II, p. 401.

[7] P. C. Trivedi, H. O. Sharma, and L. S. Kothari, J. Phys. C 10, 3487 (1977).

[8] D. L. Martin, Phys. Rev. 139, A150 (1965).

[9] See, for example, D. C. Wallace, Phys. Rev. 178, 900 (1969); V. Bortolani and G. Pizzichini, Phys. Rev. Lett. 22, 840 (1969); W. M. Shyu, K. S. Singwi, and M. P. Tosi, Phys. Rev. B 3, 237 (1971); S. N. Singh and S. Prakash, Physica 58, 71 (1972); B. Prasad and R. S. Srivastava, Phys. Rev. B 6, 2192 (1972); P. L. Srivastava and N. Mishra, J. Phys. F 2, 1046 (1972); P. K. Sharma and N. Singh, Physica 59, 109 (1972); W. C. Topp and J. J. Hopfield, Phys. Rev. B 7, 1295 (1973); S. K. Srivastava, Aus. J. Phys. 28, 403 (1975); J. P. Perdew and S. H. Vosko, J. Phys. F 6, 1421 (1976).

[10] W. Shyu and G. D. Gaspari, Phys. Rev. 163, 667 (1967).

[11] A. O. E. Animalu, Solid State Theory Group Report, Cavendish Laboratory, Cambridge, England, 1965 (unpublished).

[12] V. Heine and I. Abarenkov, Philos. Mag. 9, 451 (1964); I. Abarenkov and V. Heine, *ibid.* 12, 529 (1965).

[13] L. J. Sham, Proc. R. Soc. A 283, 33 (1965).

[14] J. Hubbard, Proc. R. Soc. A 240, 539 (1957); 243, 336 (1958).

[15] A. O. E. Animalu, Philos. Mag. 11, 379 (1965); A. O. E. Animalu and V. Heine, 12, 1249 (1965).

[16] A. O. E. Animalu, F. Bonsignori, and V. Bortolani, Nuovo Cimento 44, 159 (1966).

[17] A. O. E. Animalu, Proc. R. Soc. A 294, 376 (1966).

[18] G. L. Squires, Ark. Fys. 25, 21 (1963).

[19] J. M. Keller and D. C. Wallace, Phys. Rev. 126, 1275 (1962).

[20] P. K. Sharma and N. Singh, Physica 59, 109 (1972).

[21] D. L. Martin, Proc. R. Soc. A 254, 444 (1960).

[22] D. L. Martin, Proc. R. Soc. A 254, 443 (1960).

[23] C. A. Krier, R. S. Craig, and W. E. Wallace, J. Phys. Chem. 61, 522 (1957).

[24] J. D. Filby and D. L. Martin, Proc. R. Soc. A 284, 83 (1965).

[25] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1974), p. 219.

[26] R. Brout, Phys. Rev. 113, 43 (1959).

[27] A. D. B. Woods, B. N. Brockhouse, R. H. March, A. T. Stewart, and R. Bowers, Phys. Rev. 128, 1112 (1962).

[28] R. A. Cowley, A. D. B. Woods, and G. Dolling, Phys. Rev. 150, 487 (1966).

[29] J. R. D. Copley, B. N. Brockhouse, and S. H. Chen, in *Proceedings of International Conference on Inelastic Neutron Scattering* (IAEA, Vienna, 1968), Vol. I, p. 209.

[30] H. G. Smith, G. Dolling, R. M. Nicklow, P. R. Vijayaraghavan, and M. K. Wilkinson, Bull. Am. Phys. Soc. 13, 451 (1968).