pressions become

$$C_1 \approx \frac{\pi^2}{3} k^2 T N_1(\zeta_0) \times \left\{ 1 - \frac{n}{N_1(\zeta_0)} e^{-E_p/kT} \left[\frac{1}{N_1} \frac{dN_1}{dE} \right]_{E=\zeta_0} \right\} + O(T^3) + \cdots, \quad \text{(A8)}$$

$$\Delta C \approx (nE_p{}^2/kT^2) e^{-E_p/kT}. \quad \text{(A9)}$$

C_1 is expressed as usual in an odd-power series in T, but the coefficients are modified by the addition of terms in $e^{-E_p/kT}$. These extra terms will in general be small compared to the usual terms, so that the effect of the electron energy level at E_a upon C_1 will be negligible. In the expression for ΔC, $|E_a-\zeta+T\zeta'|$ has been replaced by E_p; this approximation is of the same order as the replacement of $|E_a-\zeta|$ by E_p.

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Critical Fields of Superconducting Tin, Indium, and Tantalum*

R. W. Shaw,† D. E. Mapother,‡ and D. C. Hopkins
Physics Department, University of Illinois, Urbana, Illinois

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Precise ballistic-induction measurements of the critical field curves of tin, indium, and tantalum are reported. The measurements were made to provide more accurate data on the deviation of the critical field curves from the parabolic law. The resulting deviation functions are generally within the range of uncertainty of earlier measurements. The main experimental error in the observed deviation now arises from uncertainty in the extrapolation of the measurements to 0°K from the present lower limit of 1.1°K. Measurements at lower temperatures which will eliminate some of this uncertainty are to be desired.

I. INTRODUCTION

ALL pure superconductors have critical field curves which approximate the parabolic relation, $H_c = H_0[1-(T/T_c)^2]$. Experimental measurements have shown[1] (and theory has predicted[2]) deviations from this relation. Observations on lead[3] and mercury[4] have been of particular interest in showing deviations of the opposite sense from those found in the majority of superconductors and predicted by theory. The present work reports critical field measurements on superconducting elements all of which deviate from the parabolic H_c relation in the sense predicted by the BCS theory. These measurements achieve a significant improvement in accuracy over earlier results and also show differences in detail among the several elements.

II. EXPERIMENTAL

The two tin specimens measured differed both in purity and preparation. Sn-1 was reagent grade material (99.97%) from Allied Chemical Company. It was cast and grown as a nearly single crystal in a graphite coated Pyrex tube and in a vacuum of 10^{-5} mm Hg. The tube was later etched off in hydrofluoric acid. Sn-2 was formed from 99.9998% pure tin from Vulcan Detinning Company. It was vacuum cast and grown in a carefully cleaned and outgassed crucible of pure graphite. The outside of the crucible was slotted to allow it to be broken away from the specimen with a minimum of damage. This specimen was then vacuum annealed near the melting point to minimize the effects of strains introduced during the removal of the crucible.

Two indium specimens were also prepared, both from high purity indium supplied by the Indium Corporation of America. Sample In-0-8 was prepared in the same manner as Sn-1 and the preparation of In-2 and Sn-2 similarly corresponded. Semiquantitative spectrographic analysis by the Detroit Testing Laboratory indicated a total metallic impurity of 0.03% in In-0-8 and 0.05% in In-2. This difference is thought to result from a higher initial purity of the slug used in forming In-0-8 rather than the difference in fabrication techniques. The dimensions of the tin and indium specimens were approximately the same: cylinders of diameter 0.070 in. and length 1.5 in.

The tantalum was kindly provided by Dr. J. I. Budnick who reported a resistance ratio for the material between 20°C and 0°K of 1400. It was in the form of 0.010-in. diameter wire which was cut with a razor blade into approximately 1.5-in. lengths. No doubt some strained regions with altered super-

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† Present address: Physics Department, Rensselaer Polytechnic Institute, Troy, New York.

‡ Alfred P. Sloan Fellow.

[1] See, for example, M. A. Biondi, A. T. Forrester, M. P. Garfunkel, and C. B. Satterthwaite, Revs. Modern Phys. **30**, 1109 (1958).

[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[3] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958).

[4] D. K. Finnemore, D. E. Mapother, and R. W. Shaw, Phys. Rev. **118**, 127 (1960).

TABLE I. Summary of critical field data. The footnotes indicate the random experimental error in measured values.

	Sn-1			In-0-8			Ta	
	T[a]	H_c[c]		T[a]	H_c[c]		T[a]	H_c[d]
Transitions	°K	oersted	Transitions	°K	oersted	Transitions	°K	oersted
3	3.6922	4.342	4	3.3576	7.650		Six strands	
3	3.6344	12.788	3	3.2253	27.408	5	4.1761	100.20
3	3.5468	25.54	4	3.0682	50.02	3	3.9828	160.19
2	3.3591	52.28	3	2.7526	93.04	3	3.7046	243.15
3	3.2260	70.42	3	2.5164	122.82	2	3.3928	331.29
3	3.0683	91.25	4	2.3053[b]	147.59	3	3.1034	407.99
3	2.7520	130.72	3	2.0304	177.16	2	2.8242	476.92
3	2.5158	158.19	5	1.7587[b]	203.20	3	2.5309	544.16
2	2.3079	180.61	3	1.4162[b]	231.09	3	2.0403	642.43
3	2.0307	208.16	3	1.2310[b]	244.18	3	1.7966	684.15
3	1.7565	232.55	3	1.0736	254.29	3	1.5452	722.17
3	1.4132	258.54	5	3.3874	3.099	3	1.2723	757.00
3	1.2287	270.42				4	1.0991	776.23
3	1.0700	279.77						
3	3.3869	48.36						
	Sn-2			In-2			One strand	
5	3.6767	6.873	5	3.3499	8.851	4	4.1870	96.42
5	3.6636	8.842	5	3.3264	12.38	6	2.0418	641.88
5	3.6442	11.622	3	3.1022	45.35			
5	3.5190	29.70	5	3.3819	4.038		Four strands	
4	3.3509	53.43	3	3.2274	27.24	4	4.1739	100.41
3	3.3273	56.66	5	2.9087	72.54	6	4.4411	13.57
3	3.1019	86.92	3	2.7066	99.36	6	4.4085	24.39
5	3.6926	4.432	3	2.5231	122.32	6	4.3618	40.00
3	3.3811	49.31	3	2.3518	142.72	7	4.2635	71.80
3	3.2268	70.43	3	2.1206[b]	167.43	2	1.6966	699.52
3	2.9113	111.47	3	1.8982	190.66	2	1.4176	738.83
3	2.7088	136.17	3	1.6584	212.07	2	1.1806	766.35
3	2.5228	157.63	3	1.5041	224.72			
3	2.3495	176.60	3	1.3537	236.16			
3	2.1207[b]	199.46	3	1.2254	244.82			
3	1.8978	220.67	3	1.1064	252.46			
3	1.6578	240.60						
3	1.5038	252.28						
3	1.3526	262.90						
3	1.2257	270.88						
3	1.1040	278.09						

[a] Temperature uncertainty = ±0.0005°K.
[b] Abnormal temperature uncertainty = ±0.002°K.
[c] Magnetic field uncertainty = ±0.05 oersted.
[d] Abnormal field uncertainty = ±0.2% of H_c. See text for explanation.

conducting properties[5] existed near the cut ends. However, for the present length to diameter ratios, the effect of these regions should be quite small. In order to form a readily measurable specimen several of these strands were stacked together within the same coil.

The ballistic induction techniques are those used in the earlier research on lead[3] and mercury.[4] Most of the present measurements were carried out in the cryostat used for the mercury measurements. However, T_c for tantalum is somewhat above the normal boiling point of helium and for this range the cryostat from the lead measurements was used.[6] By operating at an overpressure points close to T_c could be taken while using the helium vapor pressure for temperature indication. All temperatures were deduced from the 1958 He^4 Scale of Temperatures.[7]

III. RESULTS AND DISCUSSION

Table I gives the critical field and temperature values for each specimen together with the number of transitions measured at each point. For the tin and indium specimens the random uncertainties in each point are ±0.0005°K and ±0.05 oersted but this is somewhat dependent upon the number of transitions measured and the temperature. In particular, near the lambda point (2.18°K) temperature regulation is sometimes difficult, leading to a considerably larger uncertainty. Points for which this is true are indicated by a footnote.

A typical transition cycle (S-N-S) for tantalum is shown in Fig. 1. Note that the S-N curve clearly

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[5] J. I. Budnick, Phys. Rev. (to be published). See also D. P. Seraphim and R. A. Connell, Phys. Rev. **116**, 606 (1959).

[6] R. R. Hake, D. E. Mapother, and D. L. Decker, Phys. Rev. **112**, 1522 (1958).

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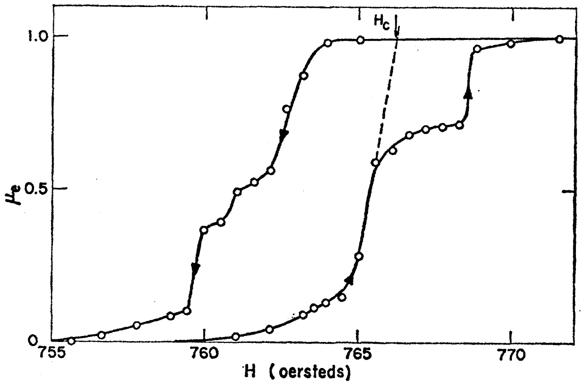

FIG. 1. A typical transition cycle for a specimen composed of four strands of tantalum wire.

shows regions in the transition in which no change of μ_e occurs when the applied field is changed. No detailed study of this phenomenon has been made but it can be interpreted as indicating slightly different critical fields for various parts of the specimen. A single strand of tantalum wire also showed this same type of behavior. The method chosen for determination of H_c, extrapolation of the lower approximately linear portion of the curve to $\mu_e = 1$, represents a compromise among the various ways this curve might be interpreted. A comparable uncertainty is caused by the presence of hysteresis in the transition. In lead a separation of S-N and N-S transitions, such as is shown in Fig. 1 for tantalum, indicates a reversible critical field midway between the two transitions.[3,8] A comparison of samples with differing amounts of hysteresis has not been made for tantalum and we are reluctant to apply the lead findings to this case. Thus the tantalum critical field values may easily be in error by half of the hysteresis width, or approximately 0.2% of the critical field value. Further measurements on other tantalum specimens are planned.

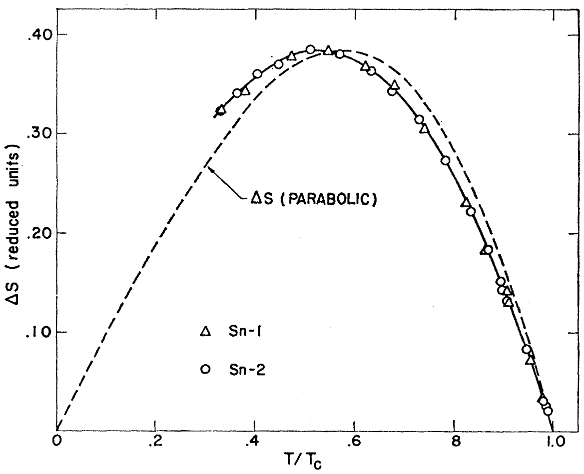

FIG. 2. Entropy change in the S-N transition of tin calculated from the data of Table I, together with the same curve for a hypothetical superconductor with parabolic critical field curve (dashed curve). ΔS (Reduced units) $= \Delta S[V_{\mathrm{mol}} H_0^2 / 2\pi T_c]^{-1}$.

The solenoid constant was measured by proton resonance techniques following the last run of this work. The systematic error from this and other sources is thought to be less than the approximately 0.1% maximum difference in critical fields observed between samples of the same element. The values quoted for the purer samples (Sn-2 and In-0-8) are to be preferred. Where applicable, corrections have been made for thermomolecular pressure difference,[9] field inhomogeneity, and field interference among samples.[6]

Table II gives the values of T_c, H_0, and γ (the coefficient of the normal electronic specific heat) derived from the critical field measurements of each specimen. Determination of H_0 requires an extrapolation to the absolute zero which has been accomplished by assuming a linear H_c vs T^2 curve below the lowest measured points. γ is determined, basically, from the limiting slope of the entropy difference curve[10]:

TABLE II. Constants derived from the critical field data.[a]

Specimen	T_c (°K)	H_0 (oersteds)	γ (cal/mole°K²)×10⁻⁴
Sn-1	3.7214±0.0005	308.8±0.5	4.75±0.3
Sn-2	3.7224±0.0005	308.6±0.5	4.69±0.3
In-0-8	3.4075±0.0005	285.7±0.5	4.57±0.3
In-2	3.4085±0.0005	285.7±0.5	4.55±0.3
Ta	4.4820±0.0008	830 ±4.0	15.5 ±1.0

[a] All errors quoted indicate only the approximate internal consistency of each set of data.

$$\gamma = \lim_{T \to 0} \frac{d\Delta S}{dT}.$$

Figure 2 shows the curve of ΔS vs T based upon the data for tin in Table I. It is clear that ΔS does not define γ unequivocally.[4] Similar curves can be constructed for indium and tantalum with the same conclusion.

The H_0 and γ values of Table II should soon be superseded when a He³ refrigerator, now being built at this laboratory, becomes operational. For this reason curve fitting and more detailed extrapolation procedures have not been carried out at this time. The values of H_0 and γ listed here are large relative to those given in earlier papers.[11] This is due, in part, to the lower temperatures reached here and the continuous increase

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[8] R. W. Shaw and D. E. Mapother, Phys. Rev. **118**, 1474 (1960).

[9] T. R. Roberts and S. G. Sydoriak, Phys. Rev. **102**, 304 (1956).

[10] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937).

[11] For tin see E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957). For indium see E. Maxwell and O. S. Lutes, Phys. Rev. **95**, 333 (1954), and J. R. Clement and E. H. Quinell, Phys. Rev. **92**, 258 (1953). For tantalum see D. White, C. Chou, and H. L. Johnston, Phys. Rev. **109**, 797 (1958) and reference 5.

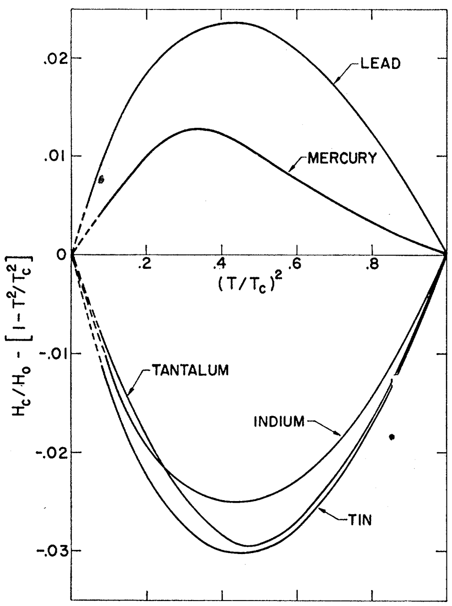

FIG. 3. Deviation of critical field curves of several superconductors from parabolicity. For clarity the curves for individual samples of tin and indium are not shown (since the differences in D amount to 0.0014 or less).

found in $-dH_c/dT^2$ as temperature is lowered. Whether this behavior will extend into the range below 1°K remains to be seen.[12]

The deviation, $D(t)$, of the critical field curve from parabolicity is defined as the difference between the true critical field curve and a parabola drawn through the experimental values of H_0 and T_c:

$$D(t)=\frac{H_c(t)}{H_0}-(1-t^2),$$

Such curves are shown in Fig. 3 for the materials discussed here as well as for lead and mercury. It is clear that the differences among tin, indium, and tantalum are small. The amplitudes of these curves are sensitive to the choice of H_0 and thus are affected by the uncertainty in the extrapolation to 0°K. Measurements below 1°K will be required before the differences in amplitude of $D(t)$ for these elements can be considered to be clearly established. Further measurements, if extended to sufficiently low temperatures to yield reliable γ values, will also permit the deduction of the temperature dependence of C_{es} (the superconducting electronic specific heat) from the shape of $D(t)$.

IV. ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of D. K. Finnemore in taking the measurements. Discussions with Professor C. A. Swenson, Dr. J. I. Budnick, and Dr. M. Garfinkel have been most helpful.

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[12] It should be pointed out that the work of E. A. Lynton, B. Serin, and M. Zucker on tin indicates that a value of γ in better agreement with calorimetric data results if critical field data are extrapolated to 0°K by means of an expression which takes explicit account of the exponential temperature dependence of the superconducting electronic specific heat.

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Anisotropic Superexchange Interaction and Weak Ferromagnetism

TÔRU MORIYA*
Bell Telephone Laboratories, Murray Hill, New Jersey

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A theory of anisotropic superexchange interaction is developed by extending the Anderson theory of superexchange to include spin-orbit coupling. The antisymmetric spin coupling suggested by Dzialoshinski from purely symmetry grounds and the symmetric pseudodipolar interaction are derived. Their orders of magnitudes are estimated to be $(\Delta g/g)$ and $(\Delta g/g)^2$ times the isotropic superexchange energy, respectively. Higher order spin couplings are also discussed. As an example of antisymmetric spin coupling the case of $CuCl_2\cdot 2H_2O$ is illustrated. In $CuCl_2\cdot 2H_2O$, a spin arrangement which is different from one accepted so far is proposed. This antisymmetric interaction is shown to be responsible for weak ferromagnetism in α-Fe_2O_3, $MnCO_3$, and CrF_3. The paramagnetic susceptibility perpendicular to the trigonal axis is expected to increase very sharply near the Néel temperature as the temperature is lowered, as was actually observed in CrF_3.

INTRODUCTION

WEAK ferromagnetism of mainly antiferromagnetic crystals, represented by α-Fe_2O_3 and the carbonates of Mn and Co, has been a controversial problem for a decade. Néel[1] proposed an explanation of this phenomena based on an impurity effect, possibly magnetite. Many years later, Li[2] proposed a different explanation based on antiferromagnetic domains with magnetized walls. As he pointed out, however, the formation of antiferromagnetic domains is not energeti-

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* On leave of absence from Tokyo Metropolitan University, Tokyo, Japan.

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[2] Y. Y. Li, Phys. Rev. 101, 1450 (1956).