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Plasmons and high-temperature superconductivity in alloys of copper oxides

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The two-dimensional character of the electronic structure of M-N-Cu-O alloys, with M = La,Y and N = Ba,Sm, . . . , is shown to favor the formation of "acoustic" plasmons at energies above the acoustic phonons. Providing that the Fermi energy intersects a small pocket of electrons (or holes) in addition to the expected occupation of a primary electron (or hole) band, the plasma oscillations of the secondary charge carriers may provide a mechanism for room-temperature superconductivity.

The recent discovery of alloys which remain superconducting at high temperatures has spurred a remarkable surge of interest and research activity. The initial low-key report[1] of a superconducting transition near 30 K in La-Ba-Cu-O compounds set the stage for a rapidly escalating series of measurements and reports of new materials such as Y-Ba-Cu-O with transition temperatures of $T_c \simeq 90$ K.[2] Superconducting features at even higher temperatures have been reported in *The New York Times*, and the quest for a room-temperature superconductor has been rejuvenated with intense and spirited rivalry.

Prior to these developments, the superconducting properties of most metals were explained by the BCS theory,[3] which invokes a phonon-mediated interaction between electrons to form superconducting pairs under certain circumstances. A slightly modified form of the weak coupling result for the transition temperature can be written as

$$T_c \cong 0.7\theta_D \exp\left(-\frac{1+\lambda}{\lambda-\mu^*}\right) , \tag{1}$$

where θ_D is a Debye frequency representing the lattice vibrations, λ is the electron-phonon coupling parameter, and the modified Coulomb repulsion μ^* is defined by

$$\mu^* = \frac{\mu}{1+\mu\ln(E_F/\theta_D)} . \tag{2}$$

In typical metals the phonon frequencies are much smaller than the Fermi energy E_F, and thus the effect of the average Coulomb repulsion μ between electrons is reduced to a small correction of order $\mu^* \simeq 0.1$. Hence if the electron-phonon coupling λ can be of order unity, and if $\theta_D \simeq 300$ K, it is reasonable to expect that $T_c \simeq 20$ K. However, considerably higher transition temperatures are difficult to envision for the phonon spectra of ordinary metals.

An exceptional case which has long been regarded as a candidate for a room-temperature superconductor is metallic hydrogen. By virtue of its light ion mass the hydrogen phonon vibrations may extend to very high values, say $\theta_D \simeq 3000$ K, and thereby enhance the T_c prospects as seen in Eq. (1). Calculations[4] of the corresponding λ and μ^* parameters for metallic hydrogen support the hope of $T_c \simeq 200$ K, and thus lend impetus to the challenge of creating a metallic hydrogen state in the laboratory.

Other excitations with much higher frequencies, such as excitons and plasmons have also been examined in the past, but they suffer a dual handicap. On the one hand, if the equivalent "Debye" energy θ is too large, say $\theta \simeq E_F$, then the Coulomb repulsion between electrons is not reduced as much as in the phonon case; a glance at Eq. (2) illustrates the most direct consequence of the high-energy modes. Furthermore, the Migdal theorem becomes doubtful and a much more detailed analysis of the dielectric screening is required. Yet another difficulty arises for very high-frequency excitations from the solutions of the Eliashberg equations for superconducting pairing. These yield an expression for the boson-mediated electron pairing parameter.

$$\lambda = 2\int \frac{\alpha^2 F(\omega)}{\omega} d\omega , \tag{3}$$

where $F(\omega)$ is the boson density of states and α^2 represents the coupling strength between electrons and bosons. From this relation, it appears that λ is reduced in the case of commonplace high-frequency bosons. Hence, elevating the boson energy too far has the combined destructive influence in reducing the electron-electron attraction λ, increasing their repulsion μ^*, and thereby dramatically lowering the exponential term in Eq. (1); the result is a negation of the positive influence on T_c achieved by a larger prefactor θ.

Incidentally, the above considerations provide part of the motivation for the commonly used "soft" phonon mechanism for enhancing T_c, in the sense that very low-energy phonons may enhance the λ parameter sufficiently to overcome a smaller prefactor θ in that case.

An alternate mechanism for electron pairing mediated by intermediate energy acoustic plasmons in transition metals was originally proposed by Fröhlich.[5] A review of research efforts to establish the possible existence of these modes in metals is presented in Ref. 6.

The recently discovered high-T_c superconductors are notable for an extreme sensitivity to alloy composition. For example, La_2CuO_4 is not superconducting, whereas $La_{2-x}Ba_xCu_4$ has $T_c \simeq 40$ K under pressure with $x \simeq 0.2$, and $(Y_{1-x}Ba_x)_2CuO_4$ has $T_c \simeq 90$ K providing $x \simeq 0.4$.[2] This unusual behavior provides the principal clue to our investigation, especially since bulk properties such as the averaged phonon spectrum or the ordinary plasmon response are not expected to vary dramatically over such a small impurity concentration range.

We propose that the superconductivity of the La-M-Cu-O alloys may be attributed to low-energy plasmon excitations extending to corresponding values of $\theta_{\rm pl} \simeq 3000$ K. The prospects for creating such modes are greatly enhanced by the two-dimensional nature of the electronic energy spectrum which gives rise to an "acoustic" plasmon branch, in the sense that the plasmon energy behaves as

$$\omega_q \simeq (aq + bq^2)^{1/2} , \tag{4}$$

where the coefficients a and b are determined by the dielectric screening and the branch remains well defined outside the electron-hole continuum up to a cutoff momentum q_c.[7,8] However, we emphasize that a single branch, appropriate to La_2CuO_4 for example, is not a likely candidate for inducing superconducting electron pairing because of its very high frequency ($\theta \sim 2$ eV) and the arguments cited above. Hence, we are led to examine a secondary, lower energy, plasmon branch which may be created by proper alloying.

A likely situation for the formation of the low-energy plasmon models is illustrated in Fig. 1 where the representation of the electronic structure near the Fermi energy has been patterned after the current band-structure results[9,10] for La_2CuO_4. The key feature of these electron bands is the two-dimensional nature of the electron dynamics. Thus, within the plane of motion, we may approximate the energies as $E_h = (k_x^2 + k_y^2)/2m_h^*$ and $E_l = (k_x^2 + k_y^2)/2m_l^*$, where the effective masses m_l^* and m_h^* refer to the curvature of the l and h bands, respectively. The two-dimensional character of the bands greatly favors the criterion for creating undamped plasmon modes at intermediate energies with a dispersion relation of Eq. (4), which is reminiscent of acoustic modes with their $\omega \simeq cq$. If the Fermi energy intersects only the E_l band, as shown in Fig. 1 for the La_2CuO_4 compound, then a single plasmon branch will appear. However, the interesting possibility regarding high-T_c superconductivity is the situation where the Fermi energy intersects both bands, thus creating a small pocket of h charge carriers which can oscillate at intermediate energies and mediate the pairing interaction of the l electron (or hole) states.

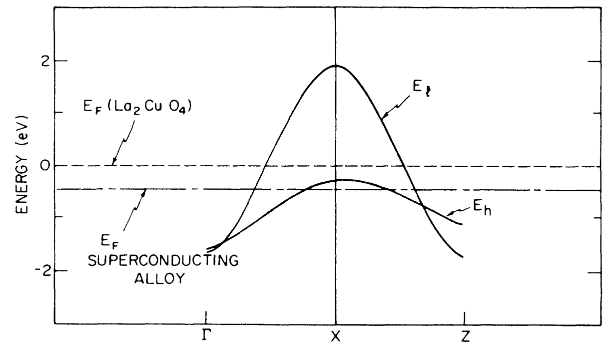

FIG. 1. Representation of the electron energy as a function of momentum. The shape of E_l and E_h, as well as the Fermi energy E_F, for La_2CuO_4 is patterned after the band-structure calculations of Refs. 9 and 10. The influence of alloying may lower the Fermi energy as shown by the dot-dash line intersecting both bands.

The plasmon spectrum for the two-band case follows readily from the dielectric function $\epsilon(q,\omega)$ in two dimensions. A convenient choice of dimensionless variables is to measure wave vectors in units of k_F and frequencies in units of $2E_F/\hbar$. Then, introducing $\alpha \equiv 0.22 r_s$, where r_s is the usual average electron spacing, and the variables $\nu_\pm = \pm\omega/k - k/2$, the dielectric function for a single band can be evaluated to find[7,8]

$$\mathrm{Re}\,\epsilon(q,\omega) = 1 + \frac{2\pi\alpha}{k^2}[k + \mathrm{sgn}(\nu_+)\theta(\nu_+^2 - 1)(\nu_+^2 - 1)^{1/2} + \mathrm{sgn}(\nu_-)\theta(\nu_-^2 - 1)(\nu_-^2 - 1)^{1/2}] , \tag{5a}$$

and

$$\mathrm{Im}\,\epsilon(q,\omega) = \frac{2\pi\alpha}{k^2}[\theta(1-\nu_+^2)(1-\nu_+^2)^{1/2} - \theta(1-\nu_-^2)(1-\nu_-^2)^{1/2}] . \tag{5b}$$

The total dielectric function is $\epsilon_{\rm total} = \epsilon_l + \epsilon_h$, and the individual l and h contributions naturally include their respective screening parameters r_s, E_F, and k_F. The plasmon dispersion in this two-dimensional case is quite different from the usual three-dimensional "optic" plasmon counterpart. From Eq. (5), even a single electron band will generate an "acoustic" plasmon mode[7,8] with the energy spectrum $\omega_{\rm pl} = (aq + bq^2)^{1/2}$, where $a \equiv \pi\alpha$ and $b = 0.75$ in these units. The resulting two-band spectrum can be readily calculated from Eq. (5), using the band-structure model appropriate to alloys of La-M-Cu-O. The results are shown in Fig. 2, where the two shaded regions of the l and h electron-hole continuum indicate the values of ω and q where Landau damping of the plasmons would be possible by virtue of the nonvanishing imaginary part $\mathrm{Im}\,\epsilon(q,\omega)$. The small pocket of h charge carriers shifts the l-plasmon branch somewhat, but this higher-frequency mode is expected to persist whether or not the Fermi energy intersects both l and h bands, and therefore may be present in nonsuperconducting alloys in the La-M-Cu-O series. However, the lower-energy h-plasmon branch becomes a candidate for a superconductivity mechanism only if the Fermi energy intersects the E_h band as well. In that case, the screening of the h electrons (or holes) by the primary l carriers tends to shift the "acoustic" h branch to higher frequencies, as illustrated in Fig. 2. Since this h branch of the plasmon spectrum may have a corresponding "Debye" energy of $\theta_{\rm pl}^h \sim 3000$ K, it has many of the desirable features which are anticipated for a plasmon-mediated mechanism for high-temperature superconductivity.

Finally, we estimate the corresponding electron pairing

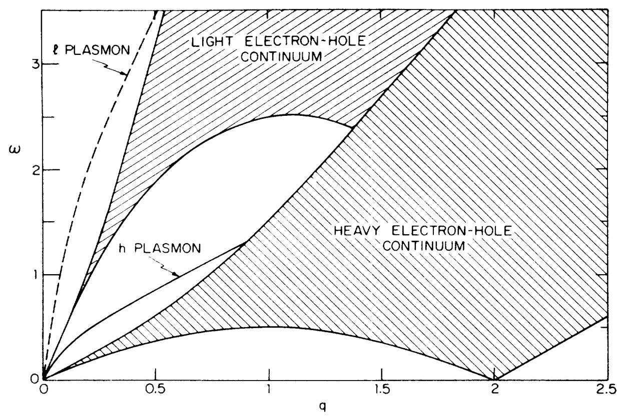

FIG. 2. Excitation spectrum proposed for certain alloys of the La-M-Cu-O series. The energy ω and the momentum q are scaled to the Fermi energy measured from the top of the E_h secondary band pocket. Thus the lower "acoustic" h plasmon may extend to an energy of order $\omega_{\rm pl}^h \simeq 0.25$ eV $=3000$ K. The primary l plasmon is expected to extend to much higher energies, $\omega_{\rm pl}^l \simeq 2$ eV, and should be present in La_2CuO_4, while the lower-energy h-plasmon branch is predicted only for the high-T_c superconducting alloys.

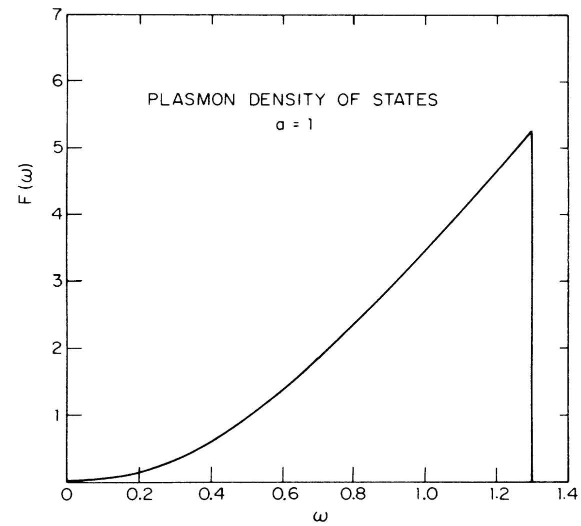

FIG. 3. The plasmon density of states $F(\omega)$ shown for the two-dimensional dispersion relation using $a=1$ and $b=1$. By comparison, two-dimensional acoustic phonons would have $F(\omega) \propto \omega$.

parameter λ and μ^* corresponding to the "acoustic" plasmon exchange process. Our analysis resembles the calculations for metallic hydrogen.[4] For the μ^* defined in Eq. (2) we have the standard definition of the averaged Coulomb repulsion.

$$\mu = N(0) \int_0^{2q_F} \frac{v_q q\, dq}{q_F^2 \epsilon(q,0)} , \tag{6}$$

where v_q is the Coulomb interaction, $N(0)$ is the density of states at the Fermi energy, and $\epsilon(q,0)$ is the static limit of Eq. (5). For parameters appropriate to the placement of the Fermi energy in Fig. 1 (for the superconducting alloy) we estimate $\mu=4.6$ and $\mu^* \simeq 0.4$. As long as the h-plasmon energy $\theta_{\rm pl}^h$ remains below 3000 K, the μ^* parameter is thus reasonably small. Computation of the electron-plasmon interaction follows the Eliashberg equation solution of Eq. (3) with $\alpha^2 = N(0)\langle q v^2(q)\rangle$, and $F(\omega)$ is the density of states for the h-plasmon branch. Here a secondary benefit of the two-dimensional electron dynamics becomes evident because the restricted dimensionality enhances the phonon density of states at lower frequencies and thus enhances λ. The density of states $F(\omega)$ is shown as a function of the dimensionless frequency in Fig. 3 for the h-plasmon dispersion of Eq. (4). For comparison, a truly acoustic-plasmon branch, with $a=0$, would give $F(\omega) \propto \omega$ in two dimensions and such a pristine mode would increase λ by a factor of 2 over the present case. It is worth mentioning that the three-dimensional analog would be $F_{\rm 3D}(\omega) \propto \omega^2$ which yields considerably smaller values. For the case depicted in the figures in this paper we thus estimate $\lambda \simeq 1.4$ and therefore $T_c \simeq 200$ K. The transition temperature is very sensitive to changes in the plasmon frequency $\theta_{\rm pl}^h$. The current model gives the following correlations: for $\theta_{\rm pl}^h = 1800$ K, $\lambda=1.5$, $\mu^*=0.36$, and $T_c=107$ K; for $\theta_{\rm pl}^h=1200$ K, $\lambda=1.4$, $\mu^*=0.30$, and $T_c=60$ K; for $\theta_{\rm pl}^h=600$ K, $\lambda=0.76$, $\mu^*=0.26$, and $T_c=32$ K. Hence T_c is strongly related to the position of the Fermi energy and this novel feature suggests interesting experimental tests which may probe the validity of the two-band plasmon mechanism proposed here.

It should be noted that the above estimate of T_c is crude and should be examined independently by including exchange and correlation corrections to the electronic screening as well as more sophisticated analysis of the Eliashberg equations.[11]

Experimental probes of these predicted low-energy plasmon modes in La-M-Cu-O and Y-Ba-Cu-O superconductors may elucidate the optimum conditions for achieving higher transition temperatures. Of course their existence should be established first, and possible measurements include electron tunneling spectroscopy, electron loss, infrared absorption, and high-frequency acoustic attenuation studies. Neutron scattering may indirectly reveal structure in those optical phonons which intersect the plasmon branch.

A limitation on the plasmon mechanism is imposed by the electron scattering rate which may be influenced by impurities, lattice defects, phonon scattering, and possibly by other means. Thus, the intrinsic plasmon damping will be sensitive to crystal disorder and alloy composition. Also, alloying may shift the Fermi energy or the relative separation of the energy bands in such a way as to allow decay of the lower branch into the electron-hole continuum.

The present results indicate that other materials with two-dimensional electronic structure are likely candidates for high-temperature superconductivity, providing that two appropriate energy bands coexist near the Fermi energy. Naturally, the three-dimensional electron plasma considered originally by Fröhlich[5] and others[6] should also be reexamined in view of the recent discoveries of high-T_c alloys. In this connection, it is worth mentioning that the anomalous concentration dependence of T_c in the oxides referred to as tungsten bronzes, i.e., $M_x WO_3$, has been attributed to an acoustic-plasmon mechanism.[12]

Our conclusions will hopefully serve to stimulate cooperative efforts by experts in band calculations and many-body theorists. The electronic structure provides a valuable guide to the choice of materials which may exhibit acoustic-plasmon oscillations, and their role in superconducting electron pairing merits further study in regard to higher-order screening corrections. Finally, strong coupling solutions of the Eliashberg equations should be examined to ascertain the credibility of the plasmon mechanism as a candidate for room-temperature superconductivity.

After this manuscript was submitted, supporting evidence for the two-band structure envisioned here was obtained for the Y-Ba-Cu-O superconductors from the Mattheiss band-structure calculation[13] and resonant photoemission spectroscopy data.[14]

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