EFFECTS OF ELECTRON CONCENTRATION AND MEAN FREE PATH ON THE SUPERCONDUCTING TRANSITION TEMPERATURES OF ZINC ALLOYS*

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We have found the superconducting transition temperature (T_c) of dilute alloys based on zinc to vary strongly with mean free path, indicating an anisotropy of the energy gap much larger than that observed for other metals, while at constant mean free path T_c varies rapidly with electron/atom ratio (x). A simple model for the gap anisotropy, involving an enhanced value of the gap for the portions of the Fermi surface that have overlapped the (002) faces of the Brillouin zone, leads to a dependence of T_c on electron concentration close to that observed.

The transition temperatures of single-phase solid-solution alloys are shown in Fig. 1, which includes data for alloys of the atomic composition 97.5% Zn, y% Al, and $(2.5-y)$% Ag, for which the mean free path varies only slightly with y. T_c was determined inductively in a helium-3 cryostat, the temperatures being measured by a 30-ohm Speer carbon resistor whose calibration curve was corrected slightly for each run by observing the transitions of pure zinc and pure cadmium. The widths of the transitions of the alloys ranged up to 20 millidegrees; the accuracy of measurement of the mean temperature is estimated at ±5 mdeg.

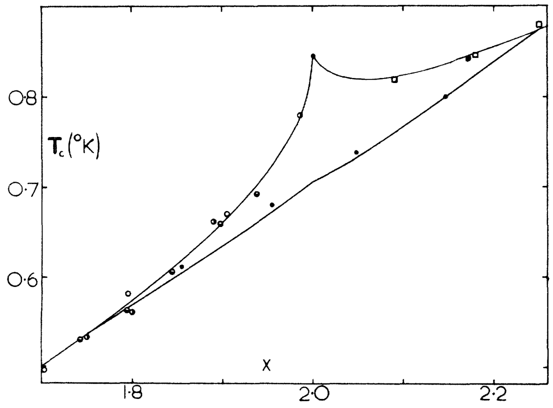

FIG. 1. Experimental values (points) for T_c of binary and ternary zinc alloys plotted against electron concentration, x (electrons/atom), with theoretical values (curves) calculated from (1) for binary Zn-Al and Zn-Ag and ternary Zn-Ag-Al alloys using the values of parameters given in the text. Filled circles: Zn-Ag-Al; open circles: Zn-Ag; squares: Zn-Al; half-filled circles: Zn-Au (vertical) and Zn-Cu (horizontal).

The dependence of T_c on mean free path has been treated theoretically by several authors,[1,2] following Anderson's original suggestion[3] that it is due to the reduction of energy-gap anisotropy brought about by impurity scattering. Markowitz and Kadanoff[1] (hereafter MK) take account of the anisotropy by choosing a simple form for the matrix elements coupling pairs formed from states with momenta $\pm\vec{p}$ and $\pm\vec{p}'$:

$$V_{\vec{p}\vec{p}'} = -\langle \vec{p}', -\vec{p}' | V | \vec{p}, -\vec{p} \rangle$$
$$= [1 + a(\vec{\Omega})] V_{av} [1 + a(\vec{\Omega}')], \qquad (1)$$

where $\vec{\Omega}$ is a unit vector along p and the mean value a_{av} is zero. This choice leads to an energy gap varying as $[1 + a(\vec{\Omega})]$. We have assumed that the difference (ΔT_c) between the transition temperatures of an alloy and the pure metal is the sum of two terms, one depending on mean free path through the function $I(\chi)$ calculated by MK, the other proportional to the electron/atom ratio (x); so that

$$\Delta T_c = (a^2)_{av} T_c I(\chi) + k(x-2). \qquad (2)$$

k is assumed to be the same for all the solutes we used, and $\chi = \hbar / k_B T_c \tau_a$ where τ_a is a time characteristic of the effect on energy-gap anisotropy of electron scattering. If we suppose that τ_a is the same as the relaxation time associated with electrical conduction, then we can use the results of Fawcett[4] to estimate for zinc $\chi = 66\rho$ where ρ is the residual resistivity in $\mu\Omega$-cm.

The curves in Fig. 1 have been calculated for silver and aluminum in zinc using for the values of the parameters

$$k = 5.8^\circ\text{K (electrons/atom)}^{-1},$$
$$(a^2)_{av} = 0.047, \quad T_c = 0.845^\circ\text{K}.$$

There is close agreement between our results and the calculated curves, even though k/T_c and $(a^2)_{av}$ are exceptionally large (more than twice the values derived from data for tin[5] and indium[6] alloys). The data for the binary Au and

Cu alloys may be compared with the curve for Ag, since their calculated curves would differ from it by less than 0.015°K.

We turn now to a discussion of the origin of the term k, that is, of the sensitivity of T_c to electron concentration at constant mean free path. Use of the BCS expression

$$T_c = 1.14\theta_D \exp[-1/N(E)V_{av}]$$

and a free-electron variation of $N(E)$, the density of states, gives a variation of T_c with x of only 0.8°K (electrons/atom)$^{-1}$. The success of a nearly-free-electron model in interpretations of properties of zinc depending on the detailed topology of the Fermi surface means that a breakdown of our assumption about $N(E)$ is unlikely.

The variation of Debye temperature (θ_D) with x is less easily estimated; we shall assume that it makes only a minor contribution to k. A naive application of the Lindemann melting point relation would give a small decrease of T_c with increasing x.

We are led to consider whether variation of V_{av} with x, rather than of $N(E)$ or θ_D, may not be responsible for the greater part of the quantity k, and have investigated a simple model by the use of which k_v, the variation of T_c caused by changes of V_{av} with electron concentration, can be calculated from the value of $(a^2)_{av}$ for the pure metal.

Since the anisotropy observed in the (001) plane[7] is small, the large value of $(a^2)_{av}$ implies that the energy gap for directions close to [001] is very different from the average value. This is the direction in which the Fermi surface overlaps the (002) face of the Brillouin zone. (The second zone for the close-packed-hexagonal lattice in the extended zone scheme is shown in Fig. 2 together with the segments of the free-electron sphere for $x = 2$ cut off by the zone planes.) We shall write Eq. (1) as

$$V_{\vec{p}\vec{p}'} = V_{mm'} = (1 + a_m)V_{av}(1 + a_{m'}),$$

where $m = 2$ when $\vec{p}$ lies in the segment of the Fermi sphere overlapping the (002) faces of the zone, $m = 1$ when $\vec{p}$ lies anywhere else, and for a given m, a_m is assumed constant. We further assume that V_{22} and V_{11} are independent of electron concentration. With increasing electron concentration the solid angle 2ω subtended at the origin by the regions 2 increases, partly because of the increase in diameter, but mainly because the Brillouin zone contracts along the [001] direction. In terms of the c/a ratio (r) of the hexagonal crystal lattice

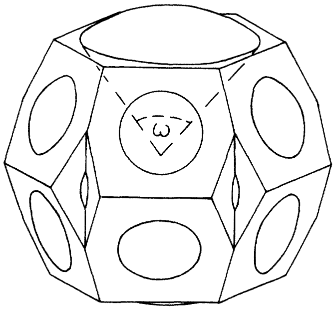

FIG. 2. The Brillouin zone for the close-packed hexagonal lattice with $c/a = 1.83$ and a free-electron Fermi surface for 2 electrons/atom.

$$1 - \omega/2\pi = (3.63/xr^2)^{1/3} = b, \text{ say.}$$

Then

$$(a^2)_{av} = ba_1^2 + (1-b)a_2^2$$

and

$$V_{av} = V_{11}[b + (1-b)\,v^{1/2}]^2$$

where $v = V_{22}/V_{11}$. We obtain the result

$$k_v = \frac{T_c}{N(E)V_{av}^2}\frac{\partial V_{av}}{\partial x}$$

$$= \frac{2T_c}{3N(E)V_{av}}\left(\frac{1}{x} + \frac{2}{r}\frac{\partial r}{\partial x}\right)\frac{1}{1-b+(v^{1/2}-1)^{-1}}$$

$$= 4.0°\text{K (electrons/atom)}^{-1}.$$

Using $(a^2)_{av} = b(1-b)(1-v^{1/2})^2[b + (1-b)v^{1/2}]^{-2} = 0.047$, we find $V_{22} = 2.65V_{11}$. θ_D was taken as 325°K and the crystallographic parameters[8] were taken to be $r = 1.83$ (at 4.2°K) and $dr/dx = 1.77$ (electrons/atom)$^{-1}$, giving $b = 0.176$.

Combining this value of k_v with a free-electron variation of $N(E)$ and ignoring any effects of changes in θ_D, the calculated value of k is 4.8°K. Further support for this model comes from related work on cadmium alloys; and a fuller account of all this work will be published elsewhere.

Brillouin-zone overlaps within solid-solution ranges have previously been suggested[9-11] as a source of anomalies in T_c-composition curves; and the present work, the first on alloys of comparatively simple electronic structure, is in strong support of such suggestions.

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POSSIBILITY OF ONE-DIMENSIONAL SUPERCONDUCTIVITY*

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Recently attention has been drawn toward the possibility that long organic molecules might exhibit superconductivity.[1] At the same time the question has, however, been raised[2] of whether or not there might be special effects associated with the case of one-dimensional motion which might make the occurence of superconductivity in one dimension quite different from its occurrence in three dimensions. Indeed, there is a well-known theorem based on thermodynamic considerations that no phase exhibiting long-range order can exist in one dimension.[3] It has been suggested that this theorem is sufficiently general to cover superconductive ordering.[4] The theorem is predicated on the assumption of short-range forces and it may be argued that the Hamiltonian which forms the basis of the BCS[5] theory of superconductivity essentially involves an infinite-range force. But the actual physical system which the BCS Hamiltonian is intended to describe does, of course, only contain forces of limited range, and there are important modifications of the BCS theory which are required to take into account the terms in the interaction Hamiltonian which are omitted from the reduced Hamiltonian of BCS. These terms, as noted by Bogoliubov, Tolmachev, and Shirkov,[6] Anderson,[7] Rickayzen,[8] and Prange[9] make it possible for the system to exhibit compressional modes of vibration and to satisfy the requirements of gauge invariance. The purpose of this note is to point out that the compressional modes play a much more dominant role in one dimension than they do in three dimensions, and prevent the establishment of the long-range order which is required for superconductive phenomena.

Let the required compressional modes of vibration of particles which are constrained to move in only one direction, say along the x axis, be described by the creation and annihilation operators $a_k{}^\dagger$ and a_k where k is the wave number of the running wave. (Throughout this paper we choose units in which Planck's constant equals 2π.) In terms of these quantized operators, the particle density operator at the position x has the following standard expansion:

$$\rho(x)=\sum_k \frac{ink}{(2mn\omega_k L)^{1/2}}(a_k{}^\dagger-a_{-k})e^{-ikx}, \qquad (1)$$

where m is the mass of the individual fermions, n the linear particle density, L the length of quantization, and ω_k the frequencty of kth mode. The equation of continuity requires that there be a velocity field present which is given by the following simple equation:

$$m^{-1}q(x)=v\rho(x)/n. \qquad (2)$$

$v=\omega_k/k$ is the velocity of propagation of the compressional waves in the long-wavelength limit. $q(x)$ can be interpreted as the local value of the mean pairing momentum of the fermions in the