Quantum-solid behavior and the electronic structure of the light alkali metals

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The identification of the 9R rhombohedral phase for the low-temperature structure of lithium offers a possible resolution of observed disparities in its optical properties and new experimental opportunities for a direct determination of the electron-ion interaction. The latter is central to the construction of effective ion-ion interactions which in turn control both lattice statics and dynamics and the ultimate choice of structure. The *static* 9R phase, whose Jones zone is actually quite "spheroidal," appears electronically favored by a Hume-Rothery argument. The lattices are, however, far from static; nevertheless, the most important of the dynamic effects can still be incorporated within the definition of state-dependent effective potentials acting between quasistatic ions. From these a possible physical source of the *driving force of the transition* can be identified.

At low temperatures the light alkali metals undergo structural transformations[1,2] from body-centered-cubic[3] (bcc, here referred to by *C*) to the far less symmetric δ-Sm structure. The latter is a close-packed rhombohedral phase (9R, here referred to by *R*); its eventual identification with a possible low-temperature structure for lithium was first made by Overhauser.[4] Though quite different, the two phases can actually be connected by a continuous variation of atomic coordinates, an observation of Nagasawa's[5] that was used by Kelly[6] to treat the variation in energy of *static* sodium when the ions were taken along such a path. It was found that a weak energy barrier separates the two end points and its origin traced to the combined effects of electrostatic (Madelung) and electronic (band-structure) contributions to the ground-state energy. But, on account of their light masses, the lattices in lithium and sodium are quite far from static, even at zero temperature. One of the aims of this paper is to show that because of significant quantum-solid effects, a self-consistent inclusion[7] of electron response and lattice dynamics may actually be required to fully resolve the structural subtleties of the martensites. If the structures are indeed *equilibrium* arrangements, the problem is tractable in principle using existing techniques (see Ref. 7) but requires a reasonably accurate specification of the effective electron-ion interaction. A second objective of this paper therefore is to show that the screened electron-ion interaction v, necessary in the determination of the structural energies, is potentially accessible using optical probes, providing the metal is verifiably in a single-crystal or polycrystalline 9R phase. Furthermore, the very existence of the 9R phase leads to a possible resolution of some longstanding vagaries in the measured optical properties of lithium.

The martensitic transformations in lithium and sodium occur at temperatures sufficiently low that in discussing the thermodynamic functions the electron systems can reasonably be taken in their ground states.[8] At one atmosphere an appropriate thermodynamic function for the

structural problem is the Helmholtz free energy $F(V,T)$, where V is the volume in which there are N ions. Within the Born-Oppenheimer approximation it is a unique functional of the equilibrium ionic densities $\rho_i(\mathbf{r})$. Given two possible structures (C and R, say) phase preference at a temperature T can be examined from the behavior of the difference $\Delta F = F^C - F^R$, namely

$$\Delta F(V,T) = \Delta E_m + \Delta E_e + \Delta F_i \, , \tag{1}$$

where

$$\Delta E_m(V,T) = \frac{N}{2V} \sum_{\mathbf{q} \neq 0} \frac{4\pi e^2}{q^2} [S^C(\mathbf{q},T) - S^R(\mathbf{q},T)] \tag{2}$$

is the difference in average Madelung energy,

$$\Delta E_e(V,T) = \frac{1}{V} \sum_{\mathbf{q} \neq 0} v_{\mathbf{q}} \int_0^1 d\alpha [\langle \hat{\rho}_i^C(\mathbf{q}) \rho_e^C(-\mathbf{q};\alpha) \rangle_i \\ - \langle \hat{\rho}_i^R(\mathbf{q}) \rho_e^R(-\mathbf{q};\alpha) \rangle_i] \tag{3}$$

is the electronic response energy, and

$$\Delta F_i(V,T) = \tfrac{1}{2} \sum_{\lambda,\mathbf{q}} \hbar\omega_\lambda^C(\mathbf{q}) \\ + k_B T \sum_{\lambda,\mathbf{q}} \ln\{1 - \exp[-\beta\hbar\omega_\lambda^C(\mathbf{q})]\} \\ - \left[\tfrac{1}{2} \sum_{\lambda,\mathbf{q}} \hbar\omega_\lambda^R(\mathbf{q}) \right. \\ \left. + k_B T \sum_{\lambda,\mathbf{q}} \ln\{1 - \exp[-\beta\hbar\omega_\lambda^R(\mathbf{q})]\} \right] \tag{4}$$

is the difference in lattice vibrational free energies in the small oscillations problem. In (2) the quantities $S(\mathbf{q},T) = N^{-1}\langle \hat{\rho}_i(\mathbf{q})\hat{\rho}_i(-\mathbf{q}) \rangle - N\delta_{q,0}$ are the static density-density correlation functions for the respective dynamic lattices, one of them (C) a Bravais lattice with three acoustic branches $[\omega_\lambda(q); \lambda=1,2,3]$, the other ($R$)

possessing a basis of three atoms (see below) and thus an additional six optic branches [$\omega_\lambda(q)$; $\lambda=1,\ldots,9$]. The induced electron density [$\rho_e(\mathbf{q};\alpha)$ in (3)] is considered coupled to the ions by a pseudopotential[9] v_q, but at strength α ($0<\alpha<1$). The density operator for these ions is $\hat{\rho}_i(\mathbf{q})$; the averages $\langle\ \rangle_i$ in (3) are over their states. If the electron response density is itself developed in the pseudopotential, then $\rho_e(-\mathbf{q};\alpha)=\alpha\chi(q)v_q\hat{\rho}_i(-\mathbf{q})+\cdots$, where $\chi(q)$ is the linear response function for the fully interacting electron gas. It is customary to combine (2) and (3) at this level of linear response[10] to give

$$\Delta E_p = \Delta E_m + \Delta E_e = \frac{N}{2V}\sum_{q\neq0}\phi(q)[S^C(\mathbf{q},T)-S^R(\mathbf{q},T)]\ ,$$

(5)

with $\phi(q)$ being the Fourier transform of an effective pair interaction between ions, i.e.,

$$\phi(q)=(4\pi e^2/q^2)\{1+(v_q/v_{cq})^2[\epsilon^{-1}(q)-1]\}\ ,$$

(6)

where $\epsilon(q)$ is the dielectric function of the electron gas and v_{cq} a point-ion potential. Ion dynamics is now seen to enter both directly in ΔF_i but also indirectly in the correlation functions $S(\mathbf{q},T)$. Many treatments[10] of the theoretical basis for the observed structures in the simple metals take $S(\mathbf{q},T)$ to be given by its *static*-lattice value, that is, $S(\mathbf{q},T)=N\sum_K f_K\delta_{qK}$, where $\{\mathbf{K}\}$ is the set of reciprocal-lattice vectors for the lattice and $f_\mathbf{K}$ is the (geometric) structure factor per atom if the structure has a basis. Then E_m and E_e reduce to lattice sums which can be evaluated by relatively standard procedures. Typical static-lattice structural *differences* in energy ($\Delta E_m+\Delta E_e$) amount to $\lesssim10^2$ K/atom, depending on the system. In the present example the occurrence of the 9R structure at low temperatures can be supported for a *static* lattice by a standard Hume-Rothery argument, since with 38 zone planes (see below) more of the lower-energy electrons are in states of higher density and the overall electronic energy is expected to be reduced. Such an argument marginally favors 9R over the hexagonal-close-packed (hcp) structure, for example, though the differences are certainly small.

But as is known from the existence of both strong and markedly temperature-dependent diffuse x-ray scattering in simple metals, $S(\mathbf{q},T)$ must actually be quite far from a sequence of δ functions. This is especially so for the light "quantum metals," lithium and sodium, as is evident from Figs. 1 and 2, where the quantity

$$S(\mathbf{q},T)=\sum_\mathbf{R} e^{-i\mathbf{q}\cdot\mathbf{R}}e^{-2w}e^{\langle\mathbf{q}\cdot\mathbf{u}(0)\mathbf{q}\cdot\mathbf{u}(\mathbf{R})\rangle_i}$$

(7)

is plotted for both. Equation (7) represents the form taken by the correlation functions for Bravais lattices in either the harmonic or self-consistent harmonic approximations.[12] Here e^{-2w} is the usual Debye-Waller factor and $\mathbf{u}(\mathbf{R})$ is the displacement of an ion near lattice site $\mathbf{R}$. Significant quantum solid behavior in these metals is very clear from the substantial values taken by $S(\mathbf{q},T)$ *between* the Bragg peaks, even at $T=0$. Figure 2, also from Ref. 12, shows the strong temperature dependence[13] of
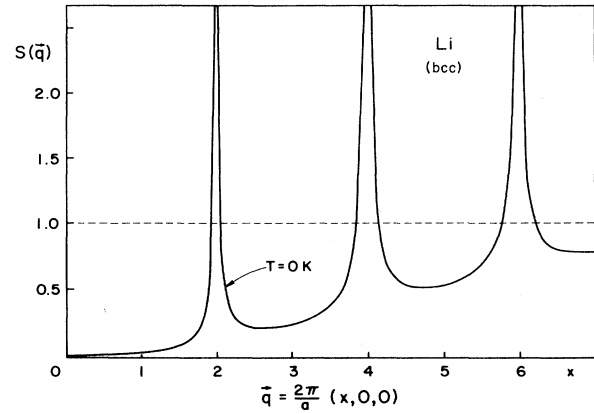

FIG. 1. Ground-state density-density correlation function $S(\mathbf{q},0)$ for bcc lithium (from Ref. 12). Here $\mathbf{q}$ is directed along the (1,0,0) direction: the strong structure between the Bragg peaks is a consequence of large zero-point motion.

the structure factor. The crucial point is this: because of the quantum nature of these metals there is a large, temperature-dependent transfer of weight from the Bragg peaks to the continuum. The complex intertwining of electronic and lattice degrees of freedom is now evident, and they must be addressed on an equal footing by, for example, the methods of Ref. 7. However, a general consequence is that differences in structural energies, *already small* for static lattices, must be diminished still further. Moreover, such differences as are present at $T=0$ are also expected to progressively decline as the temperature increases, and with it the diffuse component of $S(\mathbf{q},T)$. This matter can be investigated in detail *pro-*
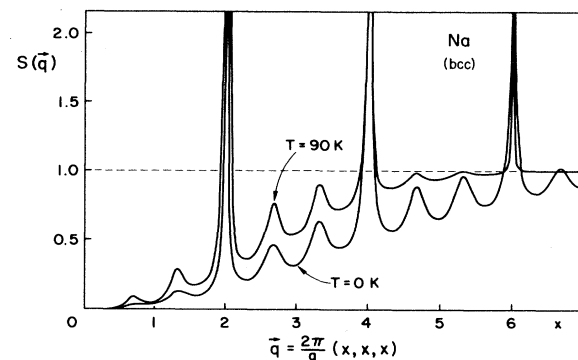

FIG. 2. Correlation functions $S(\mathbf{q},T=0)$ and $S(\mathbf{q},T=90$ K) for bcc Na (again from Ref. 12). Here $\mathbf{q}$ is along the [111] direction. The maxima between the Bragg peaks correspond to the "extra reflections" as seen in x-ray scattering (see text). They are markedly temperature dependent. In terms of diffraction, this behavior is manifested just as strongly for electrons as it is for x rays, and hence is an important factor in energetics.

vided v_q is known, but assuming for the moment that the proposition is correct, then the issue of structural preference centers on ΔF_i and especially its entropic components.

In this respect the structural manifestation in (4) of the differences between bcc and 9R is quite interesting. At high temperatures[14] the ionic free-energy difference will take the form

$$\Delta F_i/N = \Delta F_i(0)/N + 3k_BT\ln\bar{\omega}_l^C/\bar{\omega}_l^R \ , \qquad (8)$$

where $\Delta F_i(0)/N$ is the difference in zero-point energy, per atom, and $\bar{\omega}_l$ is the average over modes of the logarithms of the frequencies. Now the rhombohedral structure has a basis of three atoms per primitive cell and a zone whose volume is $\frac{1}{3}$ that of the corresponding bcc zone. After conversion from bcc to 9R, $\frac{2}{3}$ of the modes are promoted from acoustic to optic character. If one imagines embedding the 9R zone within the bcc zone, then formation of the polyatomic phase is revealed by a splitting of the branches at the inner zone faces, and a folding back of the (previously acoustic) branches. Because of the upward splitting of the optic modes, and the fact that the bcc phase is elastically quite anisotropic with low-lying Zener modes (see below), it is expected that $\bar{\omega}_l^C < \bar{\omega}_l^R$, so that from

$$\Delta F \approx \Delta E_p(T) + \Delta F_i(0) - 3Nk_BT\ln(\bar{\omega}_l^R/\bar{\omega}_l^C) \qquad (9)$$

it is apparent that a bcc phase can now be favored at high temperatures on entropic grounds even if the terms $\Delta E_p + \Delta F_i(0)$ indicate a preference for the rhombohedral structure at low temperature. Two comments may be made here: first, since the behavior of $S(\mathbf{q},T)$ is revealed in the thermal diffuse scattering, the information required to establish the importance of the relative entropies should be accessible by x-ray measurement, provided samples can be obtained entirely in a 9R phase. Second, even in the absence of this information, the required $S(\mathbf{q})$ are still calculable by the methods of Refs. 7 and 12, again provided the electron-ion coupling v_q is accurately known. But here too the existence of the 9R phase plays a very special role. In this phase the electronic structure is sufficiently different from bcc that v_q may be *directly* accessible using optical reflectivity measurements.

To see this it is necessary to establish the essential attributes of a nearly-free-electron structure in the 9R phase and to specify the reciprocal lattice. Let $\mathbf{a}_i(i=1,2,3;\ |\mathbf{a}_i|=a=7.807$ Å for lithium) be the primitive vectors of a rhombohedral cell. The corresponding vectors $\mathbf{b}_i$ of the reciprocal lattice then have magnitudes $(=|\mathbf{b}_i|)$

$$b = (2\pi/a)[(1+\cos\alpha)/(1+2\cos\alpha)(1-\cos\alpha)]^{1/2} \ , \qquad (10)$$

where α is the angle between any two $\mathbf{a}_i$. For ideal rhombohedral close packing $\alpha = \cos^{-1}\frac{35}{38} = 22.9195°$ (the experimental value for Li being 22.93°). Correspondingly, the angle β between any two of the $\mathbf{b}_i$ is given by $\cos^{-1}[-\cos\alpha/(1+\cos\alpha)]$, or $\cos\beta = -\frac{35}{73}$ for the ideal structure. An arbitrary reciprocal-lattice vector has the form $\mathbf{K} = \mathbf{K}_{lmn} = l\mathbf{b}_1 + m\mathbf{b}_2 + n\mathbf{b}_3$, and given that the

three-atom basis is $(0,0,0)\pm\frac{2}{9}(\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3)$, the structure factor per atom $f_\mathbf{K}$ is therefore

$$f(lmn) = \frac{1}{3}[1+2\cos4\pi(l+m+n)/9] \ . \qquad (11)$$

With three electrons per rhombohedral cell, the Fermi wave vector is[15]

$$k_F = (2\pi/a)[9/8\pi(1-\cos\alpha)(1+2\cos\alpha)^{1/2}]^{1/3} \ , \qquad (12)$$

or $2k_F = (2\pi/a)2.7817$ for the ideal structure. Further, the magnitude of a typical reciprocal-lattice vector is

$$K_{lmn} = (2\pi/a)(l^2+m^2+n^2)^{1/2}$$
$$\times[1+2\cos\beta(lm+mn+nl)/(l^2+m^2+n^2)^{1/2}] \ , \qquad (13)$$

from which the key dimensionless ratios $2k_F/K_{lmn}$ are determined. These are listed in Table I for those reciprocal-lattice vectors (38 in all) that establish a Jones zone by a standard Wigner-Seitz construction.

The crucial difference between bcc and 9R is now seen by selecting the shortest reciprocal-lattice vectors $\mathbf{K}$ and plotting the corresponding free-electron bands, as has been done in Fig. 3 for the static lattice. In the presence
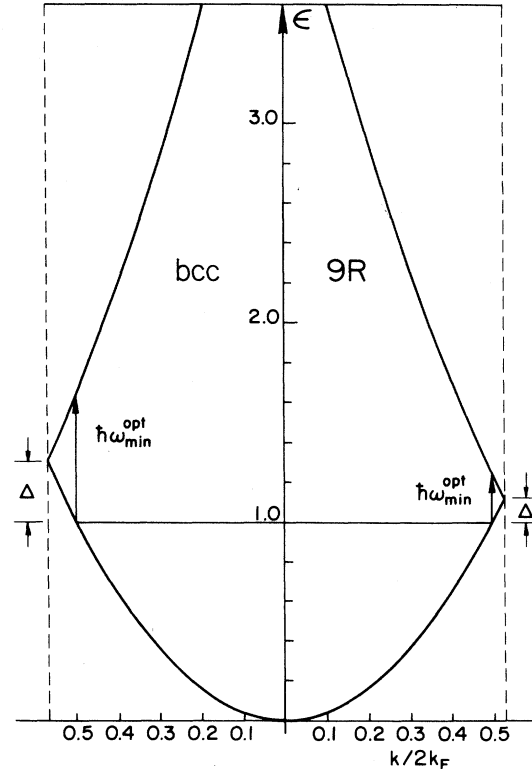

FIG. 3. Free-electron energies (in units of $\varepsilon_F = \hbar^2k_f^2/2m^*$) plotted as a function of wave vector (in units of $2k_F$) for bcc and rhombohedral structures along the shortest reciprocal-lattice vectors. Here Δ represents the smallest required splitting at the zone face by the crystalline potential for zone contact by the Fermi surface. Correspondingly, if no zone contact occurs, $\hbar\omega_{min}^{opt}$ represents (to second order in band gaps) the smallest energy for interband absorption.

TABLE I. Reciprocal-lattice and nearly-free-electron properties of the $9R$ structure (three electrons per cell) and also given below for bcc structure. Here k_{lmn} refers to the reciprocal-lattice vector $l\mathbf{b}+m\mathbf{b}_2+n\mathbf{b}_3$, where its magnitude is given in units of $2\pi/a$; the second column tabulates $2k_F/|\mathbf{K}_{lmn}|$, where $2k_F$ is the diameter of the Fermi sphere. In the third column are values of the geometric structure factor per atom. Next, is the quantity $\Delta/\epsilon_F=[\epsilon(K_{lmn}/2)-\epsilon_F]/\epsilon_F$. The quantity V_{min} is the corresponding minimum value of the magnitude of the pseudopotential component (for zone plane $\mathbf{K}_{lmn}$) required to produce contact of the Fermi surface with the zone plane. (In parentheses are the values required for Li assuming a band mass of 1.6.) Finally, $\hbar\omega_{IB}$ represents the interband absorption onset energy for the zone plane associated with $\mathbf{K}_{lmn}$. Note that the bcc structure has a zone bounded by 12 planes; the $9R$ structure has 38 planes.

$\mathbf{K}_{lmn}$	K_{lmn}/K_{100}	$2k_F/K_{lmn}$	F_{lmn}	Δ/ϵ_F	$V_{min}(lmn)/\epsilon_F$	$\hbar\omega_{IB}(lmn)/\epsilon_F$
			$9R$			
(1,0,0)	1.000 00	0.950 67	0.4491	0.1065	0.2371 (0.70)	0.2183 (0.65)
(1,1,0)	1.020 34	0.931 72	0.2931	0.1239	0.5184 (1.54)	0.3146 (0.93)
(1,1,1)	0.351 12	2.707 51	0	0.3338		
(1,1,2)	1.097 94	0.865 86	0.8440	0.4702	0.3955 (1.17)	0.7156 (2.12)
(1,2,2)	1.152 72	0.824 72	0.8440	0.8340	0.5571 (1.65)	1.0308 (3.05)
(2,2,2)	0.702 25	1.353 75	0	1.0613		
(2,2,3)	1.287 45	0.738 41	0.2931	0.2277	2.8455 (8.43)	1.9191 (5.69)
(2,3,3)	1.364 92	0.696 50	0.4491		2.3633 (7.00)	2.5025 (7.41)
(3,3,3)	1.053 37	0.902 50	1.0000		0.2277 (0.67)	0.4788 (1.42)
			bcc			
(1,1,0)	1.0000	0.877 31	1.0000		0.2933 (0.87)	0.6376 (1.89)
(2,0,0)	1.4142	0.620 35	1.0000		1.5985 (4.80)	3.946 (11.69)

of a weak periodic potential v, the degeneracies at the zone faces are split by $\pm|f_K v_K|$, where v_K is proportional to the corresponding Fourier component of v. For the light alkali metals it is known that in the bcc phase this splitting is insufficient to cause contact of the Fermi surface with the zone. However, as seen from Fig. 3 contact becomes a very likely prospect in the $9R$ phase, even allowing for any reduction caused by f_K.

This possibility can be made semiquantitative by establishing the gap (Δ) to be bridged (see Fig. 3) and the minimum value of v_{lmn} required to cause zone contact. These values are listed in Table I; it is clear that for at least eight zone planes the conditions are far easier to meet for $9R$ than is the case for the bcc phase. An immediate consequence of Fermi-surface zone contact is that interband absorption can take place *at*, rather than *near*, the zone face. If the bands happen to be parallel in that zone face, then the optical joint density of states becomes very large, in fact even singular, at $\hbar\omega=|2f_K v_K|$, as is known from the corresponding case of the polyvalent simple metals.[16] The situation is best described by comparison with the bcc case where the optical properties below a few eV are normally ascribed to intraband (Drude) excitation augmented by *weak* interband behavior. The onset of the latter is at $\hbar\omega_{IB}\doteq 4\epsilon_F(K_{110}/2k_F-1)=0.6376\epsilon_F$ and from Table I and Fig. 3 is seen to be determined almost entirely by the structure, at least to within corrections second order[16,17] in v_K. This is in notable contrast to the edge structure that develops in the zone-contact case and which appears at energies characterized by a property *not* primarily of the structure but of the electron-ion interaction itself.[16,18] If the energy bands plotted *in* the zone face depart from true parallelism, the absorption remains strong but is not singular. Instead there is a large maximum relatively close to a sharp onset[19] of absorption; this case is espe-

cially pertinent to nonlocal electron-ion interactions. Nevertheless, the optical properties still provide a *direct* measurement of v_q.

There is another very significant difference between optical response in systems with spherical Fermi surfaces (one electron per cell) and their zone-contact counterparts. In the latter the distortions of the Fermi surface from spherical are first order in v_K/ϵ_F and these lead to changes in the density of states which significantly augment contributions arising from scaling of the average bandwidth. In consequence, the optical effective mass acquires corrections that are also first order in v_K/ϵ_F, and as found for polyvalent simple metals, these corrections are substantial.[16] This again is in some contrast to the spherical Fermi-surface case, where the optical effective mass is not very different from the band mass.

These essential distinctions lead to a possible clarification of the experimental situation as it presently exists for the optical constants of lithium. Experimentally there has been little agreement on the optical properties of lithium (and in fact, in the alkali metals quite generally). However, with an alternative structure now identified and one that is separated by exceedingly small energies from bcc, one can now ask whether the less-symmetric $9R$ phase might be present in part (either in layer or composite form) at the interfaces or boundaries where the optical properties are measured. The early measurements by Hodgson[20] were by reflection from a (silica) glass-lithium interface and revealed structure around 3 eV which tallies with $\hbar\omega_{IB}$ (onset) for (110) zone faces in the bcc phase. The characteristics of the absorption were, however, somewhat atypical of the other alkali metals, and also different from the results of Mathewson and Myers[21] taken at vacuum interfaces with films deposited at *low temperatures* on both quartz and sapphire substrates. For the quartz substrate it was observed that the

optical conductivity shifted *very* noticeably with time. Mathewson and Myers noted, of course, the possibility of the nucleation and growth of a second phase and indeed in a later paper[22] the postulated case of hexagonal close packing was examined in detail. Almost contemporaneously, Inagaki *et al.*[23] published results for lithium films deposited on quartz at room temperature, the measurements being taken through the quartz-lithium interface. For the most part far more stable behavior was obtained; however, Inagaki *et al.* also presented evidence of "anomalous absorption" which seemed to be associated with an onset of structure at about $\hbar\omega \sim 1$ eV. This energy is not at all inconsistent with the corresponding onset energies inferred by Mathewson and Myers from their data, as can be seen in Fig. 4. As it now turns out, it i also quite in line with zone-contact absorption for a 9R phase, as will be discussed next.

The possibility that as a consequence of lattice matching (or of conditions of local strain, or even from a balance between bulk and surface free energies) a significant component of the 9R phase is present in the optically active region is given further weight by the observation[21,22] that the optical mass appears to increase by about 30% during the transition from the high-temperature phase, presumed to be bcc, to the less symmetric low-temperature phase. This behavior is fully consistent with the loss of Fermi-surface area brought on by zone contact. Because of possible mixed-phase or composite

FIG. 4. Examples of the real part of the optical conductivity in lithium according to deposition condition (see text). Curve *A* is taken from the work of Inagaki *et al.* (Ref. 24); curve *B* is from Mathewson and Myers (Ref. 22). The dotted curve gives the onset of nearly-free-electron optical absorption for a spherical Fermi surface; the dashed curve indicates the onset of edge structure (see Table I).

effects, it is difficult to determine the corresponding onset of 9R structure absorption with precision, but it seems to be quite near $\hbar\omega \approx 1$ eV (see Fig. 4). If this is identified with the (100) planes, then $|2f_{100}v_{100}^{R}| \approx 1$ eV and since $f_{100} = 0.4491$ (Table I) this places $|v_{100}^{R}|$ likewise at about 1 eV. But, in the bcc phase, a number of band calculations[24] also place v_{110}^{R} rather firmly in this range, and since $K_{100}^{R} \approx K_{110}^{C}$, the required condition on v_{100}^{R} for zone contact is therefore completely in line with the current view on the electron structure for the cubic structure. Further, it is apparent from Table I that the (3,3,3) planes are also candidates for zone contact; multiple structure in the optical response from a pure 9R sample may also be expected.[22]

The low-temperature data in lithium,[25] both optical mass and onset of absorption, therefore appear to be consistent with the (somewhat variable) presence of the 9R phase. If this interpretation is correct and if through lattice matching or other strategies a 9R film can be prepared on a suitable substrate,[26] then the optical properties become in principle a powerful and *direct* probe of the electron-ion interaction[27] through the onset condition $\hbar\omega|2f_{K}v_{K}|$. As discussed above, this electron-ion interaction is of central importance in determining the Helmholtz free energy F of both high- and low-temperature structures, assuming them to be equilibrium phases.

Returning therefore to the structural issue, it is possible to incorporate the dynamics into a picture that reveals very clearly the eventual likelihood of a low-temperature martensite. To do so it is only necessary to realize that the structural energy of a *dynamic* metal can formally be rewritten as a summation over a *static* lattice of a state-dependent pair interaction[28] defined by [see (5) and (7)]

$$\phi_T(0,\mathbf{r}) = \frac{1}{8\pi^3} \int d\mathbf{q}\, e^{-i\mathbf{q}\cdot\mathbf{r}} \phi(q) e^{-2w} e^{\langle \mathbf{q}\cdot\mathbf{u}(0)\mathbf{q}\cdot\mathbf{u}(\mathbf{r})\rangle} , \qquad (14)$$

with $\phi(q)$ depending noticeably on v_q. As shown in Ref. 28 for sodium, the effect of this modification is to soften the repulsive region of ϕ_T as temperature increases; or, put another way, as temperature declines, ϕ_T becomes shorter ranged and hence closer to a rigid-sphere type of interaction which is well known to possess the Zener-mode instability[29] in the bcc structure. In fact, the smallness of the associated elastic constant $c_{11} - c_{12}$ is a key feature of some Landau-theory descriptions of the transition.[30,31] Thermodynamic arguments of the kind discussed above generally do not address the issue of specific mechanisms. However, in the microscopic picture just presented, the temperature dependence of the elastic constants can actually be visualized in terms of the state-dependent pair potential ϕ_T. The structural energy appears as $\frac{1}{2} \sum_{\mathbf{R}}' \phi_T(\mathbf{R} - \mathbf{R}')$ with shear or elastic distortion now manifesting itself in the modification of the sites $\mathbf{R}, \mathbf{R}'$ themselves. Note that ϕ_T is defined with respect to an underlying lattice (and its dynamics[32]) and, being embedded in a crystalline environment is not spherically
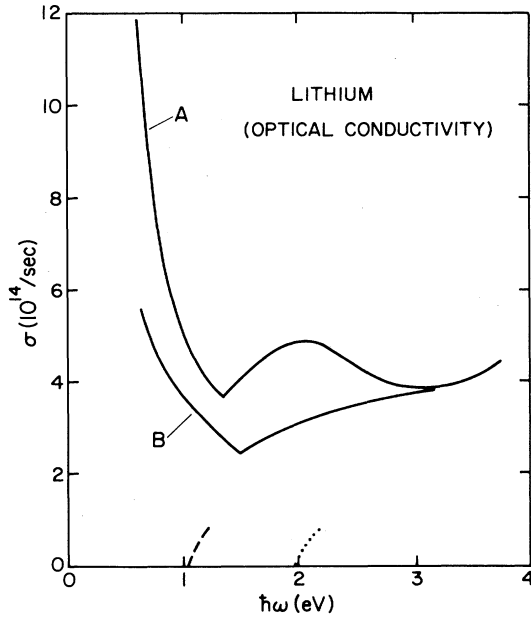
symmetric. Anisotropies in this quantity favoring a particularly low-shear constant can therefore arise not only as a direct consequence of the chosen structure, but also *indirectly* through the dynamical contributions to ϕ_T. It should be recognized that ϕ_T is just a partial contribution to the more general quantity $\delta F/\delta \rho_i(\mathbf{r})$ which *is* the effective one-body interaction arising from interactions with all other particles in the system. The gradient of $\delta F/\delta \rho_i(\mathbf{r})$ therefore gives the effective force on a particle arising from all others. Accordingly, the identification of *the driving force of the transition* must be sought in this term, at least for states near the end points. It is suggested that the complete determination of ϕ_T is a possible first step in this task.

Finally, with respect to the importance of dynamics in these metals, Overhauser[4,33] has correctly drawn attention to the curious absence of a bulk superconducting phase in lithium.[34] Actually, there are reports[35] that lithium is superconducting in thin films deposited at low temperatures, but the status of these measurements is not clear. A key quantity is the electronic density of states at the Fermi energy. Measurements of the low-temperature specific heat lead to a thermal mass (m_t/m) with a value[36] 2.3. This contains some renormalization by the electron-phonon interaction estimated to be[37] $(m_{e\text{-ph}}/m) \sim 1.4$, at least for bcc-phase phonons. This leaves a band mass of about 1.6, or, in lithium, a bandwidth of 3 eV which seems to accord well with the bcc (spherical Fermi surface) optical mass. Overhauser also makes the interesting observation that the electron-phonon-mass enhancement may actually be larger in the 9R phase. If this were the case, then to be consistent with the thermal mass the band mass would need to be correspondingly reduced. As it happens, this is quite in accord with optical mass measurements in the presumed 9R phase and the rigorous one-electron bound,[38]

$$\left[\frac{m_{\text{opt}}}{m^*}\right] \leq \left[\frac{S_F^0}{S}\right]^2 ,$$

since the actual Fermi-surface area (S_F) will be less than the spherical value (S_F^0) through the action of zone contact. Within the assumption of phonon mediated electron pairing superconductivity would then appear to be absent[39] because although the electron-phonon enhancement may be larger in 9R than in bcc the increase is evidently more than balanced by the decline in the electronic density of states.

It is clear that more experimental information on the electronic structure and lattice dynamics of the 9R phase is required in order to resolve this and other issues. The experimental challenge is whether the metals can be prepared wholly in such phases, and whether the role of interfaces and surfaces is then crucial in the matter of stability. Most certainly the 9R real-space structure leads to some new and intriguing features in the electronic structure. For example, the low-temperature galvanomagnetic properties will be crucially different from those of the bcc structure if zone contact occurs. Fermi-surface contact with the zone guarantees extended and even open orbits and extremal orbits at the contacted faces whose orbit diameters will be a small fraction of the major diametral orbits. Determination of these dimensions by galvanomagnetic methods can also fix the electron-ion interaction with considerable precision.[40] On a final experimental note, it may be observed that the less-symmetric 9R phase offers a range of interesting excitations[41] even if zone contact does *not* occur. For example, in a metal with the density of potassium, Table I indicates interband features beginning at about 0.5 eV.[42] Other stackings or even heavily faulted phases could permit similarly low excitations.

[1]C. S. Barrett, Phys. Rev. **72**, 245 (1947).

[2]C. M. McCartley, C. W. Thompson, and S. A. Werner, Phys. Rev. B **22**, 574 (1980); R. Berliner, O. Fajen, H. G. Smith, and R. J. Hitterman, Bull. Am. Phys. Soc. **33**, 615 (1988).

[3]The centered cubic phase is a common post-freezing structure and is predicted by density-wave-instability arguments [see G. Baym, H. A. Bethe, and C. J. Pethick, Nucl. Phys. **175A**, 225 (1971), and S. Alexander and J. McTague, Phys. Rev. Lett. **41**, 702 (1978)].

[4]A. W. Overhauser, Phys. Rev. Lett. **53**, 64 (1984).

[5]A. Nagasawa, J. Phys. Soc. Jpn. **40**, 1021 (1976).

[6]M. J. Kelly, J. Phys. F **9**, 1921 (1979).

[7]This point has already arisen in the context of the ground-state dynamic structure of metallic hydrogen. [See D. M. Straus and N. W. Ashcroft, Phys. Rev. Lett. **38**, 415 (1977).]

[8]This is not necessarily the case for martensites at higher temperatures; see R. E. Watson and M. Weinert, Phys. Rev. B **30**, 164 (1984).

[9]The argument is given for local pseudopotentials, but this is not a necessary simplification.

[10]See, for example, N. W. Ashcroft and D. C. Langreth, Phys. Rev. **155**, 682 (1967). The importance of terms beyond linear response is discussed by J. Hammerberg and N. W. Ashcroft, Phys. Rev. B **9**, 409 (1974).

[11]K. Lonsdale and H. Smith, Nature (London) **148**, 628 (1941). See also K. Lonsdale, Proc. Phys. Soc. London **54**, 314 (1942).

[12]D. M. Straus and N. W. Ashcroft, Phys. Rev. B **14**, 448 (1976). The pseudopotentials v_q used in those calculations were taken from liquid-state properties. The zone sums required in the evaluation of the two-site averages in (6) are evaluated using

special-point techniques.

[13]The maxima are the "extra reflections" or the Faxen-Waller structure of the x-ray case [see M. Born, Rep. Prog. Phys. **9**, 294 (1942–43)]. Their occurrence is readily understood by excerpting from (6) the one-phonon component which in an isotropic polarization-independent model is $S_1(\mathbf{q},T) = e^{-2w}(\hbar^2 q^2/2M)[\frac{1}{2}+(e^{\beta\hbar\omega_k(\mathbf{q})}-1)^{-1}]/\hbar\omega_k(\mathbf{q})$, where M is the mass of the ion and $\mathbf{k}(q)$ is the vector $\mathbf{q}$ reduced to the first zone by an appropriate reciprocal-lattice vector. Any particularly low-lying frequency will cause a sequence of temperature-dependent maxima along certain directions (see Ref. 12). The point at issue here is the degree to which the "extra spots" are manifested in electronic structure, and indeed how the band structure itself is *defined* for a highly dynamic metal. Nor is this argument restricted to the normal crystalline state. For example, though diffuse scattering must overlap Bragg scattering in a *quasicrystal* the difference in temperature dependence between the two can still be used in principle to determine the characteristics of dynamics.

[14]For high-temperature martensites the entropic preference can be approximately related to difference in coordination between the phases [J. Friedel, J. Phys. (Paris) Lett. **35**, L59 (1974)]. Though coordination is clearly a factor here, the different manifestation in F of acoustic and optic modes is the controlling factor at lower temperatures. The difference between the bcc and $9R$ phonons in Li has been discussed by Wang and Overhauser, Phys. Rev. B **34**, 8401 (1986).

[15]The volume of the primitive rhombohedral cell is $a^3(1-\cos\alpha)(1+2\cos\alpha)^{1/2}$.

[16]A. I. Golovashkin, A. I. Kopeliovich, and G. P. Motulevich. Zh. Eksp. Teor. Fiz. **53**, 2053 (1967) [Sov. Phys.—JETP **26**, 1161 (1968)]. For a detailed discussion, see N. W. Ashcroft and K. Sturm, Phys. Rev. B **3**, 1898 (1971).

[17]P. N. Butcher, Proc. Phys. Soc. London **64**, 765 (1951).

[18]For a further example, see K. Takemura and K. Syassen, Phys. Rev. B **28**, 1193 (1983).

[19]This case has been analyzed by K. Sturm and N. W. Ashcroft, Phys. Rev. B **10**, 1343 (1974).

[20]J. N. Hodgson, in *Optical Properties and Electronic Structure of Metals and Alloys,* edited by F. Abelès (North-Holland, Amsterdam, 1966), p. 60.

[21]A. G. Mathewson and H. P. Myers, J. Phys. F **3**, 623 (1973).

[22]H. P. Myers and P. Sixtenson, J. Phys. F **6**, 2023 (1976).

[23]T. Inagaki, L. C. Emerson, E. T. Arakawa, and M. W. Williams, Phys. Rev. B **13**, 2305 (1976). See also T. A. Callcott and E. T. Arakawa, J. Opt. Soc. Am. **64**, 839 (1974).

[24]See, for example, H. Bross and G. Bohn, Z. Phys. B **20**, 261 (1975).

[25]It is clear that this argument (both for $9R$ and for other stackings) applies equally to sodium where substrate-dependent reflectivities are reported. For a compilation, see A. J. Sievers, Phys. Rev. B **22**, 1600 (1980).

[26]If a $9R$ phase could be grown, for instance, on diamond, then the electron-ion interaction $\langle\mathbf{k}+\mathbf{q}|\hat{v}|\mathbf{k}\rangle$ could, in principle, be mapped out over a range of $\mathbf{q}$ by observations made at high pressure. This has already been successfully demonstrated in aluminun by Tups and Syassen [J. Phys. F **14**, 2753 (1984)], and further analyzed by Dandrea and Ashcroft [Phys. Rev. B **32**, 6936 (1985)].

[27]This information can be used, of course, to refine the existing first-principles determinations of pseudopotentials.

[28]D. Stroud and N. W. Ashcroft, Phys. Rev. B **5**, 371 (1972). Three-particle and higher interactions can be defined by going beyond linear response. In metals of low valence they are less effective in discriminating between structures.

[29]C. Zener, Phys. Rev. **71**, 846 (1947).

[30]M. J. Kelly and W. M. Stobbs, Phys. Rev. Lett. **45**, 922 (1980); P-Å. Lindgard and O. G. Mouritsen, *ibid.* **57**, 2458 (1986); R. J. Gooding and J. A. Krumhansl, Phys. Rev. B **38**, 1695 (1988). A case for temperature- and wave-vector-dependent force constants in such an approach is made by M. Sato, R. D. Lowde, G. A. Sands, and M. M. Hargreave, Proc. R. Soc. London, Ser. A **374**, 115 (1981). As noted above, the free energy F is a unique functional of the ionic density so that in place of Eqs. (1)–(4) one may write $\Delta F = F[\rho_i^C(\mathbf{r})] - F[\rho_i^R(\mathbf{r})]$ and the order-parameter approaches attempt to describe ΔF by introducing phenomenological variables whose choice is dictated by the physics of diffusionless motion of atoms along appropriate paths, and in terms of which ΔF, as T changes, may reveal first-order transitions. As an alternative, ΔF can also be treated from the standpoint of a functional expansion, again along suitably parametrized paths, as is done, for example, in the melting problem [see W. A. Curtin and N. W. Ashcroft, Phys. Rev. A **32**, 2909 (1985)]. In either case, general constraints are imposed by symmetry, as discussed by P. W. Anderson and E. I. Blount, Phys. Rev. Lett. **14**, 217 (1965).

[31]This observation is not limited to Li and Na, but might also include K. The free-energy argument given above clearly involves the mass of the ion in question (7 in Li, 23 in Na) and the possibility of an extremely low-temperature martensite in K (mass 39) cannot be excluded. [This argument is pursued by J. A. Wilson and M. dePodesta in J. Phys. F **16**, L121 (1986)]. However, the transition will be exceedingly slow, and it is doubtful that transforming samples at liquid-helium temperatures would ever reach true equilibrium on practical time scales.

[32]According to S. H. Taole, H. R. Glyde, and R. Taylor, Phys. Rev. B **18**, 2643 (1978), the frequencies are not particularly anharmonic.

[33]A. W. Overhauser, Phys. Rev. B **29**, 7023 (1984); see also A. W. Overhauser (Ref. 14).

[34]T. L. Thorp, B. B. Triplett, W. D. Brewer, M. L. Cohen, N. E. Phillips, D. A. Shirley, J. E. Templeton, R. W. Stark, and P. H. Schmidt, J. Low. Temp. Phys. **3**, 589 (1970).

[35]C. Reale, Phys. Lett. **55A**, 165 (1975).

[36]N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt-Saunders, New York, 1976), p. 48.

[37]N. W. Ashcroft and J. W. Wilkins, Phys. Lett. **14**, 23 (1965); see also N. W. Ashcroft, Phys. Rev. **140**, A935 (1965).

[38]M. H. Cohen, Philos. Mag. **3**, 762 (1958).

[39]Note that Eq. (7) leads to a conclusion that the net electron-phonon-electron interaction will also be reduced by Debye-Waller-type factors, which in Li are significant. The point is that a band structure can be established in the time-average periodic lattice, and it is the residual scattering that is important. Pairing occurs in the standard picture from a retarded interaction originating with the polarization of nuclear and electronic charge rigidly displaced by phonons. It can also arise, in part, from polarization originating with the internal dynamics of this periodically localized charge. Phonons (hence ionic mass) are still involved through Debye-Waller modification of these waves of electronic polarization, whose importance is determined by the scale of ionic polarizability. In Li this is particularly small.

[40]For an example of inversion of Fermi-surface dimensions to pseudopotentials, see N. W. Ashcroft, Phys. Rev. **140**, A935

(1965); Philos. Mag. **8**, 2055 (1963).

[41]It might be noted that the energy scale of the (100) bands in 9R structure and the (110) bands in bcc structure differ at their respective zone faces by some 17%. If, for example, spectroscopy from such a 9R structure (or even another stacking) is *interpreted* as bcc, then a corresponding error in

bandwidth would result.

[42]There is a controversial report in the literature of structure, measured on a *free* surface, at about this energy. See H. Mayer and M. H. El Naby, Z. Phys. **174**, 289 (1963). In Na the corresponding energy would be about 1 eV [see Table I and B. Hietel and H. Mayer, Z. Phys. **264**, 21 (1973)].