[6] A. M. Levelut and M. Lambert, C. R. Acad. Sci., Ser. B 272, 1018 (1971).

[7] H. Hervet, F. Volino, A. J. Dianoux, and R. E. Lechner, J. Phys. (Paris), Lett. 35, L-151 (1974); H. Hervet, F. Volino, A. J. Dianoux, and R. E. Lechner, Phys. Rev. Lett. 34, 451 (1975).

[8] J. W. Doane, in Proceedings of the Seventh International Liquid Crystal Conference, Kent, Ohio, August 1976 (to be published).

[9] J. Seliger, R. Blinc, H. Arend, and R. Kind, Z. Phys. B25, 189 (1976).

[10] R. Blinc, Phys. Status Solidi (b) 70, K29 (1975).

[11] J. Seliger, M. Mali, R. Osredkar, and R. Blinc, J. Chem. Phys. 65, 2887 (1976).

[12] Unpublished work from this laboratory.

[13] R. A. Wise, D. H. Smith, and J. W. Doane, Phys. Rev. A 7, 1366 (1973); T. R. Taylor, S. L. Aurora, and J. L. Ferguson, Phys. Rev. Lett. 25, 722 (1970).

Self-Consistent Structure of Metallic Hydrogen*

David M. Straus† and N. W. Ashcroft
Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853

(Received 23 November 1976)

A calculation is presented of the total energy of metallic hydrogen for a family of face-centered tetragonal lattices carried out within the self-consistent phonon approximation. The energy of proton motion is large and proper inclusion of proton dynamics alters the *structural* dependence of the total energy, causing isotropic lattices to become favored. For the dynamic lattice the structural dependence of terms of third and higher order in the electron-proton interaction is greatly reduced from static lattice equivalents.

Perturbation theory has been moderately successful in accounting for the structural dependence of the *static* energy in many simple crystalline metals.[1,2] In this method, the structural energy is obtained by expansion in orders of the effective conduction-electron–ion interaction (or pseudopotential), the expansion usually being truncated at the lowest term and resulting in what is referred to as the second-order band-structure energy. For perfect lattices, this term reduces to a relatively simple sum over the sites of the reciprocal lattice.

In the case of metallic hydrogen, the electron-ion (electron-proton or electron-deuteron) interaction is exactly known, and it is partly for this reason that this system has attracted theoretical attention.[3-7] Within the static-lattice approximation, perturbation theory for the structural energy has been carried through to fourth order,[7] and extensive scans of "Bravais lattice space" have been carried out in an attempt to determine, at zero pressure, the structures with lowest static energy.[3] In the latter calculations (which were at third order), Brovman *et al.*[3] concluded that static metallic hydrogen would take up structures which are so highly anisotropic that near the zero-pressure metastable density they would become "liquidlike" in certain crystal directions upon inclusion of the proton dynamics.

Since the ionic mass in metallic hydrogen is small, one expects on quite general grounds that the ionic degrees of freedom can play a rather significant role in determining the structure with lowest overall energy. It is known[3,7] that energy differences between different structures are small—much smaller, for example, than the estimate of the energy bound up in the zero-point motion of the protons. Evidently, what is required is a calculation of structural energies carried out self-consistently for various lattices disturbed by the presence of phonons. The purpose of this Letter is to report on the outcome of such an investigation: We have completed a series of calculations within the self-consistent harmonic phonon approximation[8,9] (SCHA) for a representative family of face-centered tetragonal (fct) Bravais lattices in their ground states at a density[10] of $r_s = 1.36$ [with $\frac{4}{3}\pi(r_s a_0)^3 = n^{-1}$, n being the electron density N/Ω]. Two important results emerge: First, the inclusion of ion dynamics radically alters the structural dependence of the energy so that, in the family which we consider, it is the *isotropic* lattice (fcc) that is ultimately favored. Second, by the inclusion of ion dynamics in the perturbation theory, the structural sensitivity of the terms *higher* than second order is greatly reduced from that appropriate to the static theory.

The arguments go as follows: To second order in the electron-proton interaction, the total *ground-state energy* per proton in the self-consistent harmonic approximation can be written[11]

$$E(r_s) = \frac{1}{4N} \sum_{\vec{q},j}^{\mathrm{BZ}} \hbar\omega(\vec{q},j) + \frac{1}{2} \sum_{\vec{X}\neq 0} \Phi(\vec{X}) + (\text{terms independent of structure}). \tag{1}$$

Here the sum of frequencies $\omega(\vec{q},j)$ of polarization j is taken over the first Brillouin zone (BZ), and

$$\Phi(\vec{X}) = \int \frac{d^3k}{(2\pi)^3} \frac{4\pi}{k^2\epsilon(k)} \exp[-\tfrac{1}{2}k_\alpha k_\beta \lambda_{\alpha\beta}(\vec{X})]\exp(i\vec{k}\cdot\vec{X}), \tag{2}$$

where

$$\lambda_{\alpha\beta}(\vec{X}) = 2[\langle u_\alpha(\vec{X})u_\beta(\vec{X})\rangle - \langle u_\alpha(\vec{X})u_\beta(0)\rangle] = \frac{\hbar}{MN} \sum_{\vec{q},j}^{\mathrm{BZ}} (1-\cos\vec{q}\cdot\vec{X})e_\alpha(\vec{q},j)e_\beta(\vec{q},j)\omega^{-1}(\vec{q},j), \tag{3}$$

with the brackets indicating an average over *harmonic* states. In Eq. (2), $\epsilon(k)$ is the dielectric function of the interacting electron gas taken, as is customary, in its static limit. The small ionic displacements $\vec{u}(\vec{X})$ are defined by $\vec{u}(\vec{X}) = \vec{R} - \vec{X}$, where $\vec{R}$ is the instantaneous position of the ion, and $\vec{X}$ the lattice site to which it is attached. Notice that the first term in (1) is the kinetic energy of the ionic system whereas the second is the potential energy averaged over the ions, motion. To carry out this averaging, we require both the frequencies $\omega(\vec{q},j)$ and the polarization vectors $\vec{e}(\vec{q},j)$ of the self-consistent phonons; and these are given by the solution of

$$M\omega^2(\vec{q},j)e_\alpha(\vec{q},j) = \left\{ \sum_{\vec{X}\neq 0} (\cos\vec{q}\cdot X - 1) \int \frac{dk}{(2\pi)^3} \frac{4\pi}{\epsilon(k)k^2} k_\alpha k_\beta \exp[-\tfrac{1}{2}k_\mu k_\nu \lambda_{\mu\nu}(\vec{X})] \exp(i\vec{k}\cdot\vec{X}) \right\} e_\beta(\vec{q},j). \tag{4}$$

Evidently, the *static* energy can be formally recovered by setting $\lambda = 0$ in Eqs. (1)–(3), and by omitting the phonon kinetic energy in Eq. (1). The harmonic approximation, on the other hand, can be obtained by expanding in powers of λ and retaining the terms linear in λ. In metallic hydrogen however, the root-mean-square proton displacement is substantial,[12] and such an expansion (implicit in Ref. 3) is open to question. The second-order static energies[13,14] (to which, in the harmonic approximation, the phonon energies are simply added) are shown in Fig. 1, plotted against c/a for the fct system (solid line). Note that there is noticeable structure in the curve not found, for example, in an ordinary simple metal (e.g.,[15] Al). In agreement with Ref. 3, we find a structure with $c/a < 1$ to have the lowest static energy. However, when we compute the dynamic energy self-consistently, the situation changes markedly. It is important to note that the solutions of (4) do not always admit *real* frequencies: The arrows in Fig. 1 indicate three such lattices; the dashed line gives the *total* energy[16,17] [Eq. (1)] for the c/a values for which Eq. (4) *can* be solved. The reason for the apparent failure of the SCHA is simply that, for certain values of the parameter c/a, the small-oscillations problem is not well defined. For example, lattices corresponding to c/a values lying in the range $0.5 < c/a < 0.7$ are associated with a portion of the static-energy curve (Fig. 1) that is removed from a local minimum and for which the second derivative (with respect to c/a) is negative. In these lattices, the existence of *stable* small oscillations of the protons cannot be presumed, and the occurrence of imaginary frequencies in the SCHA is an indication that they do not. For values of c/a near 1.5,

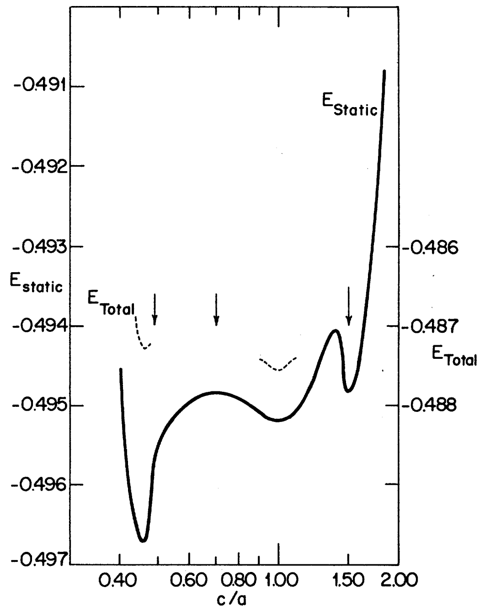

FIG. 1. Static energy and total self-consistent energy for fct metallic hydrogen (at $r_s = 1.36$ and $T = 0$°K) as a function of c/a (all energies are in hartree atomic units). Total (right-hand scale) is given by the dashed line. Arrows refer to particular values of c/a for which the crystal is unstable.

the absence of stable oscillations is already suggested by the results of the harmonic approximation, for which imaginary frequencies are found everywhere in the BZ. Although there is a minimum in the static energy near $c/a = 1.5$ (Fig. 1), the SCHA can still fail because in the wider Bravais lattice space referred to earlier this point can be situated at a saddle on the energy surface, in contrast to the regions corresponding to the dashed curves which evidently reflect local minima (as required for stability).

The total energy is minimized at $c/a = 1$ corresponding to the fcc structure, which is the most symmetric of the class considered. Since the sharp variations of static-lattice energy found in Fig. 1 and in the plots of Ref. 3 occur over values of c/a comparable to the ratio of $\{\langle \vec{u}^2 \rangle\}^{1/2}$ to a nearest-neighbor distance, it is not unreasonable to expect similar behavior for other families of Bravais lattices such as those investigated by Brovman, Kagan, and Kholas.[3] Evidently, we may conclude that in the metallic phase of hydrogen, lattice dynamical effects completely alter the structural dependence of the energy: In a self-consistent calculation, it is isotropic lattices that are favored. (Indeed, it is worth noting that *none* of the structures corresponding to the minima of the static energy in Fig. 1 is stable in the simple-harmonic approximation.) Finally, the energy of motion, defined by $E - E_{\text{static}}$, is[18] 0.0076 hartree units per proton for the fcc structure. This is a substantial fraction of the zero-pressure binding energy[3,7] which, depending on estimates of electron-gas correlation energy, is in the range 0.02 to 0.03 hartrees per proton.

We now come to the structural dependence of terms in the energy of third and higher order in the electron-ion interaction, which have been omitted from (1). In the SCHA the *total* second-order band-structure energy can be written

$$E_b^{(2)} = \frac{1}{2\Omega} \sum_{\vec{k} \neq 0} S(\vec{k}) \frac{4\pi}{k^2} \left[\frac{1}{\epsilon(k)} - 1\right], \qquad (5)$$

where the static structure factor $S(\vec{k})$ is given by[17]

$$S(\vec{k}) = \sum_{\vec{X}} e^{i\vec{k}\cdot\vec{X}} \exp[-\tfrac{1}{2} k_\alpha k_\beta \lambda_{\alpha\beta}(\vec{X})]. \qquad (6)$$

This function is plotted in Fig. 2 for fcc metallic hydrogen ($r_s = 1.36$) with $\vec{k}$ along the [100] direction. The large weight between peaks (and the correspondingly sharp reduction in the strength of the Bragg peaks themselves) can be traced to the value of the Debye-Waller factor e^{-2W} where

$$2W = \langle \vec{u}^2 \rangle = \frac{\hbar}{MN} \frac{1}{2} \sum_{\vec{q}, j}^{\text{BZ}} e_\alpha(\vec{q}, j) e_\beta(\vec{q}, j) \omega^{-1}(\vec{q}, j) \qquad (7)$$

is appreciable.[12] This transfer of weight from the Bragg peaks to the continuum in between means that the *dynamic* second-order energy is *less* sensitive to structure than the corresponding static lattice quantity. Now, in third and higher orders this effect is compounded: It is easy to show[15,18] that the dynamic third-order band-structure energy has three Debye-Waller factors, the fourth has six such factors, and so on. The extent to which the dynamics *reduces* the structural sensitivity is more marked at each successively higher order. Thus, for purposes of calculating the *structural* dependence of the energy, perturbation theory converges more quickly in the dynamic case than in the static counterpart. Perturbation theory does not, of course, say whether the assumption of a crystalline ground state for metallic hydrogen is valid. However within such an assumption, it offers a means for deciding on the preferred lattice; and in this context the calculations described above appear to be the first for a metal that go beyond the harmonic approximation.

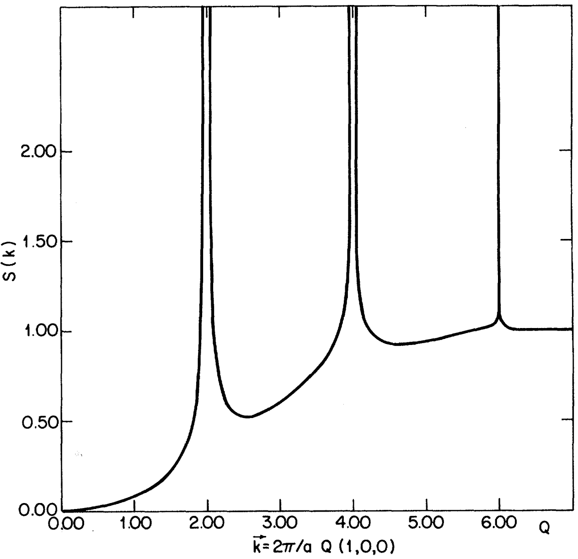

FIG. 2. Structure factor $S(\vec{k})$ for fcc metallic hydrogen (at $r_s = 1.36$ and $T = 0$°K) for $\vec{k}$ along [100]. The frequencies and polarization vectors used to compute $S(\vec{k})$ are the solutions of the self-consistent equations.

---

*Work supported by the National Aeronautics and

Space Administration under Grant No. NGR-33-010-188 and in part by the National Science Foundation through the facilities of the Cornell University of Materials Science Center (Grant No. DMR-72-03029), Technical Report No. 2749, and Contract No. DMR 74-23494.

†Present address: Department of Meterology, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

[1] V. Heine and D. Weaire, *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 250.

[2] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

[3] E. G. Brovman, Yu Kagan, and A. Kholas, Zh. Eksp. Teor. Fiz. 61, 2429 (1971), and 62, 1492 (1972) [Sov. Phys. JETP 34, 1300 (1972), and 35, 783 (1972)].

[4] L. G. Caron, Phys. Rev. B 9, 5025 (1974).

[5] G. A. Neece, F. J. Rogers, and W. G. Hoover, J. Comp. Phys. 7, 621 (1971).

[6] T. Schneider, Helv. Phys. Acta 42, 957 (1969).

[7] J. Hammerberg and N. W. Ashcroft, Phys. Rev. B 9, 409 (1974).

[8] N. S. Gillis, N. R. Werthamer, and T. R. Koehler, Phys. Rev. 165, 951 (1968). For a recent review, see T. R. Koehler, in *Dynamical Properties of Solids*, edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1975), p. 1.

[9] P. Choquard, *The Anharmonic Crystal* (Benjamin, New York, 1971).

[10] This corresponds to a representative pressure of about 1.7 Mbars.

[11] For a static lattice, the energy (to second order) is conventionally written as $E = E_0 + E_\mathrm{M} + E_b^{(2)} + \cdots$, where E_0 is the energy of the homogeneous interacting electron gas, E_M the Madelung energy, and $E_b^{(2)}$ the second-order band-structure energy. To obtain Eq. (1), we must not only include dynamics but also combine E_M and $E_b^{(2)}$ so that they each contribute to the potential Φ.

[12] The ratio of $\{\langle \vec{u}^{\,2}\rangle\}^{1/2}$ to nearest-neighbor distance is readily calculated (from the self-consistent frequencies and polarizations) to be 0.1687 for the fcc structure at $r_s = 1.36$ [see D. Straus, thesis, Cornell University Materials Science Laboratory Report No. 2739 (unpublished)]. This should be compared to the value for Na which for *melting* ($p = 0$) is 0.123 [D. Stroud and N. W. Ashcroft, Phys. Rev. B 5, 371 (1972)].

[13] A plot of the static ground-state Gibbs energy G (at a pressure corresponding to the fcc crystal of Fig. 1) looks almost identical to the static-energy plot of Fig. 1; and minimization of G at constant p is, in this case, essentially equivalent to E at constant r_s.

[14] We have used for $\epsilon(k)$ the Hubbard-Geldart-Vosko form, and in the structure-*independent* terms of Eq. (1) we have used the Nozières-Pines approximation to the correlation-energy contribution.

[15] C. Friedli and N. W. Ashcroft, Phys. Rev. B 12, 5552 (1975).

[16] Full details of the calculational methods are found in Straus, Ref. 12. The important point is that the correlation functions $\lambda_{\alpha\beta}(\vec{X})$ were computed using the techniques of D. M. Straus and N. W. Ashcroft [Phys. Rev. B 14, 448 (1976)], except that the *full* directional dependence rather than the angular average of the $\vec{q}\to 0$ portion of the integrand in Eq. (3) has been completely included.

[17] D. M. Straus and N. W. Ashcroft, Phys. Rev. B 14, 448 (1976).

[18] Straus, Ref. 12.

Renormalized Pair Interactions and Three-Body Polarization Forces in Solid Hydrogen*

S. Luryi and J. Van Kranendonk
Department of Physics, University of Toronto, Toronto, Ontario M5S 1A7, Canada

and

J. Noolandi
Xerox Research Centre of Canada Limited, Mississauga, Ontario L5L 1J9, Canada

(Received 18 November 1976)

We find that the inclusion of the pseudo-three-body forces between all neighbors does not remove the difficulty of obtaining a consistent analysis of the microwave spectrum of solid hydrogen observed by Hardy and Berlinsky. We propose a novel anisotropic interaction, due to the deviation from axial symmetry of the pair distribution function of neighboring molecules, leading to a satisfactory interpretation, and yielding new information about lattice dynamics.

The intermolecular interactions and the rotational and lattice-vibrational motions of the molecules in solid hydrogen have been studied extensively in recent years; and attempts at comprehensive theoretical treatments have also been published.[1-3] An important advance in our knowledge in this field is the recent observation by Hardy and Berlinsky[4] of the microwave spectrum of bound pairs of ortho molecules in a parahydrogen crystal. These authors interpreted this spectrum on the basis of previous theoretical work of Harris,[3] but they came to the conclusion that the