

could be based on only three parameters such as the Cd-ion core shift $\Delta E^{\text{core}}(\text{Cd})$, the Te-ion core shift $\Delta E^{\text{core}}(\text{Te})$, and the shift in the symmetric component of the [111] Fourier coefficient of crystal potential away from its first-principles value, $\Delta v_s(111)$. Here $\Delta E^{\text{core}}(\text{Cd/Te})$ denotes a common shift of all Cd/Te-ion core levels away from their respective first-principles values. The adjusted band structure shown in Fig. 1 was so constructed that the following three experimental transition energies were reproduced exactly: $E(\Gamma_{1c}) - E(\Gamma_{15v}) = 1.8$ eV {direct band gap, based on electroreflectivity data [M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. **154**, 696 (1967)]}; $E(L_{1c}) - E(L_{3v}) = 3.6$ eV {based on optical [M. Cardona and D. L. Greenaway, Phys. Rev. **131**, 98 (1963)] and electroreflectivity [Cardona, Shaklee, and Pollak, *loc. cit.*] data}; and $E(\Gamma_{15c}) - E(\Gamma_{15v}) = 6.1$ eV (based on present interpretation of S1 shoulder in our photoemission data). Further theoretical work now in progress is aimed at

including the spin-orbit splitting throughout the zone and at determining the complex dielectric response function for CdTe.

¹³F. Herman, C. D. Kuglin, and R. L. Kortum, to be published.

¹⁴W. E. Spicer and R. E. Simon, Phys. Rev. Letters **9**, 385 (1962), and many subsequent papers.

¹⁵Cardona and Greenaway, Ref. 12.

¹⁶N. B. Kindig and W. E. Spicer, Rev. Sci. Instr. **36**, 759 (1965); R. J. Powell and W. E. Spicer, to be published.

¹⁷J. L. Shay, dissertation, Stanford University, 1966 (unpublished).

¹⁸J. L. Shay and W. E. Spicer, to be published.

¹⁹Cardona, Shaklee, and Pollak, Ref. 12.

²⁰E. O. Kane, J. Phys. Soc. Japan Suppl. **21**, 37 (1966).

²¹W. E. Spicer, Phys. Rev. **154**, 385 (1967).

²²F. Herman, C. D. Kuglin, K. F. Cuff, and R. L. Kortum, Phys. Rev. Letters **11**, 541 (1963).

NEW APPROACH TO LATTICE DYNAMICS APPLIED TO SOLID He³ AT 0°K

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The expansion of a crystal potential in terms of a set of three-dimensional polynomials orthogonalized with respect to the weight function $f^2(\vec{r}_1, r_2, \dots, r_N) \exp[(r_i - \vec{R}_i) \cdot \mathbf{G}_{ij} \cdot (\vec{r}_j - \vec{R}_j)]$ is shown to be a logical generalization of the previously introduced self-consistent harmonic approximation which is particularly appropriate for highly anharmonic systems. Explicit expressions for the calculation of the ground-state energy and phonon spectrum of a crystal at 0°K are given and certain numerical results for solid He³ at 0°K are presented.

The theory of the self-consistent harmonic approximation was introduced in a previous Letter.¹ This theory combined the idea, originally due to Born,² of finding the optimum harmonic Hamiltonian

$$H^{(h)} = -\frac{1}{2}\lambda \sum_i (\nabla_i^\alpha)^2 + V_0 + \frac{1}{2} \sum_i q_i^\alpha \Phi_{ij}^{\alpha\beta} q_j^\beta / \lambda^2 \quad (1)$$

with which one can approximate a true crystal Hamiltonian

$$H = -\frac{1}{2}\lambda \sum_i (\nabla_i^\alpha)^2 + \frac{1}{2} \sum_{i \neq j} V_{ij} \quad (2)$$

with certain computational techniques introduced by the author.³ The essential result is the self-consistent condition that one should choose $\Phi_{ij}^{\alpha\beta} = \lambda^2 \langle 0 | \nabla_i^\alpha \nabla_j^\beta V | 0 \rangle / \langle 0 | 0 \rangle$ in order to minimize $E_0 = \langle 0 | H | 0 \rangle / \langle 0 | 0 \rangle$.

In the above, λ^2 is an expression for the mass, q_i^α is the α th Cartesian component of the displacement of the i th particle, whose coordinate is \vec{r}_i , from its equilibrium position \vec{R}_i , $V_{ij} = V(|\vec{r}_i$

$-\vec{r}_j|)$ is a suitable interatomic potential, and $V = \frac{1}{2} \sum_{i \neq j} V_{ij}$. The ground-state eigenfunction of $H^{(h)}$ is given by $|0\rangle \propto \exp[-\frac{1}{2} q_i^\alpha G_{ij}^{\alpha\beta} q_j^\beta / \lambda^2]$, where $\mathbf{G}^2 = \Phi$.

While one could probably calculate the ground-state properties of a substance with the anharmonicity of, for example, solid neon using perturbation theory based upon the eigenfunctions of $H^{(h)}$, it is clear that the Gaussian character of $|0\rangle$ will not at all be adequate for a treatment of highly anharmonic systems such as solid helium. A generalization of theory which remedies this deficiency will be presented in the following.

If one considers the identity

$$\int f(x) H_n(x) e^{-x^2} dx = \int \left[\frac{d^n}{dx^n} f(x) \right] e^{-x^2} dx,$$

where H_n is a Hermite polynomial, it is clear that a term of the form $\langle 0 | \nabla_i^\alpha \nabla_j^\beta V | 0 \rangle$ is proportional to the second term in the expansion

of the crystal potential in a set of three-dimensional harmonic oscillator wave functions.⁴ If one performs such an expansion and selects the particular set of wave functions to satisfy $\partial E_0/\partial G_{ij} = 0$, the self-consistent condition results.

If one now feels that $|0\rangle$ is not a good enough approximation to the ground-state wave function one could try $\Psi_0 = f(r_1, r_2, \dots, r_N)|0\rangle$ where, for example, f could be chosen to introduce short-range correlation. One could then expand the potential in terms of a new set of three-dimensional polynomials orthogonalized⁵ with respect to the weight function Ψ_0^2 .

A few detailed results of this approach are readily derived and one obtains an expression for the ground-state energy of a crystal

$$E_0 = \frac{1}{4} \text{Tr}(\mathbf{G}) + \langle 0 | V_{\text{eff}} | 0 \rangle / \langle 0 | f^2 | 0 \rangle, \quad (3)$$

where

$$V_{\text{eff}} = f^2 \left[V - \frac{1}{4} \lambda^2 \sum_i (\nabla_i^\alpha)^2 \ln f \right]. \quad (4)$$

This result is similar to that obtained by Nosanow,⁶ the essential difference being due to the use of a correlated Gaussian wave function here.

The requirement $\partial E_0/\partial G_{ij}^{\alpha\beta} = 0$ yields

$$(\mathbf{G}^2)_{ij}^{\alpha\beta} = \lambda \frac{\langle |\nabla_i^\alpha \nabla_j^\beta V_{\text{eff}} | \rangle \langle |f^2| \rangle - \langle |\nabla_i^\alpha \nabla_j^\beta f^2| \rangle \langle |V_{\text{eff}}| \rangle}{\langle |f^2| \rangle^2}. \quad (5)$$

If f has the symmetry of the crystal potential, the lowest excited states, which are obviously to be identified with one-phonon states, are given by $|k^\alpha\rangle = S_{ki}^{\alpha\beta} q_i^\beta f|0\rangle$, where S is a unitary matrix which diagonalizes the matrix whose elements are $\Phi_{ij}^{\alpha\beta} = \langle 0 | q_i^\alpha q_j^\beta f^2 | 0 \rangle / \langle 0 | 0 \rangle$. The phonon energies are given by

$$\nu_k^\alpha = \frac{1}{2} \lambda^2 \left[(\mathbf{S} \Phi \mathbf{S}^\dagger)_{kk}^{\alpha\alpha} \right]^{-1}. \quad (6)$$

It is interesting that the phonon energies are not equal to ω_k^α , the roots of the matrix \mathbf{G} , as would be obtained if one made the most obvious combination of the work of Nosanow and Werthamer⁷ with that of I—that is, if one simply substituted V_{eff} for V in I. However, one can show that $\nu_k^\alpha \rightarrow \omega_k^\alpha$, $k \rightarrow 0$.

The self-consistency condition, Eq. (5), is sufficient to provide two desirable results: $\langle k^\alpha | H | k^\beta \rangle \propto \delta_{kk}^{\alpha\beta}$ and $\langle 0 | H | k^\alpha, k^\beta \rangle = 0$. Thus, the matrix elements of H between nonidentical

one-phonon states and between the ground state and all two-phonon states are identically zero, a feature which is not present in Ref. 7.

In applying the above theory to a numerical calculation of certain properties of bcc He³ we have partially followed the approach of Nosanow⁶ and have taken $f = \prod_{i>j} u(|r_i - r_j|)$ with $u_{ij} = \exp(-\frac{1}{2} c V_{ij})$. The integrals were then evaluated retaining only the lowest order term in a cluster expansion based on the method of Van Kampen.⁸ Recent studies⁹ have shown that higher order terms in this cluster expansion are small when f is as given here. We used $c = 0.089$ and $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ with $\sigma = 2.556 \text{ \AA}$ and $\epsilon = 10.22^\circ\text{K}$ as was done in Ref. 6, 7, and 9. (Then $\lambda^2 = \hbar^2/m\sigma^2\epsilon$.)

The numerical results for E_0 and for the [110] phonon dispersion curves at a specific volume of 21.5 cc/mole are shown in Figs. 1 and 2, respectively, by the curves labeled SC (self-consistent). These are to be compared with the curves labeled NCG which are calculated with $|0\rangle$ a noncorrelated Gaussian wave function (i.e., $\mathbf{G} = aI$ with a chosen to minimize E_0) according to the theories of Refs. 6 and 7.

The most notable numerical result is the improvement in E_0 . This obtains much more from the introduction of a correlated Gaussian wave function in this work than from the fulfillment of Eq. (5). One can obtain almost as low a value of E_0 if one uses $\mathbf{G} = ax$ (an arbitrary "reasonable" matrix) and minimizes with respect to a .

It is apparent that calculations of the velocity of sound by the two theories are in close

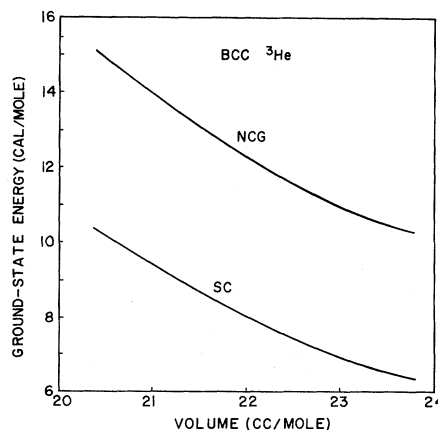


FIG. 1. Ground-state energy versus molar volume. The curve labeled SC is the result of the theory presented in this paper and the curve labeled NCG is the previous result of Ref. 6.

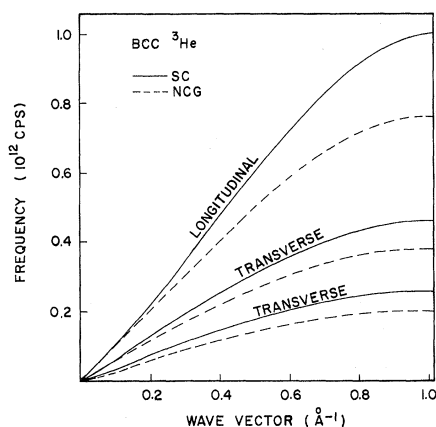


FIG. 2. Phonon dispersion curves in the [110] direction at a specific volume of 21.5 cc/mole. The solid curves are results of this paper, the dashed curves are computed from the theory of Ref. 7.

agreement. However, the calculated phonon energies differ significantly near the edge of the Brillouin zone. These results also obtain at other densities.

We feel that the theoretical approach outlined here offers a unified method of treating both highly anharmonic and slightly anharmonic systems by the expansion of the potential in general three-dimensional orthogonal polynomials or three-dimensional Hermite polynomials, respectively. In addition, the latter expansion has definite advantages over the conventional Taylor series expansion,¹⁰ although the mathematical techniques of II are required to perform it. In contrast with the theories of Refs. 6 and 7, one is provided here with a clear-cut

procedure for extending the calculation since the orthogonal polynomials provide a complete set of wave functions so that perturbation theory can be used. Thus, one could expect to obtain an improved value of E_0 and to calculate phonon lifetimes.

The author has enjoyed discussing various aspects of this work with N. S. Gillis, N. R. Werthamer, W. J. Mullin, and L. H. Nosanow.

¹T. R. Koehler, Phys. Rev. Letters **17**, 89 (1966); this paper will be referred to as I.

²M. Born, in *Festschrift zur Feier des zweihundert-jährigen Bestehens der Akademie der Wissenschaften in Göttingen. I. Mathematisch-physikalische Klasse* (Springer-Verlag, Berlin, 1951), p. 1; D. J. Hooton, Phil. Mag. **46**, 422 (1955).

³T. R. Koehler, Phys. Rev. **144**, 789 (1966); this paper will be referred to as II.

⁴One constructs these wave functions by multiplying $|0\rangle$ by three-dimensional polynomials in the q_i^α which are products of Hermite polynomials in the normal coordinates Q_k^α .

⁵When $f=1$ this process recovers the traditional harmonic oscillator wave functions.

⁶L. H. Nosanow, Phys. Rev. Letters **13**, 270 (1964); Phys. Rev. **146**, 120 (1966).

⁷L. H. Nosanow and N. R. Werthamer, Phys. Rev. Letters **15**, 618 (1965).

⁸N. G. van Kampen, Physica **27**, 783 (1961).

⁹J. H. Hetherington, W. J. Mullin, and L. H. Nosanow, Phys. Rev. **154**, 175 (1967).

¹⁰For example, in perturbation theory, the n th term in the expansion of the potential has matrix elements only between states in which the total number of phonons is n so that ground-state expectation values of higher order terms are eliminated.

BAND STRUCTURE OF CUBIC ZnS (KORRINGA-KOHN-ROSTOKER METHOD)

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Calculating the band structure of semiconductors crystallizing in the diamond or ZnS structure is a very interesting but also a difficult problem. Self-consistent calculations as performed by Herman¹ are extensive and until now only completed for Ge, Si, and grey tin (a perturbation calculation had to be added a posteriori). Results obtained with the aid of the pseudopotential-interpolation scheme have been published for 14 semiconductors by Cohen and

Bergstresser² (hereafter referred to as CB). But in spite of the striking success of this paper, the method is not fully satisfactory, since it is an empirical one and depends on a great deal of experimental data which must be interpreted properly.

To adopt a middle course—not as extensive as orthogonalized-plane-wave self-consistency but starting nearly from first principles—we undertook an application of the Green's func-