Acoustical Plasmons, Phonon Anomalies, and Superconductivity in Transition-Metal Systems*

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It is shown that the concept of acoustical plasmons may be useful for understanding the anomalous behavior of the phonon dispersion curves of superconducting transition-metal systems with high T_c (5–10°K). The value of the velocity of plasmon sound obtained from the phonon calculations for Nb is quite close to that needed to explain the specific-heat anomaly by the acoustical-plasmon mechanism.

Pines[1] has pointed out that it is possible under certain conditions to obtain a plasmon dispersion curve for which $\omega(q)\rightarrow 0$ as $q\rightarrow 0$. Radhakrishnan[2] and Fröhlich[3] postulated that the acoustical-plasmon (AP) concept might be important for superconductivity, with the AP's playing the role of phonons in standard BCS theory. Rothwarf[4] demonstrated that AP's may explain the specific-heat anomaly observed in several transition-metal systems. In this Letter we show that the anomalies in the phonon dispersion curves of many high-T_c superconductors may also be related to acoustical plasmons. We were unaware of Rothwarf's work at the time of our initial calculations on Nb, and it was reassuring to find that our value of the plasmon velocity of sound could be chosen to agree well with his.

Phonon anomalies in transition-metal systems were first observed by Nakagawa and Woods[5] in Nb. A characteristic feature of the anomalies is a dip in the LA mode, [001] dispersion curve. Since this work on Nb, other transition-metal systems[6] have been found to exhibit the anomalies. The transition-metal carbides are particularly interesting in that traces of the anomalies also appear in the optical modes. A ten-neighbor Born–von Karman analysis yields a good fit to the dispersion curves in the transition metals, but the meaning of the numerous force constants is obscure. Attempts to fit the carbide results with a modified shell model[7] and with a screened pseudopotential approach[8] have attained some success, but they have failed thus far to account for the "anomalous wiggles." The systems exhibiting the anomalies are high-T_c superconductors with high electronic heat coefficients γ, which in turn indicate a high electronic density of states at the Fermi surface, $N(0)$. Superconductivity trends in these systems suggest the need for including the electron-phonon interaction self-consistently in the lattice dynamics. This can be done through the ω- and q-dependent dielectric response function $\epsilon(\vec{q}, \omega)$. To simplify the analysis we restrict ourselves to the free-electron approximation, but we shall see that even this is sufficient to produce the anomalies.

The dielectric function can be written as

$$\epsilon(\vec{q}, \omega)=1+4\pi(\alpha_s+\alpha_d+\alpha_0+\alpha_L), \tag{1}$$

where α_s and α_d are the ω- and q-dependent polarizabilities of two distinct groups of electrons, which we shall refer to loosely as s and d, while α_0 contains all other contributions to the electronic polarizability, e.g., from interband transitions. For systems with complicated, hybridized band structures, the breakup of the polarizability in Eq. (1) is highly simplified, but we feel it should contain the essential physics of the problem. α_L is the polarizability of the lattice. An approximate dispersion relation for the bare AP's can be obtained in the free-electron approximation.[9] For $qv_d<\omega<qv_s$, we get

$$\omega_{\rm pl}{}^2=(\epsilon_0 q^2 v_s{}^2+3\omega_{0s}{}^2)^{-1}\omega_{0d}{}^2 v_s{}^2 q^2. \tag{2}$$

ω_{0s} (ω_{0d}) is the unscreened s (d) plasmon frequency, and v_s (v_d) is the velocity of the s (d) electron at the Fermi surface (FS). We have neglected the screening by ionic plasmons since the effect is orders of magnitude smaller than that of s-electron screening. We now let the AP's and the phonons interact and examine two cases.

(I) Low-q case.—Here the AP can still exist as a collective excitation, and the approximate dis-

persion relations for phonons and plasmons are

$$\overline{\omega}_{\rm ph}{}^2 \simeq \omega_{\rm ph}{}^2 + \omega_{\rm ion}{}^2\omega_{\rm pl}{}^2(\omega_{\rm ph}{}^2 - \omega_{\rm pl}{}^2)^{-1}, \qquad (3)$$

$$\overline{\omega}_{\rm pl}{}^2 \simeq \omega_{\rm pl}{}^2 - \omega_{\rm ion}{}^2\omega_{\rm pl}{}^2(\omega_{\rm ph}{}^2 - \omega_{\rm pl}{}^2)^{-1}, \qquad (4)$$

$$\omega_{\rm ph}{}^2 = \Omega^2 + \omega_m{}^2/\epsilon_1(q) \equiv \Omega^2 + \omega_{\rm ion}{}^2, \qquad (5)$$

$$\omega_{\rm pl}{}^2 = \omega_{0d}{}^2/\epsilon_1(q). \qquad (6)$$

Ω is the contribution from the "core-core interaction," ω_m is the frequency of the "unscreened ion plasma," and $\epsilon_1(q) = \epsilon_0 + 4\pi\alpha_s$. Because of the phonon-AP interaction, the phonon frequencies are increased and the plasmon frequencies decreased at low q. A more complete discussion of many of the preceding quantities and equations is given in Ref. 4 [see particularly Eq. (2.33), from which our Eqs. (3)–(4) can be obtained].

(II) High-q case.—Here the AP has ceased to exist as a collective mode. The phonon frequency is given by

$$\overline{\omega}_{\rm ph}{}^2 \simeq \omega_{\rm ph}{}^2 - 4\pi\alpha_d\omega_m{}^2/\epsilon_1(\epsilon_1 + 4\pi\alpha_d), \qquad (7)$$

so that for large q the phonon frequencies are reduced. We note in passing that phonons of large q are important for the BCS theory of superconductivity. We also note that from Eqs. (5) and (7) we can obtain

$$\overline{\omega}_{\rm ph}{}^2 = \Omega^2 + \omega_m{}^2/(\epsilon_1 + 4\pi\alpha_d). \qquad (8)$$

Those electrons which were involved in the formation of the AP's at low q are free to participate in the screening of the ions at high q.

Figure 1 shows one set of results for the [001] LA modes in Nb. The curves were obtained by programming the full Lindhard expressions for the dielectric constant, approximating $\omega_{\rm ph}$ by $aq + bq^2$ and finding the zeros of $\epsilon(\vec{q}, \omega)$. The unperturbed plasmons were found from $\epsilon(\vec{q}, \omega)$ when α_L was omitted. The perturbed plasmons were obtained from Eqs. (3) and (4). The points show the experimental data taken as best we could from the first paper of Ref. 5. We have done no least-squares fitting to these data, but we have varied the electronic parameters and the coefficients a and b to put the dip in about the right place and to give a fairly good overall fit. We find the velocity of sound for our perturbed plasmons in this calculation to be 1.58×10^5 cm/sec, in agreement with the value of 1.55×10^5 cm/sec found by Rothwarf to explain the specific-heat anomaly. Although this very close agreement is undoubtedly somewhat fortuitous, is does show that, within the framework of our simple model, Rothwarf's value is not inconsistent with the phonon data.

Other calculations of ours indicate that the plasmon sound velocity may vary considerably from the above value without destroying the *overall* fit although the position of the dip may be shifted somewhat.

At present we feel there is little evidence for AP-induced superconductivity in transition-metal systems. A low isotope effect, which might have been a springboard for the AP mechanism, now appears to be accounted for by the pseudopotential parameter μ^* in the Eliashberg[10]-McMillan[11] (EM) theory. Matthias's rule, relating the number of valence electrons per atom to T_c, is likely due to the variation of the electronic density of states at the FS. The Debye temperature required for the AP mode to account for both the phonon and specific-heat anomalies[4] is much smaller than the phonon $\Theta_{\rm D}$; AP's are essentially low-q excitations. This implies that if AP-induced superconductivity prevails, only a *very* small fraction of electrons near the FS take part. Recent tunneling experiments[12] strongly suggest that the phonon mechanism is the only one operative in Ta, and it would seem reasonable to expect similar results for Nb. It has been customary to interpret the observed anomalies in tunneling[13] and ultrasonic attenuation[14] in Nb by a "two-gap" BCS model. However, re-

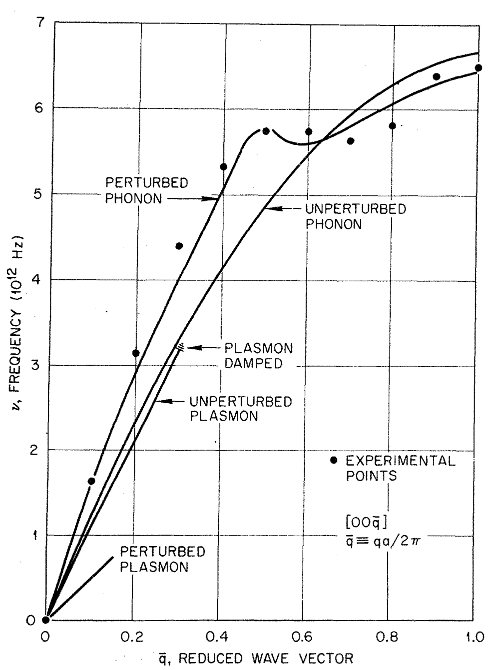

FIG. 1. Plasmon and phonon dispersion curves for Nb. The experimental data are taken from the first paper of Ref. 5.

TABLE I. Parameters for some transition-metal systems. The data are taken from Ref. 11.

System	T_c (°K)	Θ_D (°K)	γ (mJ/mole °K^2)	λ	Phonon anomaly
Nb	9.22	277	7.8	0.82	yes
Mo	0.92	460	1.83	0.41	no
Ta	4.48	258	6.0	0.65	yes
W	0.012	390	0.90	0.28	no
$Nb_{0.85}Mo_{0.15}$	5.85	265	6.3	0.70	yes
$Nb_{0.60}Mo_{0.40}$	0.60	371	2.87	0.41	not large
$Nb_{0.20}Mo_{0.80}$	0.095	461	1.49	0.33	no

cent thermal-conductivity measurements in Nb[15] and NbC[16] lend little support to the existence of two gaps. The striking agreement between the calculated μ^* and that obtained from the observed isotope effect[17] leads us to believe that the EM theory is valid for transition-metal systems. The close agreement between the density of states calculated from EM theory and the results from band calculations[18] reinforces this feeling. The correlations evident in the data in Table I can be qualitatively understood through the EM theory. Empirically, the EM theory gives

$$\lambda \simeq \mathrm{const}/M\langle\bar{\omega}_{\mathrm{ph}}^2\rangle \tag{9}$$

for bcc transition metals. This indicates that the coupling is governed by the phonon factor and not *directly* by $N(0)$. However, the observed variation of T_c with $N(0)$ led McMillan to conclude that, "··· the high-density-of-states materials are elastically softer." This conclusion can be understood, qualitatively, through Eq. (5), which states that for high $N(0)$ the screening of the ion plasma is more effective. Also the same effects which may produce the AP's at small q produce an additional softening of phonons at high q and may increase T_c.

The condition for a high density of states at a point on the FS is that the velocity is small or vanishing (critical point). Our results, like those of Rothwarf, indicate that in certain transition-metal systems there are low-velocity electrons at or very near the FS which contribute to the polarizability in a fundamentally important way. Furthermore, the values of our electronic parameters lead us to believe that the number of such electrons is relatively small and that an important quantity is likely to be the density of states as a function of $\vec{k}$, $N(E,\vec{k})$. Possible sources of low-velocity electrons in Nb may be the hole pockets at the N points in the third Brillouin zone.[18] A detailed calculation of $\epsilon(\vec{q},\omega)$ based on a realistic band structure, though very complex, now seems possible and should constitute a major step forward in the quantitative analysis of these systems.

We conclude by reiterating our present viewpoint. The electronic properties which produce high T_c's in some transition-metal superconductors may also lead to phonon anomalies and, in some cases, to the existence of AP's. These plasmons, which are low-q excitations, manifest themselves through anomalies in various other physical properties such as the specific heat, resistivity, and ultrasonic attenuation.

Note added in proof.—We have recently been informed that the authors of Ref. 7, in collaboration with U. Schröder, have obtained the phonon anomalies in TaC by further modification of the shell model.

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Evidence for Large Antisymmetric Superexchange in Tetrameric Copper Complexes

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Transition metal cluster complexes often combine high local symmetry about individual magnetic ions with low spin-pair symmetry. These complexes should therefore enrich greatly the field of study of highly anisotropic, particularly asymmetric, exchange phenomena of low order. We illustrate by presenting evidence indicating strongly that the tetrameric copper complex $Cu_4OCl_6[OP(C_6H_5)_3]_4$ provides the first example in the literature of large (lowest-order) antisymmetric superexchange between orbitally degenerate magnetic ions.

The possible existence of contributions to magnetic insulator exchange asymmetric with respect to the spins involved has long been recognized in the literature. In particular we are familiar with the Dzialoshinski-Moriya antisymmetric bilinear coupling of the form $\vec{S}_1 \cdot \overleftrightarrow{K}_A \cdot \vec{S}_2$, where $\overleftrightarrow{K}_A$ is an antisymmetric exchange tensor.[1,2] Such an interaction exists only when spin-pair crystal symmetry is sufficiently low. In simple inorganic magnetic crystals this low spin-pair symmetry seems always, via space-group restrictions, to lead to low local symmetry about individual magnetic ions, producing in turn an orbitally quenched magnetic ground state. Asymmetric exchange contributions then occur only via exchange coupling through excited states and are consequently small; rarely larger than a few percent of the symmetric exchange and usually even smaller.

There has recently been increasing recognition of the value of using organic spacer molecules in crystals to "isolate" chains or planes of magnetically coupled ions and elevate the study of physics in less than three dimensions from the realm of academic interest.[3,4] We wish to point to particular advantages concerning asymmetric exchange to be gained from this principle when taken a step further to "isolate" small clusters of magnetic ions by embedding them in an organic-ligand matrix.

First, the severe geometric restrictions imposed on magnetic ions in simple inorganic crystals by space-group symmetry are removed in cluster-complex crystals where only clusters as a whole are subject to translational symmetry conditions. In particular, high local symmetry (and orbital degeneracy) is not necessarily incompatible with low spin-pair symmetry, enriching greatly the potential field of study of highly anisotropic and particularly asymmetric exchange phenomena of low order. Additional advantages of cluster-complex studies relate to the few-body nature of the associated statistical problem (which is therefore particularly amenable to exact solution) and to the extensive variations of composition which can be generated to enable systematic study of exchange phenomena in terms of bond length, bond angle, ionicity, etc.

As an example of the increased opportunities afforded by these complexes for the study of asymmetric exchange, we present in this Letter evidence from magnetic-susceptibility measurements, which strongly suggests that the tetrameric copper complex $Cu_4OCl_6[OP(C_6H_5)_3]_4$ provides the first example in the literature of large (lowest-order) antisymmetric superexchange between orbitally degenerate magnetic ions.

Conditions under which effective spin-spin in-