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DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE ON CARRIER CONCENTRATION IN SEMICONDUCTING $SrTiO_3$†

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(Received 21 January 1965)

The superconducting transition temperature of reduced $SrTiO_3$[1] has been measured as a function of electronic carrier concentration, n_c, over three orders of magnitude, i.e., from 10^{18} to 10^{21} carriers/cm^3. The transition temperature exhibits a maximum in the range of carrier concentration investigated. The dependence of the transition temperature on carrier concentration can be understood on the basis of the assumption that the superconductivity arises primarily from the attractive interaction resulting from the exchange of intervalley phonons between time-reversed electron pairs, and reveals interesting screening effects arising from the free carriers.

The superconductive transitions were observed by measuring the magnetic susceptibility using an ac method at 210 Hz and 0.01-Oe measuring field, and also by four-lead resistance measurements. External fields were compensated to about 0.01 Oe.

The specimens were prepared by appropriate reduction of single crystals of $SrTiO_3$.[1] The carrier concentrations were determined from Hall-effect measurements at 300, 77, and 4°K.[2] As noted in reference 1, representative specimens were measured by x-ray diffractometer techniques to detect possible second-phase contamination, particularly Ti and TiO. To the limit of sensitivity of the technique (about ½%), specimens over the whole range of carrier concentration were shown to be single crystals of $SrTiO_3$ perovskite structure. The electrical-resistance specimens were thin slabs approximately 10×3×1 mm, and the magnetic susceptibility specimens were rough spheres of 3 mm diameter.

The specimens were cooled to temperatures as low as 0.05°K through thermal contact with a few hundred copper wires imbedded in a chromium-potassium-alum pill which was cooled by adiabatic demagnetization. The specimen temperatures were deduced from the paramagnetic susceptibility of a separate chromium-potassium-alum single-crystal sphere 3 mm in diameter which was also in thermal contact with the copper cooling wires at a position beyond the specimens. In order to reduce the time required for each run, the chrome-alum pill was electrically heated between measurements.

Typical examples of the transitions as observed magnetically and resistively are shown in Fig. 1. The electrical specimens generally first showed resistance at a temperature very nearly that of the upper end of the corresponding transition observed magnetically. The transitions are rather broad in tempera-

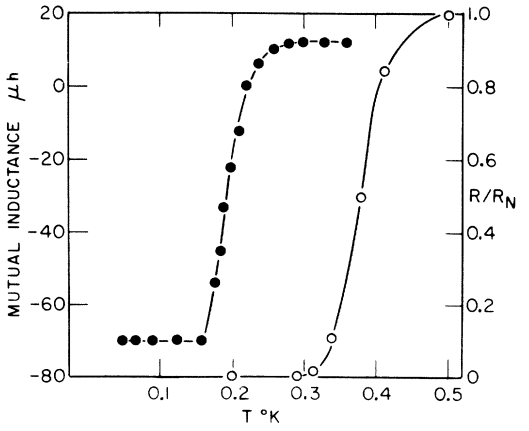

FIG. 1. Superconductive transitions at $n_c = 2.5\times10^{19}$ cm^{-3}. The left-hand ordinate (filled circles) reflects the magnetic specimen susceptibility, and the right-hand ordinate (open circles) shows the ratio of electrical specimen resistance to the normal value, which is constant up through the helium range.

ture; some broadening can be expected to arise from disorder induced in specimen preparation[3] and from strain set up during cooling.[4]

The data are plotted in Fig. 2. The limits shown denote the temperature range over which the transitions occurred and refer neither to errors nor uncertainties. The midpoints of the resistive and magnetic transitions are indicated by circles and crosses, respectively. In several cases, the transition temperature was too low for the entire transition to be observed magnetically; hence no midpoint is shown. In four samples at n_c about 2×10^{18} and 9×10^{20} cm^{-3}, no part of the transition could be observed magnetically. These are shown by the letter "N" at the lowest temperature reached by the chrome-alum sphere.

In order to understand the shape of the curve in Fig. 2 we have applied the theory of superconductivity in degenerate semiconductors,[5,6] utilizing a many-valley model[7] for the conduction band of $SrTiO_3$ with minima lying in the (100) directions near the Brillouin-zone edge. A simplified form of the BCS energy-gap equation[6] was solved to obtain estimates of the transition temperature for several values of the carrier concentration. This equation has the form

$$D_k = -\int \frac{D_{k'}}{E_{k'}} K(c,\delta) \tanh\frac{E_{k'}}{2k_B T} d\epsilon_{k'}, \qquad (1)$$

where $D_k = (k/k_F)\Delta_k$, $E_{k'} = (\Delta_{k'}^2 + \epsilon_{k'}^2)^{1/2}$, $c = k/k_F$, $\delta = (\epsilon_{k'} - \epsilon_k)/E_F$, ϵ_k and $\epsilon_{k'}$ are the energies of the states k and k', and Δ_k is the superconducting energy gap. The kernel, $K(c,\delta)$, is the product of the interaction potential and the density of states [roughly, it represents a measure of the "$N(0)V$" parameter of the BCS theory], and it is given by the algebraic sum of kernels for intravalley Coulomb, intravalley phonon, intervalley Coulomb, and intervalley phonon interactions.

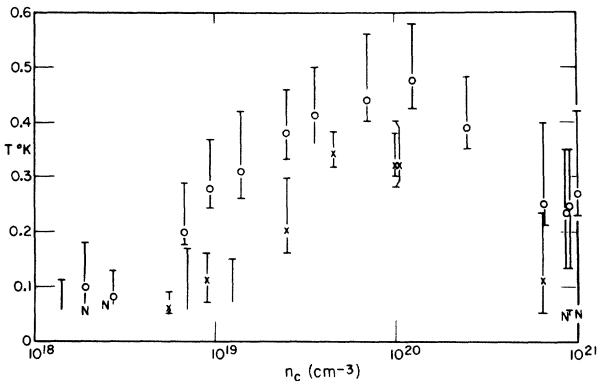

FIG. 2. Transition temperatures versus charge-carrier concentration in $SrTiO_3$. The horizontal bars are not error bars but denote the temperature range of the transition, as shown in Fig. 1. The midpoints of the resistive and magnetic transitions are indicated by circles and crosses, respectively. The lowest temperature reached in the experiments was 0.05°K.

Using the measured vibration spectrum[8] and the forms for these kernels given in reference 6, we have estimated the kernels assuming that the intervalley phonon interaction is the dominant attractive interaction. Screening by the free carriers plays an important role in these calculations and contributes to the appearance of a maximum in T_c vs n_c. The intervalley processes involve large momentum transfers, and therefore screening of the interactions involving these processes becomes appreciable at much higher carrier concentrations than those at which the intravalley interactions become screened. At low carrier concentrations, the density of states increases with carrier concentration, so that the dominant attractive intervalley phonon kernel also increases causing the total kernel to be more attractive. At higher carrier concentrations we have a large density of carriers (also large effective mass),[7] and the intervalley interactions are screened appreciably, reducing the total kernel. Another effect which is important at large concentrations is that the average momentum transfer decreases with increasing carrier concentration because the Fermi surface consists of highly elongated ellipsoids in the (100) direction. The above effects cause the total kernel, and hence the transition temperature, to decrease with increasing concentration at high concentrations.

Not only does the magnitude of the kernel change with carrier concentration, but also the form of its energy dependence is a function of carrier concentration. We have considered the above variations in the kernel and have solved Eq. (1) for several values of the carrier concentration using square-well approximations to the kernels[6] involved. We find that the dependence of the total kernel on carrier concentration causes a maximum in the transition temperature which, choosing reasonable values of the parameters involved, occurs at a concentration of about 10^{20} carriers/cm^3, in agreement with the measured transi-

tion temperatures. Our theoretical results should be considered to be preliminary as some of the parameters used in the calculation (such as the effective mass) are not known accurately for $SrTiO_3$. However, both the concentration at which the maximum transition temperature occurs and the transition temperature itself are within the range of uncertainty of the parameters used in the calculations.

†Work supported in part by the Advanced Research Projects Agency.

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‡Supported in part by the National Science Foundation.

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DE HAAS–VAN ALPHEN EFFECT AND FERMI SURFACE IN PALLADIUM*

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Palladium is a particularly interesting transition metal for several reasons. The density of states at the Fermi level, as measured by the electronic specific heat,[1] is the highest for any pure metal, and the magnetic susceptibility is both very large and has an anomalous temperature dependence.[2,3] Attempts to explain this behavior[4,5] have used a model in which the Fermi level lies just above the peak in the density of states in a narrow d band, but there has been little detailed experimental information on the band structure. The galvanomagnetic data[6] indicate that Pd has an open Fermi surface.

An experimental determination of the Fermi surface of palladium also provides a test of Mattheiss's prediction[7] that isostructural transition metals have, except for shifts in the Fermi level, very similar band structures. We show that this model accounts for both our data and the galvanomagnetic data.

We have observed de Haas–van Alphen oscillations in palladium in the (110) plane and have found that the s band contains 0.36 ± 0.01 electron. It is inferred that the d band contains the same number of holes. By postulating a band structure for palladium similar to that for copper[8] and nonmagnetic nickel[9] (all are face-centered cubic), we place the s-band electrons at Γ and two groups of d-band holes at X.[10] The measurements were made using a modulation technique[11] with modulation frequencies of 600 and 2200 cps and phase-sensitive detection of the second harmonic. Data were taken at temperatures between 1.00 and 1.7°K in a 53-kG Varian superconducting magnet. The Pd single crystal had a resistance ratio 4.0×10^3.

Two distinct sets of periods were observed, one being about 30 times the other. The periods have been converted into extremal cross-sectional areas $\mathcal{A}_0$ of the Fermi surface by using the Onsager[12] relation

$$P = \frac{4\pi^2 e}{h \mathcal{A}_0} = \frac{2.673 \times 10^{-9}}{\mathcal{A}_0},$$

where the last form gives the period in reciprocal gauss if $\mathcal{A}_0$ is measured in atomic units. Figure 1 shows these areas as a function of θ, the angle from [100] in the (110) plane. Beats are observed in the fast period around [111], and these give rise to the double values of the extremal area shown in Fig. 1(a). Clearly these large areas arise from a closed surface which is centered at Γ because the area is single-valued over most of its range. It can easily be seen that the corresponding Fermi surface has "bumps" in the [111] directions, and consequently the smaller area at [111] is the central section through Γ, while the larger comes from a noncentral orbit around the bumps. There must also be smaller bumps in the [100] directions, because $\mathcal{A}_{100} > \mathcal{A}_{111}$.

An empirical interpolation scheme with circular [111] and [100] bumps of sinusoidal cross section was used in an attempt to deduce a consistent set of radius vectors at the symmetry