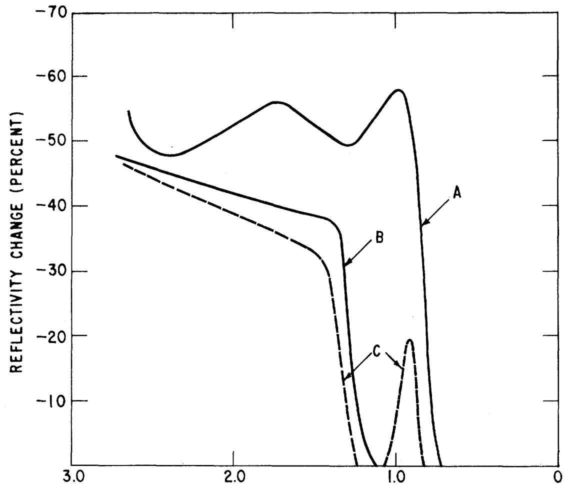

FIG. 2. Change in diffuse reflectivity of hexagonal ZnS samples produced by 3650A excitation at 80° K. *A*—ZnS:10^{-4} Ag, 2×10^{-4} Ga. *B*—ZnS:10^{-4} Au, 2×10^{-4} Ga. *C*—ZnS:10^{-4} Cu, 2×10^{-4} Ga.

in ZnS. They support an explanation in terms of hole transitions and consequently the existence of samples with a Fermi level below the middle of the forbidden band, i.e., *p*-type ZnS. By this interpretation, Figs. 1 and 2 illustrate a capability for the generation of free holes by radiative energy transfer in ZnS which, in *p*-type materials, is not restricted to the region of initial excitation. The existence of such processes must play an important role in the luminescent and photoconductive behavior of these materials.

The authors wish to thank W. W. Piper for supplying activated ZnS single crystals for this survey.

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[1] The terms "ionized luminescent center" and "unionized acceptor" are equivalent for this discussion.

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[8] "0.85-micron" radiation here refers to a band from approximately 0.7 to 1.0 microns isolated from a tungsten lamp with two Corning No. 2600 filters.

[9] 3650A radiation was isolated from a General Electric H-100-A4 Hg arc tube with a Corning No. 5860 filter.

MAGNETIC FIELD DEPENDENCE OF HIGH-FREQUENCY PENETRATION INTO A SUPERCONDUCTOR*

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Preliminary measurements on single-crystal wires of superconducting tin have been made to study the magnetic field dependence of the surface impedance at 1000 Mc/sec as a function of temperature. A microwave resonance technique similar to that of Pippard was used.[1,2] A tin wire was made the inner conductor of an open-circuited coaxial resonant cavity in which the high-frequency magnetic field was excited tangentially to the sample in a plane normal to the wire axis. A static magnetic field, H, was applied either along the sample axis (longitudinal field) or perpendicular to it (transverse field).

The results reported here indicate that this problem is more complicated than was suggested by previous investigations at 72.5 cps by Laurmann and Shoenberg[3] and at 9400 Mc/sec by Pippard.[1] They found that the penetration depth, λ, *increased* by no more than a few percent with increasing H in the range $0 \leq H < H_c$, H_c being the critical field. The surface reactance, X, at 1000 Mc/sec as a function of *transverse* H for a tin sample with crystalline orientation[4] $\alpha = 88.5°$, $\beta = 10°$ is illustrated in Fig. 1 for a few typical values of the temperature, T. Because of demagnetization effects, the measurements in transverse H represent an average over local fields with magnitudes between 0 and $2H$ for an applied field, H. A field variation of X implies a corresponding variation in λ,[1,5] and, in fact, both X and λ are even functions of H.

Several statements can be made regarding the results for this sample in transverse H. (1) X, and therefore also λ, may *decrease* as H increases; this effect will be referred to as *anomalous*. (2) X is weakly dependent on H, except perhaps for H near H_c and for T near T_c, T_c denoting the transition temperature. (3) The field variation of X may be strongly dependent

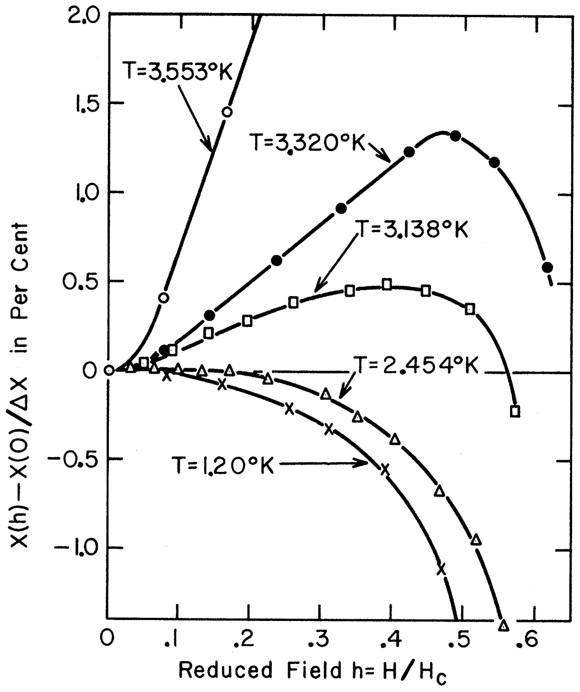

FIG. 1. Variation of the surface reactance at 1000 Mc/sec of Sn with transverse h. The ordinate represents the change in the surface reactance taken between the reduced fields h and zero relative to the change in X for the transition from the superconducting state ($h=0$) to the normal state, i.e., for the sample in the normal state the ordinate is -100%. The anomalous behavior corresponds to a positive ordinate. Hysteresis occurs for $h \gtrsim 0.6$. $T_C = 3.730^{\circ}$ K, and $H_C = 303.4$ gauss at $T = 0^{\circ}$ K.

on T, particularly near T_C. (4) There are two mechanisms operative at a given value of T and H: one, dominant at high T, causes λ to decrease with increasing H and is strongly temperature dependent; the other, prevailing at low T, causes λ to increase and has only a weak temperature dependence. Evidence for the existence of these mechanisms comes from the maxima appearing in the field plots of Fig. 1. As T decreases, these maxima diminish in magnitude and occur at lower values of the reduced field, $h = H/H_C$. (5) The anomalous behavior is not confined to high T but has been observed for temperatures as low as 2.1°K, for which the normal electron concentration, estimated from a two-fluid model, has fallen to 10% of that for $T \geqslant T_C$. (6) The changes in X, and consequently in λ, produced by transverse H as a function of T approach with zero slope a nonzero value at the lowest observed temperatures, in qualitative agreement with Bardeen's theory.[6] (7) The functional dependence of $X = X(H)$ is, in general, quite complicated; but, for T sufficiently low so that the anomalous behavior in X is suppressed, the field variation of X (and therefore also of λ) can be represented by a quadratic function of H.

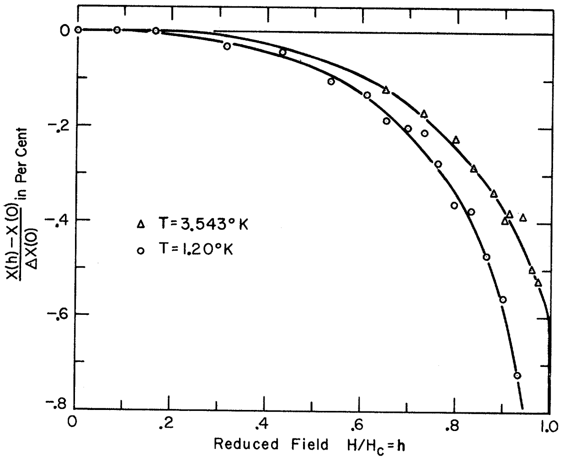

FIG. 2. Variation of the surface reactance at 1000 Mc/sec of Sn with longitudinal h. Curves obtained for 1.20° K $< T < 3.543^{\circ}$ K are similar. In this sample, the variation becomes too small to obtain reliable data for 3.55° K $< T < T_C$.

The highly anisotropic character of the field dependence of X (and λ) is exhibited by a comparison for the same sample of the variation of X in transverse H (Fig. 1) with that in longitudinal H (Fig. 2). Note the difference in scale for the two figures, the measurements of X in longitudinal H showing changes <1% for reduced fields $h < 0.9$. In a longitudinal H, this orientation of tin exhibits no anomalous behavior in $X(H)$. The functions shown in Fig. 2 decrease monotonically with H, and can be represented by a term AH^2 for $T < 3.55$°K, $h < 0.7$, and $A = A(T)$. Measurements on this sample in longitudinal H are not sufficiently precise to establish the functional form of X in the range 3.55°K $< T < T_C$. In longitudinal H, the field variation of X also approaches a nonzero limit at very low T, but smaller by about a factor of 4 or 5 than the asymptotic value in transverse H.

The anomalous decrease in X with increasing H has been observed for: (1) three widely different crystalline orientations of tin; (2) both transverse and longitudinal H in Sn; (3) tin samples prepared from a commercial 99.98% pure ingot and from a more pure zone refined ingot[7]; (4) two indium samples[8] with widely different orientations, $\alpha = 88^{\circ}$, $\beta = 26^{\circ}$, and $\alpha = 0.5^{\circ}$,

β unspecified, the first showing the anomalous behavior in transverse H, the second in longitudinal H. These experiments emphasize the large anisotropy (both in crystalline orientation and field direction) associated with this effect.

In the course of measuring the field variation of X, the corresponding variation in the surface resistance, R, was observed. Under certain circumstances $R(H)$ also shows an anomalous decrease with increasing H. A more detailed account of the complex behavior of $R(H)$ and $X(H)$ will be given at a later date.

Although no decrease in λ with increasing H was reported by Pippard, it is not certain whether this anomalous effect is altogether absent at 9.4 kMc/sec. An unfavorable choice of crystalline orientation and of magnetic field direction might have obscured detection of this behavior, particularly if at the higher frequency the effect is considerably smaller. For these reasons a detailed comparison between the experiments at 1000 Mc/sec and 9400 Mc/sec is difficult at the present time.

Efforts to explain the anomalous behavior of $X(H)$ on the basis of a size effect for the normal electron assembly (as observed in the dc magnetoresistance of thin wires of normal metals[9]) have so far been unsuccessful.

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[†] Standard Oil of Indiana Predoctoral Fellow (1955-6); Bell Telephone Predoctoral Fellow (1956-7). This work is based in part on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Chicago.

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CORRELATION AND THE ISOTOPE EFFECT FOR DIFFUSION IN CRYSTALLINE SOLIDS*

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Bardeen and Herring[1] showed that for the diffusion of the atoms of a pure crystalline solid via the random walk of lattice vacancies, the directions of consecutive jumps of each atom are correlated. The effect of such correlation on the diffusion coefficient D for this case and for other examples of diffusion in cubic cyrstals has been analyzed by Bardeen and Herring[1] and several other authors.[2-7]

We should like to suggest that the dependence of D on the isotopic mass of the diffusant is a function of the correlation between the directions of consecutive jumps of a diffusing atom. LeClaire and Lidiard[5] have shown that while this correlation is zero for interstitial diffusion, it is different from zero for diffusion by the interstice[8] mechanism as well as by the vacancy mechanism. Isotope effect measurements should therefore be useful in deciding among possible diffusion mechanisms in particular cases.

Lidiard[3] has shown that for diffusion by the vacancy mechanism of a solute atom B in infinitely dilute solution in a fcc crystal of A atoms,

$$D \cong \frac{a^2}{6}\,\frac{w_2(w_1+7k_1/2)}{w_1+w_2+7k_1/2}\,p, \qquad (1)$$

where a is the jump distance; w_2, w_1, and k_1 are the probabilities per second that a vacancy on a site next to B make an exchange with B, with any particular one of the four A atoms which are nearest neighbors of both B and vacancy, and with any particular one of the other seven A atoms adjacent to the vacancy, respectively; and p is the fraction of time during which there is a vacancy on a site adjacent to B. We may use Eq. (1) to evaluate the ratio of the diffusion coefficients for two isotopes of an element of masses m_α and m_β diffusing in the A crystal. We shall assume that w_2 depends on the isotopic