STRONG-COUPLING SUPERCONDUCTIVITY IN V_3X TYPE OF COMPOUNDS

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Recent works[1-5] have shown that the unusual physical properties of high superconducting A_3B type of intermetallic compounds, such as V_3Si and Nb_3Sn, could be understood on the basis of a very fine d-band structure. The Fermi level E_F in the normal state should fall in a very narrow peak of the density of states $n(E)$. This peak lies just above the bottom E_m of a nearly empty d sub-band (Fig. 1). Detailed calculations show that the energy range E_F-E_m of occupied states in the peak is much smaller than the width $\hbar\omega_D$ of the phonon spectrum and of the order of the superconductive gap. For instance, in V_3Si, E_F-E_m in the normal state should be equal to 18×10^{-4} eV $\simeq 22$°K. The same situation seems to arise in Nb_3Sn.

In the usual BCS theory the energy-range limitation to the attractive interaction between two pairing electrons arises from the narrowness of the phonon spectrum. On the contrary, assuming here that the d electrons are the superconducting ones,[6] we may expect the energy-range limitation to be imposed by the narrowness of the electronic spectrum. So the exact value of $\hbar\omega_D$ would not influence the energy gap, in agreement with the extreme smallness of the observed isotopic effect in Nb_3Sn.[7]

Moreover, the very large density of states near the bottom of the d sub-band is related to a Bloch energy $E(\vec{k})$ which varies slowly with the wave vector $\vec{k}$. The variation with k of the kinetic energy $\zeta=E(k)-E_F$ of the Bloch states involved is small compared with the energy gap Δ. This fact brings such compounds near to the strong-coupling limit of superconductivity where all the electrons can be involved in Cooper pairs, owing to their nearly equal kinetic energy. If Q is the small number of d electrons present in the peak of Fig. 1, and if we neglect contributions from other bands, two equations must be solved in the BCS formalism[8] to obtain the gap Δ at absolute zero:

$$Q=\int_{\zeta_m}^{\zeta_m+\hbar\omega_D}1-\zeta(\zeta^2+\Delta^2)^{-1/2}n(\zeta)d\zeta, \tag{1}$$

$$\frac{2}{V}=\int_{\zeta_m}^{\zeta_m+\hbar\omega_D}\frac{n(\zeta)d\zeta}{(\zeta^2+\Delta^2)^{1/2}}, \tag{2}$$

with $\zeta_m=E_m-E_F$. V is the BCS coupling constant; $n(\zeta)$ is the density of states for one spin direction. It is given by[1]

$$n(\zeta)=B(\zeta-\zeta_m)^{-1/2}, \tag{3}$$

where B is a normalization constant.

For small Q, all the electrons involved are in the peak of $n(\zeta)$. Thus the upper limit in Eqs. (1) and (2), being large compared with the width of this peak, is not important (Fig. 1). We shall take it as infinite.

By introducing the new variable $x=\Delta^{-1/2}(\zeta-\zeta_m)^{1/2}$, Eqs. (1) and (2) lead to

$$Q=2B^2VIJ, \tag{4}$$

$$\Delta=B^2V^2J^2 \tag{5}$$

with

$$I=\int_0^\infty\left\{1-\frac{x^2+\eta}{[(x^2+\eta)^2+1]^{1/2}}\right\}dx, \tag{6}$$

$$J=\int_0^\infty[(x^2+\eta)^2+1]^{-1/2}dx, \tag{7}$$

where

$$\eta=\zeta_m/\Delta.$$

Analogous calculations for the critical temperature T_C give

$$Q=4B^2VKL, \tag{8}$$

$$2k_BT_C=B^2V^2L^2, \tag{9}$$

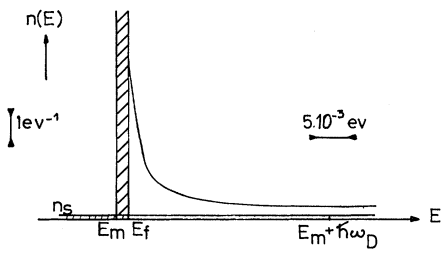

FIG. 1. Density of states and Fermi level position in the normal state.

with

$$K=\int_0^\infty \frac{dx}{1+\exp[(x^2+\eta')]}, \tag{10}$$

$$L=\int_0^\infty \frac{\tanh(x^2+\eta')}{x^2+\eta'}dx \tag{11}$$

where

$$\eta'=\zeta_m/2k_B T_c.$$

We have tabulated I, J, K, and L as functions of the parameters η and η'. Then, Fig. 2 shows the variations of $2\Delta/B^2V^2$ and $4k_BT_c/B^2V^2$ vs Q/B^2V.

We see that both Δ and T_c have a maximum for $Q=Q_M\simeq 7.5B^2V$. Their variation is very slow over a large range of Q surrounding Q_M. In this range we have $2\Delta\simeq 3.5k_BT_c\simeq 7.5B^2V^2$. It is interesting to notice that for $Q\simeq Q_M$ we also have $E_{Fn}-E_m\simeq E_{Fs}-E_m\simeq\Delta$, where E_{Fn} and E_{Fs} are the Fermi level positions in the normal and superconducting states at absolute zero.

In the limit of vanishing Q ($Q\ll Q_M$), it is easy to show that we must assume $\zeta_m\gg\Delta$ for Eqs. (1) and (2) to be consistent. On expanding in terms of Δ/ζ_m, we get from these equations

$$Q=(\tfrac{1}{4}\pi)(B\Delta^2/\zeta_m^{3/2}), \tag{12}$$

$$2/V=(\pi B/\zeta_m^{1/2}), \tag{13}$$

and thus

$$2\Delta/B^2V^2=\pi(2Q/B^2V)^{1/2}. \tag{14}$$

Analogous calculations for T_c show that in the same limit ($Q\to 0$),

$$Q\simeq 2B\pi^{1/2}(k_BT_c)^{1/2}\exp(-\zeta_m/k_BT_c) \tag{15}$$

with ζ_m given by the same equation (13).

From (14) and (15), we see that Δ and T_c have an infinite slope at the origin. But it can be shown that the energy difference between the superconducting and normal states at absolute zero is given, for $Q\to 0$, by $E_S-E_N\simeq -Q\zeta_m$.

In fact, when Q is very small, an electronic transfer may arise from the nonsuperconducting bands to the superconducting d sub-band under consideration (Fig. 1). Denoting their contribution to the density of states by n_S, we obtain

$$Q+n_S\zeta_m=\tfrac{1}{4}\pi B\Delta^2\zeta_m^{-3/2} \tag{16}$$

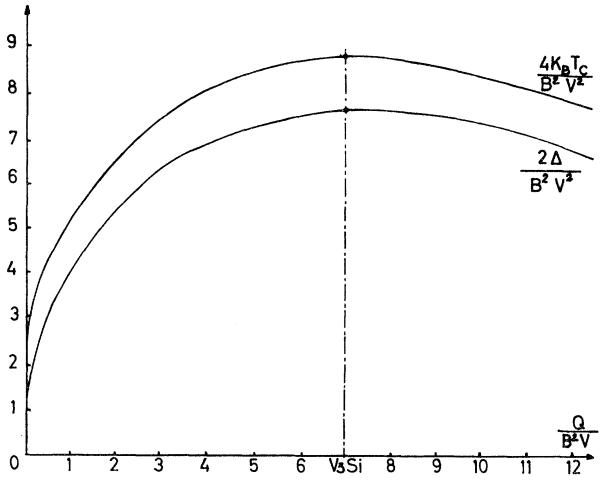

FIG. 2. Variations of the gap and the superconducting transition temperature with the small number of electrons in the narrow d sub-band.

instead of (12). Equation (13) is unchanged. This leads to

$$2\Delta/B^2V^2=\pi\sqrt{2}\,[(Q+Q_S)/B^2V]^{1/2} \tag{17}$$

with $Q_S=n_S\tfrac{1}{4}(\pi^2B^2V^2)\simeq\tfrac{1}{8}n_SVQ_M$. The condition $\zeta_m\gg\Delta$ is satisfied for $Q\ll\tfrac{1}{6}Q_M(1-2n_SV)$. With usual values of V and n_S, we have $2Vn_S\ll 1$. Thus the electronic transfer does not affect the Fermi level position appreciably, even when it is far below the bottom of the superconducting d sub-band. Its only effect is to change the effective number of electrons in the sub-band from Q to Q_S. As $Q_S\ll Q_M$, it is only for the very small Q that Δ and T_c are are appreciably increased.

Finally, when Q is large, i.e., for a Fermi level E_F far above the band edge E_m, E_F-E_m is larger than $\hbar\omega_D$. The limits of integration in (1) and (2) must be taken as $+\hbar\omega_D$ and $-\hbar\omega_D$. The density of states $n(\zeta)$ can be considered as constant over that range, and the usual BCS formula for the weak-coupling limits follows $\Delta\simeq 2\hbar\omega_D\exp\{-1/Vn(E_F)\}$ leading to a rapid decrease of the energy gap Δ with $n(E_F)$.

To conclude, we expect among the A_3B type of compounds all the situations between strong- and weak-coupling limit of superconductivity:

First, if Q is small, as seems to be the case for high superconducting A_3B type of compound (Nb_3Sn, V_3Si, V_3Ga, $\cdots$); we expect strong-coupling superconductivity with negligible isotopic effect. The gap Δ and the critical temper-

ature T_c should depend only weakly on the small number of electrons in the d sub-band and on the density of states at the Fermi level. For that reason, the martensitic phase transition observed in some of these compounds[9-11] should have only a small effect on Δ and T_c. On the other hand, in these compounds T_c could not exceed the maximum value $\simeq 2.2B^2V^2k_B^{-1}$ (Fig. 2).

We may roughly estimate the coupling constant in V_3Si, where $T_c \simeq 17°K$. From our previous estimations,[3] we have $Q \simeq 0.036$ electron atom^{-1} and $B \simeq 0.2$ state atom^{-1} spin^{-1} eV$^{-1/2}$. Thus $(Q^2/B^4V^2)(4k_BT_c/B^2V^2)^{-1} = Q^2/4B^2k_BT_c \simeq 5.6$. From Fig. 2 this corresponds to $Q/B^2V \simeq 7$ and thus $V \simeq 0.15$ eV. We see that in V_3Si, T_c is practically at its maximum value. The value for V, even though of the right order of magnitude, is smaller than the one generally admitted in the transition elements (0.4 eV). In fact, usually, V is only an average of the matrix element $V_{kk'}$ over the range $\hbar\omega_D$ of the phonon spectrum. Here the involved range is not the same, because of the drastic limitation imposed by the narrowness of the electronic spectrum, and the average of $V_{kk'}$ may be somewhat different.

In the opposite case where Q is large, i.e., the Fermi level is far from the peak of density of states, a weak-coupling superconductivity is expected, with normal isotopic effect (T_c proportional to $M^{-0.5}$).

The compounds such as Mo_3Ir, for instance, should be included in the intermediate case. For Mo_3Ir, it was experimentally found that T_c is proportion to $M^{-0.3}$.

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DISCRETE ENERGY LOSSES BY PHOTOEXCITED ELECTRONS IN SILVER AND PALLADIUM*

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Experimentally measured energy distributions of photoemitted electrons from noble and transition metals have been used to determined the optical densities of electronic states below the Fermi level.[1] In the work reported by Spicer and co-workers on Ag[2] and Pd,[3] measurements were made for incident photon energies up to 11.6 eV, the energy being limited by the use of LiF windows within the vacuum system. Using a windowless system, we have extended the range of photon energy to 22.4 eV and have found structure in the energy distribution curves for these metals which, when correlated with the available optical data, suggests that the photoexcited electrons within the metal excite collective oscillations of electron plasma (plasmons) and thereby suffer a discrete loss of energy prior to emission. This effect, when it is energetically possible, must be considered in the calculation of the optical density of states from the photoelectron energy distribution data.

Samples were prepared by the rapid evaporation of high-purity Ag or Pd wire from a triple-strand, helical tungsten coil filament onto a clean glass microscope slide. The evaporated film overlapped an area coated with a Ag-Mn alloy which was electrically connected to a Keithley model 409 picoammeter for the measurement of photoemission currents. The apparatus is essentially that described by Berning, Hass, and Madden[4]; however,