found to be approximately increased by $\approx 30\%$. Therefore, the factors $1-\gamma'/\gamma \approx 0.43$ and $m_P^{**}/m_{op} \approx 1.65$. The change in $1-\gamma'/\gamma$ will, of course, cause a modification in the numerical results for the calculated absorptivity (Fig. 2, Ref. 1), however, the change will be small (on the order of 10%) as the two parts of the second term in (9) have opposite sign (the part proportional to Γ being positive).

As stated above the main consideration in the present note is to present an alternate and simpler approach to the calculation of the far-infrared absorptivity of a metal in the ASE limit in the frequency range of greatest interest ($\omega \approx \omega_D$). With the present approach it may be feasible to consider, more explicitly, the band structure and phonon anisotropy of the metal.

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[1] H. Scher, Phys. Rev. Letters 25, 759 (1970).

[2] T. Holstein, Ann. Phys. (N. Y.) 29, 410 (1964).

[3] R. R. Joyce and P. L. Richards, Phys. Rev. Letters 24, 1007 (1970).

[4] G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) A195, 336 (1948).

[5] R. B. Dingle, Physica (Utrecht) 19, 311 (1953).

[6] The band parameters one needs to determine $v_F/\delta_f\omega$ can be derived from a measurement of the surface impedance of a pure metal ($\omega\tau_{\text{Res}} \gg 1$, where τ_{Res} is the relaxation time associated with the residual resistance) at very low temperature. In addition, one must have $\omega <<< \omega_D$, so that there are no EP effects (to be discussed below) on the value of σ/l or $\omega_p^2/4\pi v_F$ obtained from the measurement.

[7] P. B. Allen, Phys. Rev. B 3, 305 (1971).

[8] S. Nakajima and M. Watabe, Progr. Theoret. Phys. (Kyoto) 29, 341 (1963).

[9] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966), p. 314.

[10] In the ASE limit it is well known that the scattering-in contribution is negligible. As seen in (4) only the scattering-out (zero-rung diagram) contributes to the *leading* (q^{-1}) *term*. However, the scattering-in enters the q^{-2} term. Now the question is, why in the ASE limit is this scattering-in term larger than the usual transport ($\cos\psi_{kk'}$) term? A study (with T. Holstein) on this point is in progress.

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Hellmann-Feynman Theorem and Uniform Expansion of Crystals

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The applicability of the Hellmann-Feynman theorem under periodic boundary conditions is discussed. The recent result of Wannier, Misner, and Schay on the instability of metals toward uniform expansion is shown to result not so much from the inapplicability of this theorem as from the improper evaluation of a sum.

Wannier, Misner, and Schay[1] (WMS) recently used the Hellmann-Feynman theorem[2] (HFT) to consider the stability of a metal against uniform expansion. They claimed that their results showed the inadequacy of recent electronic wave-function calculations and of the nearly free-electron approach to such calculations.

Kleinman[3] (K) criticized their procedure on the basis that the HFT can be applied only to finite systems, since uniform expansion would violate the periodic boundary conditions (PBC) normally employed. He then argued that in a finite metal the structure near the surface would be distorted from the purely periodic arrangement in the interior in such a way as to provide the necessary confining force.

I believe that Kleinman has pointed out a significant inadequacy in WMS's argument, but that to see clearly where their error lies, it is more instructive to use PBC as far as possible.

Let us suppose that we have a Hamiltonian $H(p, r, R)$, where p, r stand for all the momenta and coordinates which are treated dynamically (in this case, those of the electrons: $\vec{p}_i, \vec{r}_i$), and R stands for all other coordinates which enter as parameters (say the positions $\vec{R}_\alpha$ of the nuclei).

Now let us consider a few independent changes in the Hamiltonian: (i) Move the nuclei from $\vec{R}$ to $\vec{R}/\eta$:

$$H(p, r, R) \to H(p, r, R/\eta) .$$

As Kleinman says, this cannot be done in PBC. (ii) Transform the coordinates $\vec{r}_i/\eta$ by a canonical transformation:

$$H(p, r, R) \to H(\eta p, r/\eta, R) .$$

This also cannot be done in PBC. (iii) Change the repeat vectors for the PBC from $\vec{L}_i$ to $\vec{L}_i/\eta$. This means replacing the operator $U(\vec{L}_i)=\exp(i\vec{L}_i\cdot\vec{p}/\hbar)$, which commutes with H and leaves all wave functions invariant, with $U(\vec{L}_i/\eta)$.

For a finite system we can do (i), (ii), or both. (i) leads to the special case of the HFT for uniform expansion:

$$\frac{\partial E}{\partial\eta}=\sum\vec{R}_\alpha\cdot\langle\vec{F}_\alpha\rangle\quad\text{(finite)},\tag{1}$$

where $\vec{F}_\alpha=-\partial H/\partial\vec{R}_\alpha$. (ii) leads to the virial theorem for p, r:

$$\langle\sum\vec{p}_i\cdot\vec{v}_i+\sum\vec{r}_i\cdot\vec{F}_i\rangle=0\ ,\tag{2}$$

where $v_i=\partial H/\partial\vec{p}_i$ and $\vec{F}_i=-\partial H/\partial\vec{r}_i$. If we do both (i) and (ii), H becomes

$$H_\eta(p,r,R)\equiv H\left(\eta p,\frac{r}{\eta},\frac{R}{\eta}\right)$$

and

$$\frac{\partial E}{\partial\eta}=\left\langle\frac{\partial H_\eta}{\partial\eta}\right\rangle=\langle\sum(\vec{p}_i\cdot\vec{v}_i+\vec{r}_i\cdot\vec{F}_i)\rangle+\sum\vec{R}_\alpha\cdot\langle\vec{F}_\alpha\rangle\ .\tag{3}$$

In PBC, we must do (i), (ii), and (iii). Again H becomes H_η, while the action of (ii) and (iii) on U leaves it unchanged, so that the PBC are undisturbed, and Eq. (3) holds in this case also.

For true equilibrium, of couse, all $\langle\vec{F}_\alpha\rangle$ and $\partial E/\partial\eta$ vanish, so that, in particular, for either finite crystals or PBC,

$$Q\equiv\sum\vec{R}_\alpha\cdot\langle\vec{F}_\alpha\rangle=0\ ,\tag{4a}$$

$$\frac{\partial E}{\partial\eta}=0\quad\text{(equilibrium)},\tag{4b}$$

$$\langle\sum(\vec{p}_i\cdot\vec{v}_i+\vec{r}_i\cdot\vec{F}_i)\rangle=0\ .\tag{4c}$$

Now let us suppose for a moment that for some arbitrary set of $\vec{R}_\alpha$, we have a correct solution of the electronic problem. Then in the case of a finite crystal the virial theorem (2) and the HFT (1) hold. In the PBC problem we have no guarantee that (1) or (2) hold separately. There are, however, a number of situations, which I shall call "simple" for short, where symmetry of one sort or another guarantees that all $\langle\vec{F}_\alpha\rangle$ vanish, provided only that the electronic wave function satisfied the symmetry requirements, which is normally a very simple condition to meet. Under these circumstances, we have

$$\frac{\partial E}{\partial\eta}=\langle\sum(\vec{p}_i\cdot\vec{v}_i+\vec{r}_i)\rangle\quad\text{("simple" PBC)}\ .\tag{5a}$$

This is the case for the simple metals with bcc, fcc, and hcp structures, as well as the NaCl and zinc-blende structures, for instance. This expression does not look quite as simple to evaluate as the HFT expression.

In the sense that (5) rather than (1) is the correct evaluation of $\partial E/\partial\eta$ for the conditions of WMS, I agree with K on the inapplicability of the HFT in PBC. On the other hand, failure of any of the equations (4) indicates an inadequacy of the wave function. In particular, a finite value of Q would be disturbing, especially since all $\langle\vec{F}_\alpha\rangle$ vanish by symmetry as remarked above and by K.

The fact is that WMS use not Q but, without derivation, the following:

$$Q'=\tfrac{1}{2}\sum(\vec{R}_\beta-\vec{R}_\alpha)\cdot\langle\vec{F}_{\beta\alpha}\rangle\ ,\tag{5b}$$

where $\langle\vec{F}_{\beta\alpha}\rangle$ is the expectation value of the force exerted on the βth nucleus by all the charge in the αth unit cell. They have specialized to the case of one atom per unit cell and implicitly assume PBC by supposing that the sum over α can be replaced by multiplication by the number of atoms in the crystal. In the same notation

$$Q=\sum\vec{R}_\alpha\cdot\langle\vec{F}_{\alpha\beta}\rangle\ .\tag{5c}$$

One may be inclined to argue that $\langle\vec{F}_{\alpha\beta}\rangle=-\langle\vec{F}_{\beta\alpha}\rangle$, and thus $Q=Q'$, but it is not so simple.

In general, $\langle\vec{F}_{\alpha\beta}\rangle\neq-\langle\vec{F}_{\beta\alpha}\rangle$. Since the first index refers to a nucleus and the second to a complete unit cell, Newton's third law does not apply and only a symmetry could force the equality. Such symmetry holds in PBC if each nucleus is at a center of inversion, but not for finite crystals, particularly if α or β is near the surface. Thus for a finite crystal, we find

$$Q-Q'=\tfrac{1}{4}(\vec{R}_\alpha+\vec{R}_\beta)\cdot(\langle\vec{F}_{\alpha\beta}\rangle+\langle\vec{F}_{\beta\alpha}\rangle)\quad\text{(finite)}\ .\tag{6a}$$

This comes almost entirely from the region near the surface, but the factor of $(\vec{R}_\alpha+\vec{R}_\beta)$ suffices to make it proportional to the volume.

Now let us suppose instead that we use PBC—to be concrete, suppose that the supercell for the PBC, Ω, has dimensions $L\times L\times L$. We concede that $\langle\vec{F}_{\alpha\beta}\rangle=-\langle\vec{F}_{\beta\alpha}\rangle$. Now in the case of Q, we are summing α over all nuclei in the supercell Ω, but to find $\langle\vec{F}_\alpha\rangle$ we must sum β over all space, both inside and outside Ω. There is no convergence difficulty in the sum because $\langle\vec{F}_{\alpha\beta}\rangle$ falls off like $|\vec{R}_\alpha-\vec{R}_\beta|^{-4}$, at least and like $|\vec{R}_\alpha-\vec{R}_\beta|^{-6}$ for a cubic crystal. We have written (5b) so that the same conventions apply. Thus in this case

$$Q-Q'=\frac{1}{2}\sum_{\alpha\ \text{in}\ \Omega}\ \sum_{\substack{\beta\\ \text{outside}\ \Omega}}(\vec{R}_\alpha+\vec{R}_\beta)\cdot\langle\vec{F}_{\alpha\beta}\rangle\quad\text{(PBC)}.\tag{6b}$$

Here again the rapid falloff of $\langle\vec{F}_{\alpha\beta}\rangle$ means that only if α and β are near the boundary of Ω do they contribute significantly, but the value of $(Q-Q')/L^3$ approaches a finite limit as L becomes large. This limit can be visualized by considering a unit area of a boundary plane and each line $l_{\alpha\beta}$ passing from nucleus α on, say, the left-hand side of the boundary to β on the right-hand side through that area. The sum of the forces $\langle F_{\alpha\beta}\rangle$, one for each line $l_{\alpha\beta}$, gives the value $(Q-Q')/L^3$. The value WMS find for Q'/L, viz., $0.03e^2/a^4$, is quite reasonable for this quantity.

In a paper published after the submission of these comments, Wannier and Meissner[4] have argued that the surface contribution for a finite crystal is unlikely to be important. In fact, of course, provided the crystal is large enough so that its density is no longer size dependent, $(Q-Q')/L^3$ must be the same for the finite crystal and for PBC.

In conclusion, we find that the result of WMS is invalid because they used the sum Q' instead of Q.

I have benefited from discussions with C. M. Varma and C. Herring's criticism of the manuscript.

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[1] G. H. Wannier, C. Misner, and G. Schay, Jr., Phys. Rev. 185, 983 (1969).

[2] H. Hellmann, *Einführing in die Quanten Theorie* (Franz Deuticke, Leipzig, 1937), p. 285; R. P. Feynman, Phys. Rev. 56, 340 (1939).

[3] L. Kleinman, Phys. Rev. B 1, 4189 (1970).

[4] G. H. Wannier and G. Meissner, Phys. Rev. B 3, 1240 (1971).

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Comments on Two-Phonon Resonances in Quantum Crystals*

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Recent numerical computations of the phonon spectrum of quantum crystals have demonstrated the existence of an anomalous extra phonon branch which lies above the usual acoustic modes. The purpose of the present note is to explain the physical origin of the anomalous branch in terms of two-phonon resonances, and to discuss briefly the possibility of observing these resonances in quantum crystals by neutron-scattering and Raman-scattering experiments.

It has recently been proposed that the anharmonic interactions between phonons in crystals can give rise to a two-phonon bound state whose energy lies above the two-phonon continuum. Bound phonon pairs exhibit sharp structure in the second-order phonon spectrum as observed in the Raman data on diamond,[1,2] and, in addition, may substantially modify the single-phonon spectrum as observed in the first-order Raman scattering from quartz.[3,4]

Bound states of two phonons are split off above the two-phonon continuum by the repulsive fourth-order anharmonic term in the phonon Hamiltonian providing that the anharmonicity is larger than a critical strength.[5,6] The critical value of the anharmonic strength is related to the nature of the single-phonon dispersion and involves parameters such as the curvature of the phonon spectrum near the top of the single-phonon continuum, and the "bandwidth" of the phonon branch.[5,6] If the anharmonic coupling is weaker than the critical strength, it is still possible to create two-phonon resonances[6] which give rise to considerable modifications in the spectrum within the two-phonon continuum.

The above considerations suggest that the highly anharmonic quantum crystals provide ideal systems for the formation of bound phonon pairs. However, another consequence of large anharmonicity is substantial broadening of the phonon modes which would, in general, obscure the bound-state structure. Nevertheless, if the energy widths of the two-phonon resonances are comparable to the single-phonon widths, it may be possible to observe these resonances experimentally.

Numerical calculations[7,8] of the phonon spectrum of some quantum crystals using the self-consistent harmonic approximation[9] have recently been published. In particular, the calculations for solid neon[7] and solid ^{3}He in the bcc phase[8] find a peculiar extra branch in the phonon spectrum which lies above the usual acoustic-phonon modes. Since these crystals are Bravais, the extra branch cannot be attributed to an optical phonon. In the case of ^{3}He, as shown in Fig. 1 of Ref. 8, the extra branch is situated at roughly twice the maximal single-acoustic-phonon energies. Furthermore, the anomalous peak has a width comparable to the single-phonon widths, and displays a peculiar momentum dependence.

Leath and Watson[10] have suggested that the anomalous peak may be due to the mixing of one- and two-phonon states via the third-order anharmonic coupling. Using a one-dimensional linear chain