From Eq. (A6), setting $T_c = T_{cn} = 0°\mathrm{K}$, we find

$$d_s = (\pi/2)^2 \xi_{ss}. \qquad \text{(A8)}$$

The meaning of relation (A8) is that a film with the order parameter fixed at zero on one of its boundaries will not be superconducting when its thickness is inferior to the critical thickness given by (A8). Recently, Werthamer[15] solved exactly the Ginzburg-Landau equations for a film of thickness d with the order parameter fixed at zero on both boundaries and found that the film would not be superconducting unless its thickness is greater than $d_c = \pi\delta/\kappa \simeq \pi\xi_0$ (δ is the weak field penetration depth and κ the G-L parameter). Consequently, superconductivity would disappear in a film thinner than $(\pi/2)\xi_0$ when the order parameter is fixed at zero on only one of its boundaries. Equation (A8) is therefore a very general result of the G-L theory; the discrepancy between the two numerical results is most probably due to the fact that (A8) is derived from Eqs. (A1) through (A3), which are only valid in the dirty limit ($l < \xi_0$), while the Ginzburg-Landau result was derived for pure films ($l > \xi_0$).

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[15] N. R. Werthamer, in Ginzburg-Landau Equations of Superconductivity, edited by R. D. Parks (to be published).

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Superconducting Transitions of Isotopes of Zinc*

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The effect of isotopic mass on the superconducting transition temperature T_c of Zn has been investigated in three highly purified samples with average isotopic masses of 63.96, 65.91, and 67.94. By extrapolating critical magnetic field curves to zero field, values of 0.855, 0.846, and 0.836°K were obtained for T_c of Zn^{64}, Zn^{66}, and Zn^{68}, respectively. These values were found to satisfy the relation $T_c \propto M^{-z} = M^{-0.5(1-\zeta)}$ with z taken as 0.37 and ζ as 0.25. Critical field curves measured between 0.39°K and T_c were found to have a maximum deviation from a parabola of about 5.7%. Specific heats calculated from these critical field curves are compared with direct measurements made by others. The superconducting-to-normal transition of a sample was observed to broaden as the applied magnetic field was reduced below some small value. Ratios of transition widths in "zero" field and in the earth's field ranged from about 2 to over 30, depending on the sample.

I. INTRODUCTION

The transition temperatures T_c of superconducting elements have been found to follow the relation $T_c = kM^{-z} = kM^{-0.5(1-\zeta)}$, in which k is a constant different for each element and M is the average isotopic mass of the specimen. The value of z found from the original work[1] with Hg and predicted by the simple model of Bardeen, Cooper, and Schrieffer[2] (BCS) is 0.5. ζ is the deviation from $z = 0.5$. Various authors,[3–6] using more detailed models, have made predictions of values for ζ for different elements. The value of ζ predicted for Zn is among the largest made for any nontransition element.

The previous measurement of the isotope effect in Zn by Geballe and Matthias[7] suggested that the normal isotope effect of $z = 0.5$ occurs in zinc. The work to be reported here gives a value of 0.37 for z. A slightly lower value was given in previous reports.[8,9] Since then a systematic error was found in the routine for establishing the temperature scale.

II. EXPERIMENTAL TECHNIQUES

Sample Preparation

The three samples used were obtained from the Oak Ridge National Laboratory and had average isotopic masses of 63.96 (99.85% Zn^{64}), 65.91(98.8% Zn^{66}), and 67.94(99.3% Zn^{68}). As received, the samples had residual resistivity ratios r of about 1/10, where $r = \rho(4°\mathrm{K})/\rho(297°\mathrm{K})$. A preliminary run showed that the superconducting-to-normal (S-N) transition of one of these samples in the earth's magnetic field was about 20 times as broad as that of a reasonably pure single crystal of natural Zn. The large values of r and the broad transition indicated that the samples were not adequate for studies of the isotope effect.

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* Work supported by the U.S. Atomic Energy Commission and the Wisconsin Alumni Research Foundation.

[1] E. Maxwell, Phys. Rev. **78**, 477 (1950); C. A. Reynolds, B. Serin, W. H. Wright, and L. B. Nesbitt, *ibid.* **78**, 487 (1950).

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

[3] J. C. Swihart, IBM J. Res. Develop. **6**, 14 (1962).

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[6] J. W. Garland, Jr., thesis, University of Chicago (unpublished).

[7] T. H. Geballe and B. T. Matthias, IBM J. Res. Develop. **6**, 256 (1962).

[8] R. E. Fassnacht and J. R. Dillinger, Phys. Rev. Letters **17**, 255 (1966).

[9] J. R. Dillinger, R. E. Fassnacht, and D. M. Jones, in Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966 (to be published).

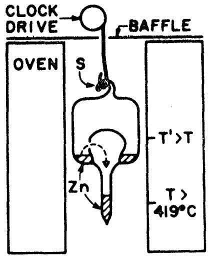

FIG. 1. Schematic diagram of apparatus used in purifying the samples by distillation.

Since zinc has a much higher vapor pressure than most other metals at any given temperature, the samples could be purified by sublimation and distillation. To sublime a sample, it was placed at the closed end of a horizontal Pyrex tube the other end of which was connected to a vacuum system through two liquid-nitrogen-cooled traps. Heated to about 370°C by an oven, the sample sublimed while the residual gas pressure remained at about 3×10^{-6} Torr. Impurities which were more volatile than Zn, such as that Cd which had not been eliminated in the original isotope separation, resolidified in the horizontal tube nearer the vacuum system, while less volatile impurities were left behind in the oven. Material from the ends of this tube was not used in subsequent purifications.

After two or three such sublimations, each sample was distilled and grown into a cylindrical specimen in a Pyrex chamber shown in Fig. 1. A light coating of carbon was deposited on the inside of the tube forming the lower part of the chamber after it was chemically cleaned. This was accomplished by thermally decomposing ethyl alcohol and served to prevent the Zn from wetting and sticking to the glass. While attached to a vacuum system at S, the chamber was outgassed, flushed with He, reoutgassed, and filled with He. After introducing the sample into the upper part of the chamber from a tube not shown, the chamber was reevacuated, heated to the melting point of Zn to outgas the metal, and then sealed off at a pressure of about 5×10^{-6} Torr.

The chamber was then placed in the oven, and the Zn was distilled into the lower section as shown by the arrow. Slowly lowering the chamber through the thermal gradient permitted the sample to crystallize. Grinding opposite sides of the tube flat, and scribing lines with a diamond point along the ground surfaces, made it possible to remove the tube by mechanically splitting it along the lines. Each sample was then annealed for over 24 h at about 200°C in a He atmosphere.

After completion of the low-temperature measurements, the samples were etched in dilute HCl to reveal crystal boundaries. To avoid effects due to the diffusion of hydrogen into the lattice, they were not etched prior to this time. The Zn^{64} sample was seen to be composed of three crystallites while the Zn^{66} and Zn^{68} samples were single crystals.

The data to be presented here were obtained after each sample had been distilled at least three times. Data obtained previous to the final distillations of the samples were essentially identical to those to be presented. In final form, the samples were cylinders about 4 mm in diameter and $6\frac{1}{2}$ cm long with residual resistivity ratios of 3.3×10^{-5} for Zn^{64}, 2.7×10^{-5} for Zn^{66}, and 3.6×10^{-5} for Zn^{68}. These values were measured by a method similar to that reported by Bean *et al.*[10] and are probably accurate to ±10%.

Following the completion of the experiments, the samples were analyzed by means of a spark-source mass spectrometer[11] to determine impurity concentrations. Table I shows values which represent, within a factor of 2–3, the upper limits of actual impurity concentrations expressed in atom parts per million (ppm). The symbol $<$ preceding a number indicates that the element in question was not observed, and the number gives the largest estimated concentration which could go undetected. Each sample was analyzed for 55 elements in addition to zinc and the 17 listed in Table I. The concentration of each of these 55 elements was found to be less than the minimum detectable which, except for F, Na, and Mg, was usually <0.06 ppm and often <0.02 ppm. The relatively large and uncertain values for Ta are attributed to the electrodes of the spark source being made of Ta. Use of Pyrex glass in the purification of the samples probably

TABLE I. Impurities in ppm detected in the samples by means of a spark-source mass spectrometer.

Impurity	Zn^{64}	Zn^{66}	Zn^{68}
Be	0.08	0.06	≤ 0.4
B	1.3	<0.15	0.50
Al	0.04	0.05	0.04
Si	<0.9	<1.2	<0.9
S	masked	≤ 0.4	≤ 0.14
K	0.08	<0.15	<0.07
Ca	0.08	0.13	0.10
Ti	0.07	0.08	<0.20
Cr	0.06	0.10	0.10
	(0.07)	(0.08)	(0.08)
Mn	<0.04	<0.05	<0.04
Fe	0.15	0.10	0.14
	(0.05)	(0.05)	(0.10)
Co	<0.04	<0.05	<0.04
Ni	0.02	<0.04	0.02
	(0.03)	(0.02)	(0.03)
Ga	<0.02	<0.09	≤ 0.07
Ta	≤ 3.0	≤ 6.0	≤ 1.5
W	<0.02	0.2	0.04
Pb	<0.03	<0.03	0.02

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[10] C. P. Bean, R. W. De Blois, and L. B. Nesbitt, J. Appl. Phys. **30**, 1976 (1959).

[11] The authors would like to thank J. C. Franklin and W. D. Harman of the Y-12 plant of Union Carbide Corp., Nuclear Division, Oak Ridge, Tennessee, for analyzing the samples.

accounts for the presence of B. Since Zn cannot be baked at a high temperature in a good vacuum, the analysis could not include the gaseous elements or C.

For samples such as those studied here with impurity concentrations of <1 ppm, experimental difficulties such as the presence of contaminating elements in the analyzer make it difficult to determine the actual impurity concentrations in the samples. Also, it is possible for various organic compounds and radicals to be formed by the spark source from contamination. This gives ions which can be mistaken for significant elements. Resistivity ratio measurements[12] and self-consistency of the superconductivity measurements on these samples were useful in pointing out some errors in the original analysis. With particular attention being given to Fe, Cr, Ni, and Ti, the samples were reanalyzed. Table I gives the final analysis. The values given in parenthesis for Cr, Fe, and Ni represent an independent analysis by another group using a different spark-source mass spectrometer.[13]

Apparatus and Thermometry

The He^3 refrigerator used here has an experimental volume $5\frac{1}{2}$ in. in diameter and 9 in. long. With no pumped He^4 bath it can run continuously down to 0.8°K and can maintain temperatures as low as 0.37°K for periods of time greater than 15 h.

To insure thermal equilibrium among them, the three samples and two thermometers were contained in four of five interconnected chambers filled with liquid He^4. Figure 2(a) is a horizontal cross-sectional view of the chambers. The samples S occupied 3 chambers separated from each other by a distance of 3 in. so that the magnetic field at any one would not be affected significantly by the state (superconducting or normal) of any other. C_1 and C_2 represent primary and secondary coils, respectively, of the mutual induction system located in each sample chamber and used to detect the S-N transitions. C_1' and C_2' are similar coils located in the fourth chamber together with the bulb of the He^3 vapor-pressure thermometer and the carbon resistor thermometer. J is a spiral of sheet copper connected to a solid rod in the fifth chamber. These served as the thermal link between the liquid He^4 in the 5 chambers and the evaporation chamber of the He^3 refrigerator.

Figure 2(b) is a vertical cross-sectional view through the centers of the three chambers containing one sample, the thermometers, and J. As indicated, the chambers were constructed of Cu and austenitic stainless steel (type 304), SS, which is sufficiently nonmagnetic for these purposes. V is the He^3 vapor-pressure thermometer, and T is the carbon resistor thermometer. Precautions were taken to use nonsuperconducting solders in the vicinity of the samples to avoid entrapment of flux with resulting distortion of the applied magnetic field. The top lids of the chambers, which were $3\frac{1}{2}$ in. from the samples, were sealed on with Cd-Bi eutectic solder which has been observed to be nonsuperconducting at temperatures as low as 0.76°K.[14] All other joints in the chambers were made with silver solder which is nonsuperconducting. Electrical leads were brought into the chambers through single-pin glass-to-metal seals L which were sealed on with soft solder. The heater H was wound noninductively on the outside of one chamber as shown and thermally attached with vacuum grease. The spiral of sheet copper and rod J were thermally connected with the evaporation chamber K of the He^3 refrigerator by means of a Cd-Bi solder joint at D. Liquid He^4 was admitted through the 0.006 in. i.d. stainless-steel capillary G in order to fill the five chambers to the level shown. Tube M was connected to a vacuum system during a run in order to pump away He^4 gas resulting from evaporation of liquid transported up through G by film flow. Without pumping, this gas would flow down G, recondense, and give rise to an intolerable heat leak. B is a thin-

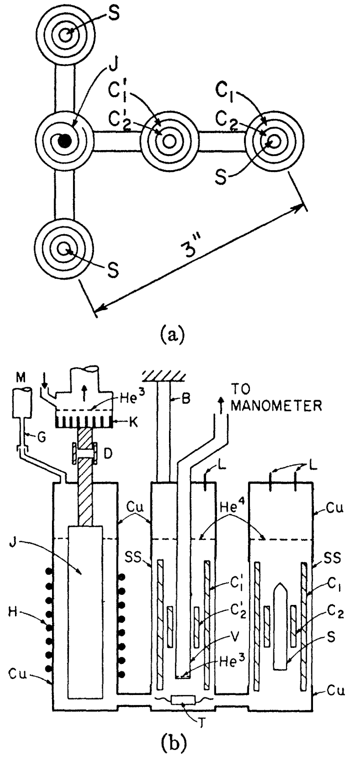

Fig. 2(a). Horizontal cross-sectional view through the five chambers. (b) Vertical cross-sectional view through three of the five chambers.

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[12] G. Boato, G. Gallinaro, and C. Rizzuto, Phys. Rev. **148**, 353 (1966).

[13] The authors would like to thank J. A. Carter and J. R. Sites of the Oak Ridge National Laboratory for the confirming analysis of the samples for Cr, Fe, and Ni.

[14] J. F. Cochran, D. E. Mapother, and R. E. Mould, Phys. Rev. **103**, 1657 (1956).

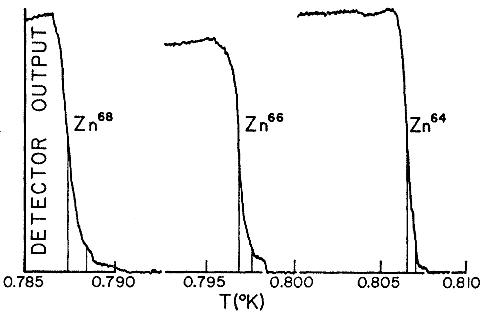

FIG. 3. *S-N* transitions of isotopes of Zn in a magnetic field of 5.02 Oe. Ordinates are outputs of a mutual induction detection system. Vertical lines are drawn to points on each curve at which the output of the detector had decreased by 50 and 90% of its maximum change.

wall stainless-steel tube to give added support to the chambers.

The magnetic fields, which were applied parallel to the axes of the samples, were produced by a single-layer sixth-order solenoid with overwound ends as described by Garrett.[15] It generated a field calculated to be uniform to 0.1% over the volume occupied by the samples. The horizontal component of the earth's field was bucked out by the use of two sets of coils placed outside of the nitrogen Dewar similar to those described by Abel *et al.*[16] There was no magnetic material near the apparatus. The existence of uniformity of magnetic field and thermal equilibrium among samples was established by interchanging the positions of the samples between runs, and obtaining no significant difference in the data.

A mutual induction system was used to detect the *S-N* transitions. The primary coils were excited by a 96 Hz signal which produced a measuring field of about 0.01 Oe at the samples. Each 30 000 turn secondary coil surrounding a sample was connected in series opposition to the dummy secondary coil C'_2 located in the center chamber. The output voltage from each pair of coils was electrically nulled when the sample was in the normal state. With the sample in the superconducting state, both the phase and amplitude of the secondary signal would be different, giving rise to a net voltage out of the nulling circuit. After amplification by a tuned amplifier and rectification, this output voltage (hereafter referred to as the detector signal) was displayed on the vertical axis of an *x-y* recorder. The *x* axis of this recorder displayed the output of a Keithley model 150A microvoltmeter which measured the imbalance of a dc Wheatstone thermometer bridge.

Four nominal 10-Ω Allen Bradley 0.1 W carbon resistors in parallel were used as the thermometer. The maximum resistance measured was about 37 000 Ω at 0.37°K. Less than 2×10^{-8} W was introduced into the system by the thermometer at 0.87°K and $<2\times10^{-10}$ W at 0.37°K. This thermometer was calibrated against the vapor pressure of liquid He^3 using the T_{62} scale.[17] The vapor pressure was measured with an MKS Baratron[18] with an ultimate pressure resolution of 0.0002 Torr. During each run the Baratron was occasionally calibrated with an oil filled manometer and a Wild precision cathetometer, and more than 15 comparisons between the thermometer and the Baratron were made in the range of 0.87 to 0.37°K. Corrections were made for the He^4 contamination[19] in the He^3 and for the thermomolecular pressure effect.[20]

These data were least-squares fitted by a computer to the equation $1/T=A/\ln R+B+C\ \ln R+D(\ln \mathrm{R})^2$. The standard deviation σ was also calculated.

$$\sigma=\{\sum_{i=1}^{n}[T(\mathrm{obs})_i-T(\mathrm{calc})_i]^2/(n-m)\}^{1/2},$$

in which n is the number of observations and m is the number of parameters. In every case σ was <0.0005°K, and was usually <0.0002°K. To avoid further corrections for the effects of magnetic fields on the resistors, each calibration point was taken in the same field at which critical field curve data were taken.

III. EXPERIMENTAL PROCEDURE

The samples were initially cooled to 77°K over a period of about 12 h by energy exchange with liquid nitrogen via radiation and conduction through an exchange gas. Cooling the refrigerator to 4.2°K, adding liquid He^4 to the chambers, and then cooling the chambers to 0.85°K by operation of the He^3 refrigerator took about 12 h more.

With the temperature just above the highest T_c, the transition detection system was nulled. Nulling at higher temperatures would lead to imbalance at the working temperature due to the increasing electrical conductivity of the samples as they cooled. After the samples had been cooled to a temperature just below the lowest T_c, the residual magnetic field at the position of the samples was nulled. This was accomplished by warming a sample until it was partially through its *S–N* transition. The currents in the vertical and two sets of horizontal coils were adjusted such that the sample became more superconducting. The temperature was then raised to return the sample to a point in the middle of its *S-N* transition. Currents in the coils were again adjusted. This process was continued to a point such that any further adjustments of the currents would drive the sample normal. At this point the residual field was null. It was found that when the field

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[15] M. W. Garrett, J. Appl. Phys. **22**, 1091 (1951).

[16] W. R. Abel, A. C. Anderson, W. C. Black, and J. C. Wheatley, Physics **1**, 337 (1965).

[17] R. H. Sherman, S. G. Sydoriak, and T. R. Roberts, J. Res. Natl. Bur. Std. **68A**, 579 (1964).

[18] Obtained from MKS Instruments Inc., 45 Middlesex Turnpike, Burlington, Masssachusetts.

[19] S. G. Sydoriak and T. R. Roberts, Phys. Rev. **118**, 901 (1960).

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

was so nulled for one sample, it was null for the other samples also.

The experimental data were taken by allowing the samples to become superconducting at some temperature, adjusting the field to a value known from previous runs to be just below the critical field for that temperature, and then slowly warming the samples through their S-N transitions. The warming rate was usually 1 to 1.5 m°K/min. A set of transitions taken with a magnetic field of 5.02 Oe applied parallel to the axes of the samples is shown in Fig. 3.

After recording each set of transitions, the imbalance voltage from the thermometer bridge, which was displayed on the x axis of the recorder, was related to thermometer resistance. This could be done by substituting a precision decade resistance box for the thermometer, and recording the imbalance voltage from the bridge on the x axis of the recorder as a function of resistance. The systematic error in the previous analysis[8,9] resulted from not properly accounting for the lead resistance in this calibration procedure when the bridge was unbalanced. The thermometer resistance in the region of 0.8°K was about 550 Ω.

Transitions observed while cooling the samples showed supercooling characteristic of good specimens. In some preliminary runs, data were taken by varying the magnetic field at various constant temperatures. This procedure gave rise to more scatter in the data than that described above and was not used.

IV. RESULTS AND DISCUSSION

Determination of T_c

When a sample went from the superconducting to the normal state, the detector output decreased by ΔV. The temperature at which each transition occurred was taken as that at which the detector had decreased by 50% of ΔV, and also by 90% of ΔV, as indicated in Fig. 3. The results in this report are based on a composite of three sets of data, each taken during a different cooldown.

TABLE II. Superconducting transition temperatures of isotopes of zinc.

Isotope	Mass	T_c (observed) °K	T_c (corrected) °K
Zn^{64} [a]	63.96	0.8545 ± 0.0004[b]	0.8548
Zn^{66} [a]	65.91	0.8448 ± 0.0003	0.8450
Zn^{68} [a]	67.94	0.8351 ± 0.0004	0.8353
Zn^{64} [c]	63.96	0.8550 ± 0.0005	0.8553
Zn^{66} [c]	65.91	0.8455 ± 0.0003	0.8456
Zn^{68} [c]	67.94	0.8361 ± 0.0003	0.8364
Zn^{64} [d]	64.0	0.864	
Nat. Zn[d]	65.38	0.855	
Zn^{68} [d]	67.9	0.840	

[a] This work based on 50% ΔV criterion.
[b] Error shown is one standard deviation of the data points from the line used in extrapolating the critical field data to zero field.
[c] This work based on 90% ΔV criterion.
[d] Values derived from graphs in Ref. 7.

TABLE III. Observed and calculated values for z and ζ.

Source	z	ζ
Observed[a,b]	0.38	0.24
Observed[c,b]	0.37	0.26
Observed[d]	0.47	0.05
Bardeen, Cooper, Schrieffer[e]	0.5	0.0
Swihart[f]	0.2	0.6
Morel and Anderson[g]	0.325	0.35
Garland[h]	0.40 ± 0.03	0.20 ± 0.06
Garland[i]	0.43 ± 0.01	0.14 ± 0.02

[a] This work based on 50% ΔV criterion.
[b] To the precision shown, z and ζ determined from the observed and corrected values of T_c are the same.
[c] This work based on 90% ΔV criterion.
[d] Values derived from graphs in Ref. 7.
[e] Reference 2.
[f] Reference 3.
[g] Reference 4.
[h] Reference 5.
[i] Reference 6.

Values of critical magnetic fields H_c versus transition temperatures were plotted for each sample, using the 50% ΔV and the 90% ΔV criteria for determining the transition temperatures. For the region $0.940<t<0.995$ in which $t=T/T_c$, straight lines were least-squares fitted to these critical field data. Extrapolating each of these 6 lines to $H_c=0$ gave 6 values of T_c, two for each isotope. The standard deviation of the data points from the fitted straight line was <0.5 m°K.

A least-squares fit of $\ln T_c=A-z\ln M$ to each set of 3 values of T_c gave two sets of values for A and z, one corresponding to the 50% ΔV criterion and one to the 90% ΔV criterion. M is the isotopic mass. The value of z determined from the 50% ΔV criterion was <3% different from that determined from the 90% ΔV criterion. The standard deviations of the values of T_c determined above, from the ones calculated using the values of A and z determined from the least-squares fits, were 0.07 m°K for those determined by the 90% ΔV criterion and 0.01 m°K for those determined by the 50% ΔV criterion.

Corrections for Impurities

The above results include no corrections for the presence of impurities in the samples. Markowitz and Kadanoff[21] have calculated the effects of nonmagnetic impurities on the transition temperatures of superconductors with anisotropic energy gaps. They find $\delta T_c=T_c\langle a^2\rangle I_c(\chi)$ in which $\langle a^2\rangle$ is the angular average of the square of the anisotropy function, $\chi=\hbar(kT_c\tau_a)^{-1}$, k is the Boltzmann constant, and $I_c(\chi)$ is an integral with a value of about $-(\pi/8)\chi$ for small χ. If τ_a is assumed to be the relaxation time associated with

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[21] D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963).

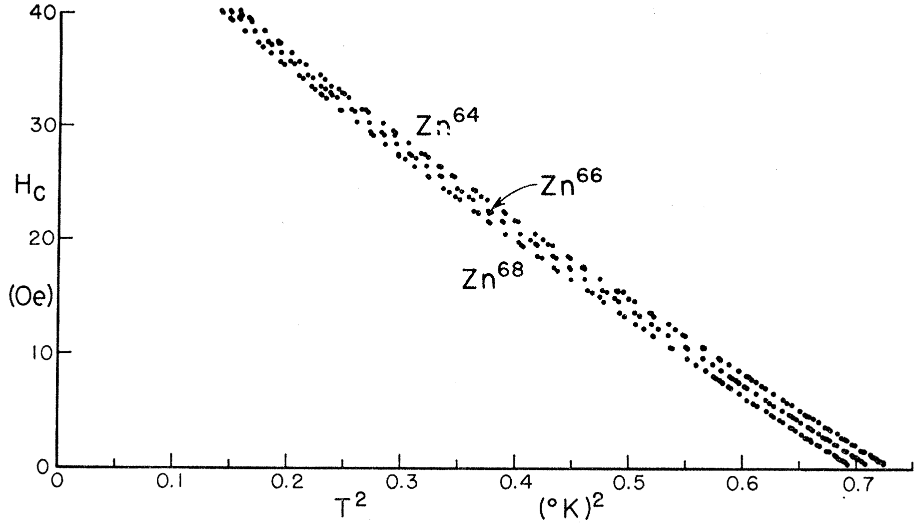

FIG. 4. Critical field data for isotopes of Zn taken during 3 different cooldowns.

electrical conductivity, using the data of Fawcett[22] for Zn, one can calculate a value of $400r$ for χ. $r=\rho(4°)/\rho(297°)$. Farrell, Park, and Coles[23] have experimentally determined $\langle a^2\rangle$ to be 0.047 for Zn.

Using the above analysis and the values of r measured for the samples used here, the corrections δT_c to the transition temperatures T_c were <0.3 m°K for all three samples. Using these corrected values of T_c, a redetermination of z gave a value within $<0.2\%$ of the previous value. These corrections changed the standard deviations between the corrected values of T_c determined from the measurements, and those determined from the new values of A and z, to 0.13 m°K for the 90% ΔV criterion and to 0.06 m°K for the 50% ΔV criterion. Table II lists both the observed and corrected values of T_c together with those reported previously. Table III lists measured and calculated values of z and ζ.

The corrections in Table II were based on the assumptions that the impurities affect T_c only by reducing the anisotropy of the energy gap, and that they do not form localized magnetic states when placed in a Zn lattice. Impurities which form localized magnetic states in Zn are known to have a drastic effect on its superconducting properties. Boato *et al.*[12] have shown that Mn and Cr depress T_c of Zn by about 315°K and 170°K per at.%, respectively. Fe, Co, and Ni, which are nonmagnetic in Zn, have $<10\%$ the effect on T_c, as does Cr.

According to the analyses summarized in Table I, Cr is the only impurity present which is known to form localized magnetic states in Zn. No corrections due to the presence of Cr were made to the values of T_c given in Table II and used in this report. This is because, despite the analysis, the actual amount of Cr present in the samples is not known, due to unknown amounts of residual background in the spectrometers. If this machine background were known, the accuracy of impurity determination is insufficient to warrant calculating a correction for T_c. Also, the effects of Cr, etc., on Zn were made in the 5 to 15 ppm concentration range[12] and it is not clear that those results can be linearly extrapolated to the concentration range in question.

If one assumes, in order to assess the possible influence of the Cr impurity, that T_c will be depressed by 170°K/at.% of Cr, and assumes the highly improbable circumstance that the indicated Cr concentration in Zn^{64} is real and that the indicated Cr concentration in Zn^{68} is all machine background, then T_c for Zn^{64} would be raised by $\sim$1.2 m°K and the values of z and ζ would be changed to 0.392 and 0.216, respectively. The presence of some Cr in the Zn^{68} and/or some machine background in the reading of Zn^{64} would reduce the difference between the correct values of z and ζ and those quoted in Table III.

Because of the improbability of observing as excellent a fit of the data to the relationship $T_c \propto M^{-z}$ as was observed, if random amounts of Cr in the concentration range indicated in the analysis were actually present; it is felt that a substantial part of Cr indicated is machine background.

Determination of H_0

Values of H_c versus T^2 plotted in Fig. 4 include all the data for $H_c > 0.3$ Oe taken during three different cooldowns. Extrapolation of these data to $T^2=0$ gave values of H_0, the critical field at 0°K, for the three isotopes. The following equation derived by Lynton,

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[22] E. Fawcett, in *Proceedings ot the Seventh International Conference on Low-Temperature Physics, 1960*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Toronto, 1960), p. 228.

[23] D. Farrell, J. G. Park, and B. R. Coles, Phys. Rev. Letters **13**, 328 (1964).

TABLE IV. Recent measurements of thermodynamic parameters for Zn. $\Delta C = C_{es} - C_{en}$, the difference between specific heats in the superconducting and normal states at $T = T_c$.

Isotope[a] and workers	Purity[b]	T_c (°K)	H_0 (Oe)	γ [mJ/mole(°K)^2]	a	b	$(dH_c/dT)_{T_c}$[c] (Oe/°K)	ΔC[c] (mJ/mole °K)
Zn^{64}		0.8553 ± 0.0005[f]	53.94 ± 0.35[g]	0.654 ± 0.019[g]	6.68 ± 0.21[g]	1.27[h]	−104.9[i]	0.677
Zn^{66}[d]	[e]	0.8456 ± 0.0004	53.77 ± 0.24	0.677 ± 0.014	6.89 ± 0.08	1.27	−105.1[i]	0.671
Zn^{68}		0.8364 ± 0.0004	53.13 ± 0.20	0.673 ± 0.012	$6.83 + 0.13$	1.27	−104.7[i]	0.659
Zavaritskiĭ[j]	[k]	0.825	52.0 ± 0.5	0.68 ± 0.03	[k]	[k]	−100[i]	0.59
Cochran *et al.*[l]	5*N*	0.875	[k]	[k]	[k]	[k]	− 83.5[i,m]	0.43
Seidel *et al.*[n]	5*N*	0.844[o]	53.4	0.640	6.40	1.27	−108	0.71[p]
Phillips[q]	5*N*	0.824[o]	51.8	0.66	5.8	1.22	−106	0.66[p]
Zavaritskiĭ[r]	6*N*	0.84	[k]	0.645−0.67	4.2[s]	1.03	−108	0.70[p]

[a] Natural Zn was used for all but the work reported in this paper.

[b] 5*N* means 99.999% pure, etc.

[c] $(dH_c/dT)_{T_c}$ and ΔC were measured by magnetic and calorimetric methods, respectively. The Rutgers's formula $[\Delta C = T_c V (dH_c/dT)^2{}_{T_c}/(4\pi)]$ [see P. Ehrenfest, Commun. Kamerlingh Onnes Lab. Univ. Leiden, Suppl. No. 75b (1933)] was used to calculate the quantity not measured in each of the studies referred to here. The value of 9.03 cm³ for V was taken from the results of H. L. Laquer, U. S. Atomic Energy Commission Report AECD-3706 (unpublished).

[d] Values given here are based on the 90% ΔV criterion as described in the text.

[e] See text.

[f] Errors in T_c are standard deviations of the points from the lines used in the extrapolation to zero field.

[g] Errors in H_0, γ, and a are 95% confidence limits assigned by the fitting program.

[h] Value taken from Ref. 25 and used to calculate H_0, γ, and a.

[i] Magnetic measurements.

[j] N. V. Zavaritskiĭ, Zh. Eksperim. i Teor. Fiz. **39,** 1193 (1960) [English transl.: Soviet Phys.—JETP **12,** 831 (1961)].

[k] Values not given.

[l] Reference 37.

[m] Measurement may be affected by transition broadening at H_c near zero. See text.

[n] Reference 25.

[o] Corrected to T_{62} He³ temperature scale.

[p] Calorimetric measurement.

[q] Reference 29.

[r] N. V. Zavaritskiĭ, Zh. Eksperim. i Teor. Fiz. **34,** 1116 (1958) [English transl.: Soviet Phys.—JETP **7,** 773 (1958)].

[s] Values of γ, T_c, and the coefficient of the exponential term given in Ref. r were used to calculate a.

Serin, and Zucker[24] was used in making this extrapolation:

$$H_c^2 = H_0^2 - (4\pi/V)\gamma T^2 \left(1 - \frac{2a}{t^2}\int_0^t dx \int_{b/x}^{\infty} \frac{e^{-u}}{u}\,du\right). \qquad (1)$$

Here γ is the coefficient of the normal electronic specific heat in $c_{en} = \gamma T$, $t = T/T_c$, and a and b are defined by the following expression for the electronic specific heat of a superconductor at temperatures well below T_c:

$$c_{es} = a\gamma T_c \exp(-bT_c/T).$$

An attempt to calculate H_0, γ, a, and b from the data failed, since the calculation did not converge correctly because of the extremely high correlation between a and b, and because of the rather limited range of temperatures over which the data extended. Setting $b = 1.27$ as determined by Seidel and Keesom[25] from specific-heat measurements, and using subroutines furnished by the University of Wisconsin Computing Center, it was possible to determine the best values for H_0, γ, and a consistent with the critical field data. These values, together with other information, are given in Table IV. Critical field data in the range $0.48 < t < 0.72$ were used in extrapolating H_c to 0°K, since Eq. (1) is valid only in the temperature range in which the electronic specific heat is exponential, and since the data of Seidel and Keesom[25] show the specific heat to be approximately exponential in this range of t.

The values of H_0 for the three isotopes are not as widely spaced as would be expected if $H_0 = k'M^{-z}$ with z taken as the value determined from the measurements of T_c, nor are they uniformly spaced. This is not surprising, since the extrapolation to 0°K is over a long range of temperature compared to the range over which useable data extends.

According to the similarity principle, values of $h = H_c/H_0$ plotted against t for all the isotopes of an element should lie on the same curve. This principle has been shown to be valid for tin[26] and indium.[27] A sensitive method for testing the validity of this principle is to plot $D = h - (1 - t^2)$ versus t^2 for all isotopic samples. Figure 5 shows D versus t^2 using values of H_0 determined by assuming that the extrapolated value of H_0 for Zn^{66} was correct, and that H_0 for Zn^{64} and Zn^{68} could be determined from the relation $H_0 = k'M^{-z}$ in which z was determined from measurements of T_c. Except for points which were eliminated to reduce

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[24] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3,** 165 (1957). The equation as published is slightly in error and should be as given here.

[25] G. Seidel and P. H. Keesom, Phys. Rev. **112,** 1083 (1958).

[26] J. M. Lock, A. B. Pippard, and D. Shoenberg, Proc. Cambridge Phil. Soc. **47,** 811 (1951).

[27] H. R. O'Neal, N. M. Senozan, and N. E. Phillips, in *Proceedings of the Eighth International Conference on Low Temperature Physics, 1961,* edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 403.

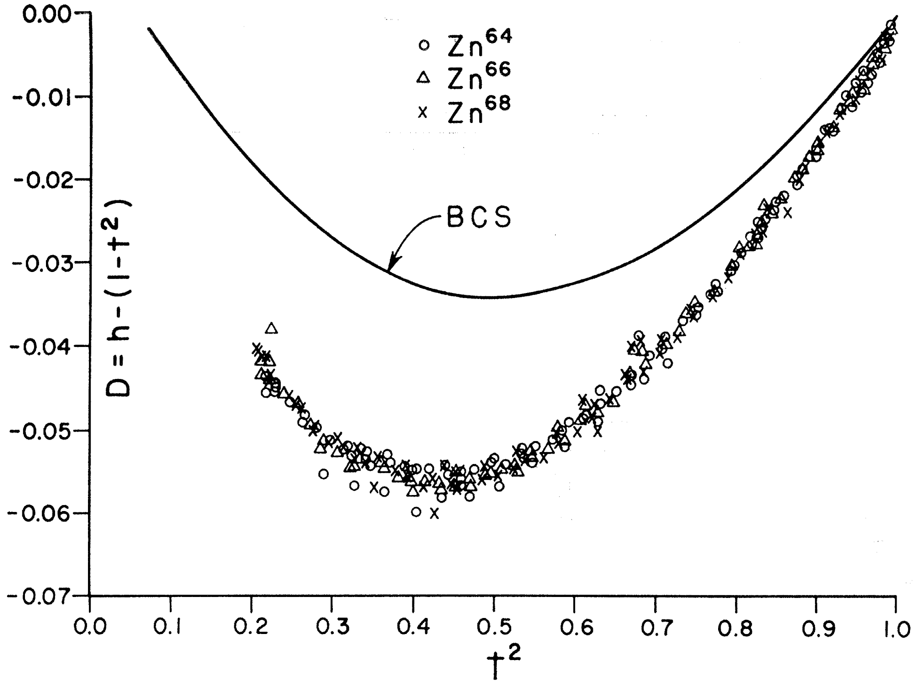

FIG. 5. D versus t^2 using values of H_0 calculated from the relation $H_0=k'M^{-z}$ in which z was obtained from measurements of T_c. k' was determined by using the value of H_0 for Zn^{66} obtained by extrapolation of critical field data. The curve marked BCS is from calculations made by Muhlschlegel (see Ref. 31).

congestion, all points taken for all 3 isotopes during 3 different cooldowns are plotted. A plot (not shown), using values for H_0 determined by extrapolation of the low-temperature critical field data in the manner described previously, was similar, but the agreement between the curves was not as good as the plot in Fig. 5.

Plots were made of the polynomials in $1-t^2$ which were fitted to data for D for the three isotopic samples, and which had the smallest standard deviation when compared to that data. These curves agreed closely and are not shown in Fig. 5 in order to reduce congestion. If the validity of the correspondence principle is assumed, the excellent agreement of the D versus t^2 curves for the three isotopes over the entire measured temperature range, when H_0 is assumed $\propto M^{-z}$, would indicate that the value of z determined from the measurements of T_c was correct. It will require measurements at lower temperatures from which more exact extrapolations of H_c to 0°K can be made to investigate further the validity of this principle in Zn.

The curve labelled BCS in Fig. 5 is the plot of D, predicted by the BCS model,[2] using the calculations of Mühlschlegel.[28] There is a larger deviation from a parabolic critical field curve for Zn than is predicted by BCS. This is in agreement with critical field curves for Zn derived from the specific-heat measurements of Seidel and Keesom[25] and of Phillips.[29]

Recent theoretical work by Clem[30,31] has shown that such a deviation is to be expected from a weak-coupling superconductor having an anisotropic energy gap. Using the critical field curves, T_c, H_0, $(dH_c/dT)_{T=T_c}$, and γ in Clem's theory, it is possible to derive values for the anisotropy parameter $\langle a^2\rangle$ in three independent ways.[32] For all three isotopes these values are in fairly good agreement with each other and with the value 0.047 determined by Farrell, Park and Coles[23] from the shift in T_c with the addition of impurities. However, since the determinations of $\langle a^2\rangle$ from these data all depend on accurate extrapolation of the critical field curves to 0°K, further measurements at lower temperatures must be taken before a good test of the theory can be made.

Specific Heat

The difference between the total specific heat of a sample in the superconducting and normal states can

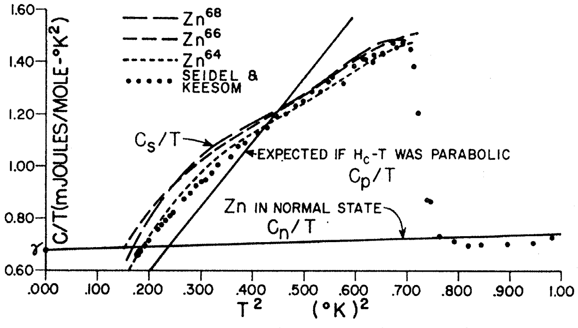

FIG. 6. Specific heat of Zn isotopes calculated from critical magnetic field curves compared with that determined for natural Zn from calorimetric measurements.

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[28] B. Mühlschlegel, Z. Physik **155**, 313 (1959).
[29] N. E. Phillips, Phys. Rev. Letters **1**, 363 (1958).
[30] J. R. Clem, Ann. Phys. (N.Y.) **40**, 268 (1966).
[31] J. R. Clem, Phys. Rev. **153**, 449 (1967).
[32] J. R. Clem (private communication).

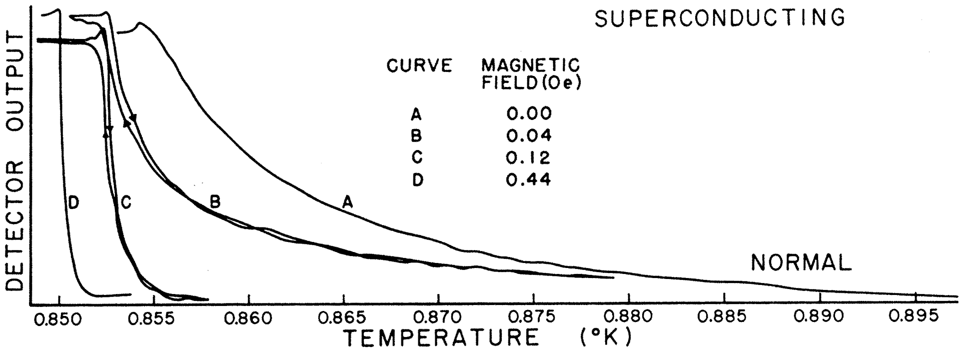

FIG. 7. *S-N* transitions of Zn^{64} in small magnetic fields.

be determined from critical magnetic field curves, since the difference can be expressed as[33]

$$c_s - c_n = (TV/8\pi)[d^2(H_c^2)/dT^2].$$

Comparison of these data with those measured calorimetrically serves as a check on the accuracy and validity of magnetic measurements.

The critical field curve can be expressed as a parabola plus a deviation D from the parabola. Following Mapother[34] $c_s - c_n$ can then be expressed as the sum of that due to a parabolic critical field, c_p, and that due to the deviation. Since $c_s - c_n$ is related to the second derivative of the square of the critical field, the nonparabolic part will also contain cross terms. Expressed in this manner,

$$c_s - c_n = c_p + TVH_0^2$$
$$\times [D'^2 + DD'' + D''(1-t^2) - 4D'T/T_c^2 - 2D/T_c^2]/4\pi.$$
$$c_p = TVH_0^2(3t^2-1)/(2\pi T_c^2),\ D' = dD/dT,\ D'' = d^2D/dT^2,$$

and V is the molar volume. Mapother also showed that $c_s - c_n$ calculated in this manner is not very sensitive to errors made in the determination of H_0. The data for D in Fig. 5 were least-squares fitted to a series of polynomials in $1-t^2$. That polynomial which had the smallest standard deviation when compared to the data was used to calculate $c_s - c_n$.

Having determined $c_s - c_n$ from critical field data, c_s can be obtained by using values of c_n calculated from $c_n = \gamma T + 660T^3$. The electronic-specific heat coefficient γ was determined from our measurements as described in the previous section of this paper, and the coefficient of the lattice term was taken as 660 mJ/mole $(°\mathrm{K})^4$ from the work of Seidel and Keesom.[25] Measurements of c_s/T determined in this way for each isotope are presented in Fig. 6. Calorimetric measurements made by Seidel and Keesom[25] on naturally occurring zinc are also plotted for comparison. A line representing c_n/T as calculated above is drawn in. It is seen that specific heats determined from our critical field data agree rather well with those determined calorimetrically both in the superconducting and normal states. The value of γ determined from our critical field data serves as a suitable intercept for a line through the calorimetrically determined values for c_n/T. A line is also drawn in to represent c_p/T, in which c_p would be the specific heat if the critical field curve had been parabolic and the values of T_c and H_0 had been the same as those determined from the actual critical field curve for Zn^{66}.

The shape of the curves for c_s/T determined from our critical field data was found to be somewhat dependent on the degree of the polynomial used to fit the data in Fig. 5. However, for all the polynomials tried, the agreement with the calorimetrically measured values of c_s/T was good at higher temperatures, and at lower temperatures, values of c_s/T determined from critical field data were slightly higher than the calorimetrically measured values as seen in Fig. 6.

Broadening of Transitions near $H_c = 0$

At critical fields H_c of <0.3 Oe the *S-N* transitions become broad in a fashion unrelated to isotopic composition of the samples. Thus, data for $H_c < 0.3$ Oe were not used in arriving at any of the results reported above. With the transition temperature defined as that at which the detector output had decreased by 50% or 90% of ΔV as discussed previously, use of data for $H_c < 0.3$ would have greatly reduced values of $(dH_c/dT)_{T=T_c}$ and changed values of T_c such as to make the determination of an isotope effect impossible.

Figure 7 shows *S-N* transitions for Zn^{64} for several magnetic fields. The other two samples showed a similar but smaller effect. *S-N-S* transitions measured in small and zero fields, such as shown in Fig. 7, showed little of the supercooling type of hysteresis which characterized such transitions at higher fields. Figure 8 shows the width of the *S-N* transitions of the three samples as a function of magnetic field. For this plot the width of a transition is defined as the difference in temperature between that at which the detector output had changed by 10% and by 90% of its maximum change. With the circuitry used, it was not possible to determine whether or not the detector

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[33] See, for example, E. A. Lynton, *Superconductivity* (Methuen and Company, Ltd., London, 1962), Sec. 2.1.

[34] D. E. Mapother, Phys. Rev. **126**, 2021 (1962).

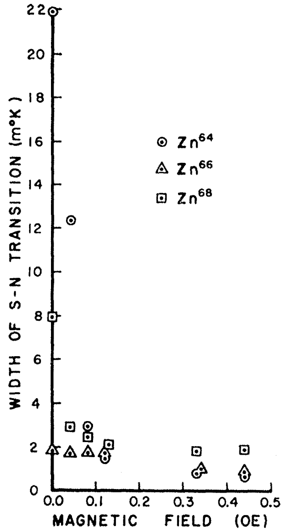

FIG. 8. Width of *S-N* transitions versus magnetic field.

signal observed in the broadened transitions was due to the real or imaginary parts of the susceptibility being different in the superconducting than in the normal state.

Between two of the cooldowns, the Zn^{64} sample was chemically polished in a nitric-phosphoric acid solution.[35] On the cooldown following the polish of Zn^{64}, the width of the small field *S-N* transition of Zn^{64} was reduced while those of the untreated Zn^{66} and Zn^{68} remained as in previous cooldowns. The behavior of the Zn^{64} at fields >0.3 Oe was unaffected by the polish. Data plotted in Fig. 8 were obtained before the polish.

A similar broadening of the *S-N* transition has been observed for aluminum by Cochran and Mapother.[36] and Cochran, Mapother, and Mould,[14] and was probably also observed for zinc by Cochran and Mapother.[37] In the latter experiment, the minimum temperature reached was too close to T_c to indicate how wide the transitions were in appreciable magnetic fields. Seidel and Keesom[25] observed that the decrease in the specific heat of Zn near T_c was spread over a considerable temperature range, and this spread was not affected by annealing the sample. Their measurements were made with the sample located inside a chamber coated with superconducting solder to reduce the field in its interior. The specific-heat measurements of Phillips[29] in an unspecified but presumably nonzero magnetic field showed a rather sharp decrease at the *S-N* transition. From the results of our work and that of Cochran and Mapother,[36] it would appear that the broadening in small fields is related to the condition of the surface and can not be accounted for in terms of strains and/or impurities.

Because of the high electrical conductivity of the samples in the normal state, the measuring field at 96 Hz penetrated only about 5×10^{-3} cm into the samples. Thus, only about 5% of the volume of each sample was subjected to the measuring field. Since only this thin shell of material was actually investigated, the surface condition of the samples might be expected to influence the results appreciably. However, except for measurements taken at very small fields, the transitions were unaffected by treatment which should have produced appreciable changes in the surface. This treatment included a complete redistillation and regrowing of the samples, and chemical polishing of the Zn^{64}. It should be noted that care was taken not to strain or otherwise damage the samples and that they were annealed before data were taken.

In view of the high quality of these samples, it might be expected that a rather large and reversible differential paramagnetic effect (DPE)[38,39] would be observed in the *S-N* transitions. Except for a very slight increase in detector signal just before the transitions occurred, no such effect was observed. Shoenberg[38] found that the magnitude of the DPE was reduced when the magnitude of the measuring field was reduced and/or when the frequency was increased. Since the measuring technique used in obtaining the results reported here employed both lower measuring fields and higher frequencies than those used by others who observed a sizeable DPE, it is not surprising that only a small effect was noted.

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[35] M. A. Biondi, M. P. Garfunkel, and W. A. Thompson, Phys. Rev. **136**, A1471 (1964).

[36] J. F. Cochran and D. E. Mapother, Phys. Rev. **111**, 132 (1958).

[37] J. F. Cochran and D. E. Mapother, Phys. Rev. **121**, 1688 (1961).

[38] D. Shoenberg, Proc. Cambridge Phil. Soc. **33**, 559 (1937).

[39] R. A. Hein and R. L. Falge, Jr., Phys. Rev. **123**, 407 (1961).