Magnetic Properties of $ZrZn_2$ between 120°K and 0.1°K. Search for Superconductivity

R. L. Falge, Jr., and R. A. Hein
U. S. Naval Research Laboratory, Washington, D. C.
(Received 4 March 1966)

The incremental magnetic susceptibilities of two samples of a zinc-zirconium alloy have been measured as a function of the temperature from 120°K down to 0.1°K. These data indicate a Curie point of 32°K for a powder sample and 24°K for a solid sample. The magnetic moments of these samples were studied as a function of magnetic field at 77, 4.2, 1.2, and 1.0°K. These data indicate that the ferromagnetic compound $ZrZn_2$ has a magnetic moment of $0.10\mu_B$ per molecule. Neither the susceptibility measurements nor the direct electrical-resistivity measurements give any indication of superconductivity in $ZrZn_2$ at temperatures above 0.1°K.

INTRODUCTION

During the past seven years several theoretical and experimental reports have appeared concerning the possible existence of superconducting ferromagnets.[1] Measurements of the magnetic moment in fields of 10 800 and 3900 Oe as a function of the temperature, between room temperature and liquid-helium temperature, showed[2] that the intermetallic compound $ZrZn_2$ was ferromagnetic. These data indicated a Curie temperature of about 35°K. The magnetic moment per molecule was calculated[2] to be about 0.13 Bohr magneton, μ_B. With only a few exceptions, an alloy or a compound of two superconducting elements is itself a superconductor.[3] Thus, the present work was initially an experimental effort to ascertain if $ZrZn_2$ is superconducting at temperatures below 1°K.

The region below 1°K is of special interest because (a) Zn and Zr are superconductors with transition temperatures of 0.86 and 0.55°K, respectively; (b) Ginzburg[4] points out that superconducting ferromagnets are feasible if $B_0=4\pi M_0<H_c(0)$. $H_c(0)$ is the superconducting critical magnetic field at the absolute zero of temperature. M_0 is the spontaneous magnetization at absolute zero. Using a value of $0.13\mu_B$ per molecule as the saturation magnetization of $ZrZn_2$ leads to a value of approximately 300 G for B_0. Such a value for B_0 is not prohibitively large when compared to known $H_c(0)$ values for type-II superconductors.

Electrical-resistivity measurements[5] between 2.2 and 295°K failed to reveal any anomaly. Hence these measurements could not confirm the reported magnetic ordering in $ZrZn_2$ at 35°K. An earlier unpolarized neutron diffraction study[6] had also failed to support independently the existence of a magnetic state at 4.2°K. More recent polarized-neutron diffraction studies[7] have confirmed the existence of a magnetically ordered state at 4.2°K. This latter study yields a derived spin density of an unusual nature,[8] which is taken as evidence for itinerant electron ferromagnetism in $ZrZn_2$.[7,8] It has been suggested that in $ZrZn_2$ we have an example of ferromagnetism which is due solely to the free-electron gas.[9] In view of this history regarding the magnetic properties of $ZrZn_2$, we felt it would be of interest to (1) extend our measurements to temperatures as high as 120°K, and (2) to include some observations of the magnetic moment as a function of magnetic field.

EXPERIMENTAL DETAILS

Samples

Two zirconium-zinc alloys (nominally $ZrZn_2$) were obtained from the Bell Telephone Laboratories. The samples were prepared in a manner described elsewhere.[6] The first of these alloys was in the form of an approximately cylindrical solid piece and the second alloy was in the form of a powder. From these alloys the three samples reported in the present study were made.

When the sample (rod) was first investigated, a superconducting transition was noted at 4.6°K. By means of x-ray fluorescence measurements tantalum was found to be present in the sample. In the hope that this was a surface contamination, we had the sample machined to a smaller diameter. The superconducting transition was still present and none of the other measured properties of the sample changed on machining. It was subsequently found (see the section below) that tantalum was present throughout the sample. Henceforth, we refer to this machined sample as the rod.

The powder alloy was examined as supplied and we refer to this simply as the powder. Our third sample (which we shall refer to as the pressed powder) was formed by compacting the powder at room temperature, without binder, under a pressure of 20 kbar. Four short sections of gold wire were situated in the powder before

[1] A bibliography on this subject is to be found in Report No. RADC-TDR-64-18V, of the Research and Technology Division, Griffiss Air Force Base, New York (unpublished).
[2] B. T. Matthias and R. M. Bozorth, Phys. Rev. **109**, 604 (1958).
[3] B. W. Roberts, *Progress in Cryogenics* (Heywood and Company, Ltd., London, 1964), pp. 161–231.
[4] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **31**, 202 (1956) [English transl.: Soviet Phys.—JETP **4**, 153 (1957)].
[5] C. E. Olsen, J. Phys. Chem. Solids **19**, 228 (1961).
[6] S. C. Abrahams, Z. Krist. **112**, 41F (1959).
[7] S. J. Pickart *et al.*, Phys. Rev. Letters **12**, 444 (1964).
[8] G. Shirane *et al.*, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and The Physical Society, London, 1965), p. 223.
[9] B. T. Matthias and T. H. Geballe, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and The Physical Society, London, 1965), p. 228; also B. T. Matthias, Intern. Sci. Technol. **30**, 32 (1964).

pressing; these served as the current and potential leads for resistivity measurements.

Metallurgical Studies

Certain results obtained during the course of this study led us to have a metallurgical examination made of the two sample materials. One metallograph of each sample is shown in Fig. 1. In the metallograph of the powder material, the dark outer matrix is an epoxy resin in which the grains were impregnated prior to polishing and etching. The powder grains were observed to have three distinct phases. Although the identifications of these phases are somewhat uncertain, we tentatively ascribe to the following: The core, only slightly alloyed zirconium, was surrounded by a shell of material of the ZrZn structure. The outer part of each grain of powder was the $ZrZn_2$ compound and this phase comprised about 80% of the sample. The grains shown in the figure are not typical of the stated relative volumes of each structure present. They were selected because they show clearly the structure encountered in the grains. While this sample is nonideal from a metallurgical point of view, we believe it is comparable to the powdered samples used by the earlier workers.

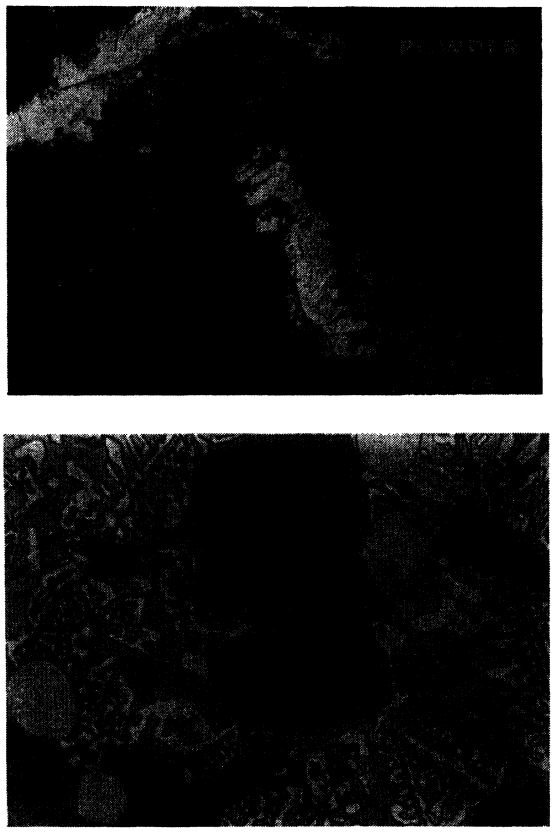

FIG. 1. Metallographs of the powder and the rod samples. Each picture covers an area of 300×400 μ. The powder grains are shown imbedded in an epoxy resin which is the dark structureless area surrounding the grains.

The rod, Fig. 1(b), appears to be largely ZrZn with a tantalum primary dendritic structure shot through it. Some eutectic platelets and a few larger ZrZn regions appear. $ZrZn_2$ is distinctly a minority component comprising less than 15% of the total volume. The single-crystal samples employed by Pickart *et al.*,[7] Abrahams,[6] and Olson[5] were all obtained from the same source. Oslon[5] detected a superconducting transition due to the presence of tantalum. The other workers do not state the purity of their samples. The tantalum impurity is apparently introduced by the use of a tantalum bomb in the growing of the single crystals.

X-ray reflection lines corresponding to $ZrZn_2$ occur[10] in both samples and confirm the presence of the compound $ZrZn_2$. The spectra also include some strong lines due to other unidentified structures and consequently the intensities of lines due to each structure cannot give evidence of the relative quantity of that component present.

Temperature Production

The sample to be investigated was cemented inside a copper sample holder (see Fig. 2; the sample holder

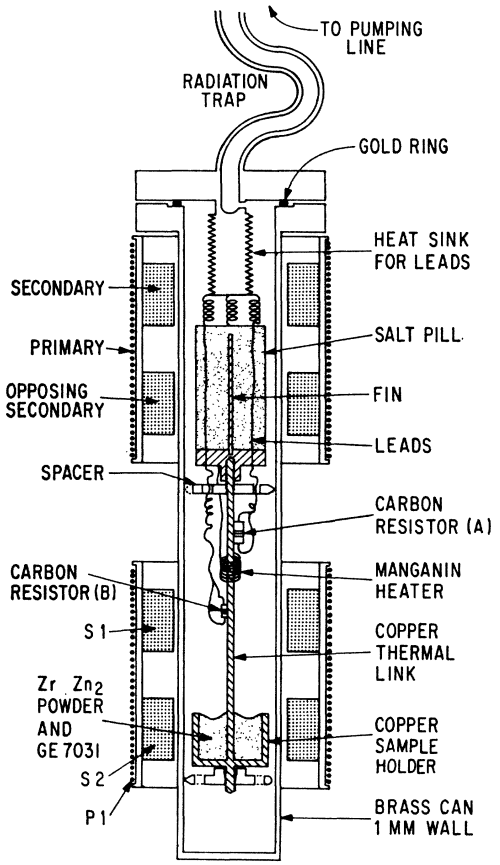

FIG. 2. A schematic of the apparatus employed in the measurement of $\Delta M/\Delta H$ over the temperature range 120 to 0.1°K.

[10] P. Chiotti and G. P. Kilip, Trans. AIME 215, 892 (1959).

shown was for the powder). The outer end of this holder was connected via a screw fitting to a system of copper fins around which a potassium chrome alum salt pill had been compressed. A manganin heater was wound between the sample and the salt pill. This interior assembly is suspended by a nylon string inside a vacuum-tight brass can which is connected to a high-vacuum exchange-gas system. A gold wire gasket is used to seal the can. The entire assembly, with its associated equipment, is placed inside a glass Dewar arrangement which allows us to immerse the can in a bath of liquid helium.

Thermometry

When feasible, the vapor pressure of the liquid-helium bath was employed as a thermometer. When this was not feasible we used either a carbon resistor or a paramagnetic salt as follows:

A precalibrated carbon resistor, chosen to have a desirable resistance-versus-temperature characteristic below 1°K, was cemented to the copper thermal link and served to demonstrate the quality of the thermal contact at the lowest temperatures attained by the sample. For measuring temperatures between 4.2 and 120°K, a second carbon resistor (B, Fig. 2) was employed. This resistor was calibrated during the course of the experiment at 77°K and several temperatures in the liquid-helium range. Interpolation between these values was made according to Clement *et al.*[11]

The magnetic susceptibility of the salt was observed by means of a dc-mutual-inductance technique.[12] The salt susceptibility is related to the temperature by Curie's law. After calibration in the liquid-helium region, susceptibility of the salt served as our primary thermometer below 1.3°K.

Magnetic Measurements

Differential-Susceptibility Measurements

For these measurements we also used a dc-mutual-inductance technique.[12] The magnitude of the deflection Θ obeys

$$\Theta = K_1 I_p \chi_{\text{inc}} + K_2 I_1,$$

where K_1 and K_2 are constants of the system. With the coils at a temperature of 4.2°K and the sample at 120°K, the variable mutual inductance is not changed for the remainder of the experiment. (K_2 is then fixed.) Thus, for a given incremental field ΔH we obtain the temperature dependence of χ_{inc} by simply observing how Θ changes with changes in the temperature of the sample. In all of the incremental-susceptibility measurements reported here, ΔH is 1.0 Oe.

Magnetic-Moment Measurements

For these measurements we used the sample displacement method with the sample immersed in a liquid-helium bath.[12] Thus, by adjusting the magnetic field, we can study the magnetic moment at constant temperature as a function of the magnetic field. Calibration of this system is done by determining the galvanometer deflections obtained using a potassium chrome alum sample, of the same size and shape as each of the alloy samples employed, at a known applied magnetic field and temperature.

Electrical-Resistance Measurements

The electrical resistance of the pressed powder sample was measured by passing a known current through the sample and measuring the potential drop occurring across two gold potential probes which had been embedded in the sample as described earlier. The current density in the sample was about 5 mA/cm^2. The real current density at the places of contact between the individual grains of powder comprising the sample may have been considerably greater than this value. While there would have been no heating at these places of contact if the ZrZn had become superconducting, one might have had a local magnetic field of non-negligible magnitude.

RESULTS

Figure 3 depicts the incremental magnetic susceptibility χ_{inc} of the powder [3(a)] and of the rod [3(b)] as a function of the absolute temperature. Although our measurements extend up to 120°K we have (since there is no temperature dependence in the omitted regions), as a matter of convenience, shown data only up to 80°K. The ordinates of these graphs are the observed galvanometer deflections plus a constant. These additive constants were chosen to render the deflections plotted for 77°K as zero.

The sudden decrease and subsequent change to negative values for χ_{inc} observed for the rod at approximately 4.6°K is suggestive of a superconducting transition. Evidence for this belief comes from two observations: (1) A deflection of −47.5 mm corresponds very closely to the deflections observed using a similar sized and shaped sample of tin. (2) This diamagnetism could be removed by sufficiently strong magnetic fields, approximately equal to the critical magnetic fields of superconducting tantalum.

Figure 3(a) is for the powder. We again note a drop in χ_{inc} with decreasing temperature. However, χ_{inc} never became negative.

Figure 4(a) shows the magnetic moment of the powder as a function of the magnetic fields for two values of the temperature. Data (not shown) were also obtained at 77 and 1.0°K. The insert of Fig. 4(a) is an enlarged plot of the 0–100-Oe data obtained for a temperature of 4.2°K. Low-magnetic-field data (i.e., values

[11] J. R. Clement *et al.*, in *Advances in Cryogenic Engineering*, edited by K. D. Timmerhaus (Plenum Press Inc., New York, 1960), Vol. 2, p. 104.

[12] Robert A. Hein and Raymond L. Falge, Jr., Phys. Rev. **123**, 407 (1961).

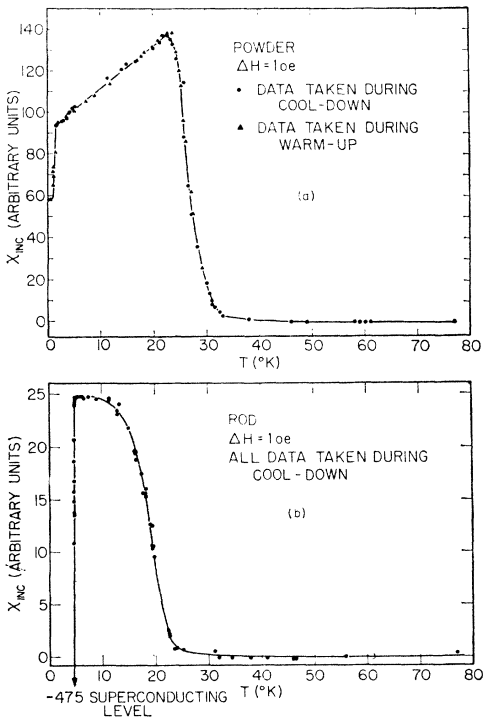

FIG. 3. Incremental susceptibility ($\Delta M/\Delta H$) as a function of the temperature for the powder (a) and for the rod (b). Galvanometer deflections are proportional to $\Delta M/\Delta H$. The constant of proportionality is different for (a) and (b).

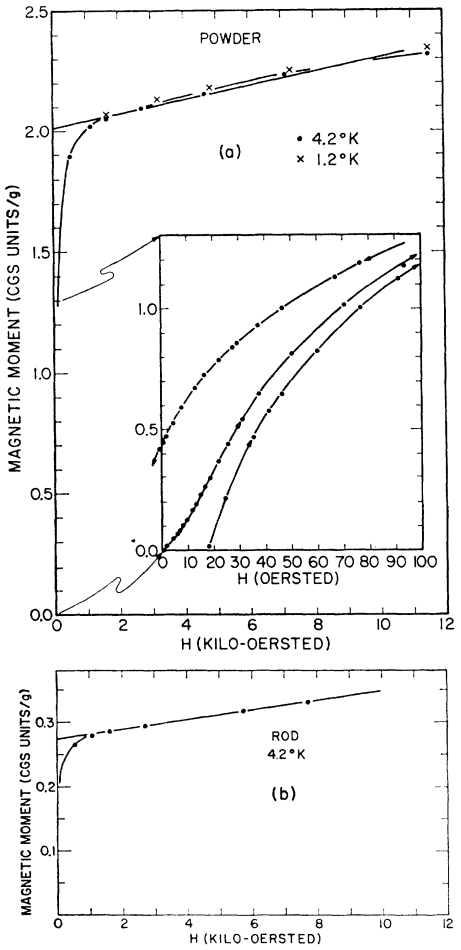

FIG. 4. The isothermal magnetic moment of the samples as a function of the applied magnetic field. The insert in (a) shows the low-field data at 4.2°K for the powder. Magnetic moment per gram refers to mass of sample, not mass of $ZrZn_2$.

of magnetic fields less than 2 Oe) obtained at 4.2 and at 1.0°K on unmagnetized samples allow us to derive values for χ_0, the initial slope of the virgin magnetization curve. Within experimental limitations, i.e., $\pm 5\%$, χ_0 is the same at 4.2 and at 1.0°K. The value of χ_0 is $8\pm 1\times 10^{-3}$ cgs units per gram. The major uncertainty in this value for χ_0 lies in the estimation of how much $ZrZn_2$ was present in our sample, i.e., 80%.

The magnetic-moment versus magnetic-field data obtained at 77°K showed no hysteresis. The magnetization curve was linear with a slope of only 0.5% of the initial slope of the magnetization curve at 4.2°K.

To investigate the possibility of superconductivity in part of the powder sample, the dc electrical resistance of the pressed powder sample was measured between 4.2 and 0.1°K. These data gave no indication of superconductivity.

DISCUSSION

Curie Temperatures

Since the original report of Matthias and Bozorth, there have been conflicting reports regarding the magnetic properties of $ZrZn_2$.[2,5–7,13] In fact there exists, in the literature, no collaborating evidence in support of the reported Curie temperature (i.e., 35°K). Figure 3(a) clearly shows that χ_{inc} for the powder increased very rapidly with decreasing temperature between 32 and 24°K. Such behavior is characteristic of a magnetic transition. The shape of the magnetization curve and its accompanying hysteresis are consistent with earlier reports, which identify this magnetic state as a ferromagnetic one. An extrapolation of the steep portion of the χ_{inc} curve back to zero intersects the temperature axis at 32°K. We will take this as the Curie temperature and feel that the agreement with the earlier reported[2] value of 35°K is very good. One could also choose the maximum in χ_{inc} as being indicative of the Curie temperature, in which case the Curie temperature for the powder would be 22°K. These data do not support the suggestion of a magnetic ordering (short-range) of temperatures above 32°K.[13]

The behavior of χ_{inc} for the rod, as a function of the temperature, is presented in Fig. 3(b). These data lead to a Curie temperature determination of 24°K (i.e.,

[13] T. Yamadaya and M. Asanuma, Phys. Rev. Letters **15**, 695 (1965).

extrapolation of the steep, 24 to 14°K, portion of the curve to $\chi_{inc}=0$). This value is 8°K below the value found for the powder.

This relatively low value for the Curie temperature of the rod is unexplained. While the metallurgical studies indicate that the majority of the tantalum impurity in the rod was present as free tantalum, it is, however, possible that some of the tantalum was alloyed in the $ZrZn_2$ phase. Vanadium in nickel reduces the Curie temperature by about 55°K per percent of vanadium.[14] Thus, it is not inconceivable that tantalum, when present to a fraction of a percent in $ZrZn_2$, could decrease the Curie temperature by 8°K.

Moments

For magnetic fields in excess of 10^3 Oe, the isothermal magnetization can usually be expressed as[15]

$$M_H(T)=M_s(T)(1-a/H-b/H^2)+CH.$$

Thus, by extrapolation of the linear high-field portion of the magnetization curve back to $H=0$, we obtain a measure of $M_s(T)$.[15] Since the reduced temperatures, $t=(T/32°K)$, for these curves are about 0.12 and 0.04 the derived values for $M_s(T)$ are good approximations to $M_s(0)=M(0)$, the saturation magnetization at absolute zero.

The powder data [Fig. 4(a)] lead to a value of $M(0)$ of $0.10\mu_B$ per molecule. We have made the assumption that (1) 80% of the sample is in the $ZrZn_2$ phase and (2) that this phase is the ferromagnetic component. This value for $M(0)$ is somewhat lower than the values quoted in the literature which range from 0.13 to $0.18\mu_B$.[2,7] We believe that this discrepancy is due, in part, to the manner in which $M(0)$ is determined from the data. We are of the opinion that Matthias and Bozorth[2] took the largest moment observed (i.e. the moment observed at $H=10\,800$, T about 4°K) as $M(0)$. Their data indicate a large field dependence between 3900 and 10 800 Oe. In order to be consistent with our determination of $M(0)$, we have extrapolated their $M_H(T\sim4°K)$ data and find a value of $M_s(4°K)$ equal to $0.11\mu_B$. Thus we feel our results are in agreement with the results of Matthias and Bozorth.

The insert in Fig. 4(a) shows the virgin magnetization curve as well as portions of the major hysteresis loop obtained for the powder at 4.2°K. The curves show behavior which is suggestive of a weak ferromagnetic or ferrimagnetic substance.

It is difficult to measure the quantity of $ZrZn_2$ present in the rod from the metallographs. $M_s(4.2°K)\cong M(0)$ found for the rod in Fig. 4(b) indicates that $ZrZn_2$ occupies 9% of the sample volume assuming that $M(0)$ per gram of $ZrZn_2$ is the same in both cases. This volume is comparable with the estimate of less than 15% by the metallography.

Superconductivity

Magnetic Measurements

At temperatures below the Curie temperature, the magnetic susceptibility data are complicated because of hysteresis effects. For this reason, the χ_{inc} data do not reflect the temperature dependence of χ_0, the initial slope of the magnetization curve. The sudden decrease and subsequent change in sign of χ_{inc}, observed at 4.6°K for the rod sample, is due to a superconducting transition. There is no doubt that this superconducting transition is the result of the tantalum impurity. It is, however, somewhat surprising that the presence of the free tantalum dendrites, see metallurgical studies, can lead to the almost "perfect" shielding observed for the rod at temperatures below 4.4°K. One can, of course, simply postulate that the "free" tantalum formed a network of closed filaments which effectively shield the bulk of the sample.

The behavior of χ_{inc} for the powder between 1.4 and 0.85°K is suggestive of superconductivity in part of the sample. This drop in χ_{inc} would be accounted for if approximately 25% of the sample's volume was exhibiting "perfect" shielding. Measurements of the magnetic moment of the sample clearly rules this out. The initial slope of the virgin magnetization curve is temperature-independent between 4 and 1.0°K. We attribute this behavior of χ_{inc} to hysteresis effects associated with the application and removal of the large magnetic field (30 000 Oe) used in the magnetic cooling process.

The constant behavior of χ_{inc} between 0.85 and 0.1°K, and the fact that χ_{inc} was always positive, can only mean that the bulk of the sample, i.e., $ZrZn_2$, is not superconducting at temperatures above 0.1°K.

Resistance Measurements

To independently check on the possibility of superconductivity in some part of the powder sample, we measured the resistivity of the pressed powder sample. The ratio of $R_{300}/R_{4.2}$ was low, ~3, as one would expect for such a sample. The resistance was essentially constant between 4 and 0.1°K, in agreement with the χ_{inc} data, and supports the belief that $ZrZn_2$ is not superconducting above 0.1°K.

CONCLUSIONS

Although $ZrZn_2$ crystallizes in the cubic structure, (type C15) which seems to favor superconductivity in Zr compounds,[16] this compound does not become superconducting down to the lowest temperature attained, i.e., 0.1°K.

Although the samples used in the present study were multiphased, the magnetic data always indicated the

[14] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), p. 721.

[15] Allan H. Morrish, *The Physical Principles of Magnetism* (John Wiley & Sons, Inc., New York, 1965), pp. 265–266.

[16] B. T. Matthias, Science **144**, 380 (1964).

occurrence of ferromagnetism at low temperatures. Data obtained on the powder sample indicate an onset of magnetic ordering at 32°K. In this ordered state the magnetic moment per molecule is 0.10 μ_B. In the case of the solid rod, we have a sample which contains Ta as a chemical impurity and which has been severely cold worked. The main effect of all this is the lowering of the Curie point by only about 8°K. Thus we cannot agree with the idea that the ferromagnetism of $ZrZn_2$ can be easily destroyed by impurities and other lattice disturbances.[17] We also find no evidence for the existence of any magnetic ordering at temperatures between 32 and 120°K.

[17] B. T. Matthias *et al.*, Phys. Rev. Letters **7**, 7 (1961).

Note added in proof: The behavior of the high-temperature susceptibility of $ZrZn_2$ has been the subject of a recent publication: E. P. Wohlfarth, Phys. Letters **20**, 253 (1966).

ACKNOWLEDGMENTS

We wish to thank B. T. Matthias for giving us the sample materials. We also wish to thank R. A. Meussner for doing the metallograph and x-ray reflection patterns. The work of K. G. Skinner in pressing the powder material into a form useful for electrical-resistance measurements was most helpful. The authors are also grateful to M. R. Pablo for his aid in taking the earlier susceptibility data.

PHYSICAL REVIEW VOLUME 148, NUMBER 2 12 AUGUST 1966

Lattice-Dynamical Calculation of the Surface Specific Heat of a Crystal at Low Temperatures

A. A. MARADUDIN
Department of Physics, University of California, Irvine, California

AND

R. F. WALLIS
U. S. Naval Research Laboratory, Washington, D. C.

(Received 28 February 1966)

A lattice-dynamical calculation of the surface contribution to the low-temperature specific heat of a crystal is presented. The free boundary surfaces of a crystal are treated as a perturbation of an unperturbed crystal in which the atomic displacements satisfy the cyclic boundary condition. The general theory developed in this paper is illustrated by applying it to a nearest- and next-nearest-neighbor central-force model of a simple cubic crystal, whose force constants are chosen in such a way that it is elastically isotropic in the long-wavelength limit. The result for the low-temperature surface specific heat obtained here agrees with the results of earlier calculations by Dupuis, Mazo, and Onsager, and by Stratton, which were based on elasticity theory.

1. INTRODUCTION

IN this paper we present a lattice-dynamical calculation of the surface contribution to the specific heat of a crystal at low temperatures.

The majority of the previous calculations of the surface specific heat of a crystal were carried out for finite or semi-infinite isotropic elastic continua. The earliest such calculation seems to have been carried out by Breger and Zhukhovitskii[1–3] who determined the normal-mode frequencies of a semi-infinite incompressible isotropic continuum, from which the frequency spectrum and consequently the specific heat were computed. The assumption of incompressibility, while unphysical, is a mathematically convenient one because only transverse waves will propagate in such a medium. The result for the specific heat obtained in this way can be written in the low-temperature limit in the form

$$C_v(T)=AVT^3+BST^2+\cdots, \qquad (1.1)$$

where A and B are constants, V is the crystal volume, and S is its surface area. The first term is just the well-known "Debye-T^3" contribution to the low-temperature bulk specific heat, and the second term is the surface contribution.

Subsequently, Montroll[4] calculated the surface specific heat of an isotropic elastic rectangular parallelepiped whose faces are clamped. The normal-mode frequencies of such a solid can be written down explicitly, and the resulting specific heat has the form given by Eq. (1.1), although the coefficient B obtained by Montroll of course differed from that obtained by Breger and Zhukhovitskii.

[1] A. Kh. Breger and A. A. Zhukhovitskii, J. Phys. Chem. U.S.S.R. **20**, 1459 (1946).
[2] A. Kh. Breger and A. A. Zhukhovitskii, Acta Physiochim. U.R.S.S. **21**, 1001 (1946).
[3] A. Kh. Breger and A. A. Zhukhovitskii, J. Chem. Phys. **14**, 569 (1946).
[4] E. W. Montroll, J. Chem. Phys. **18**, 183 (1950).

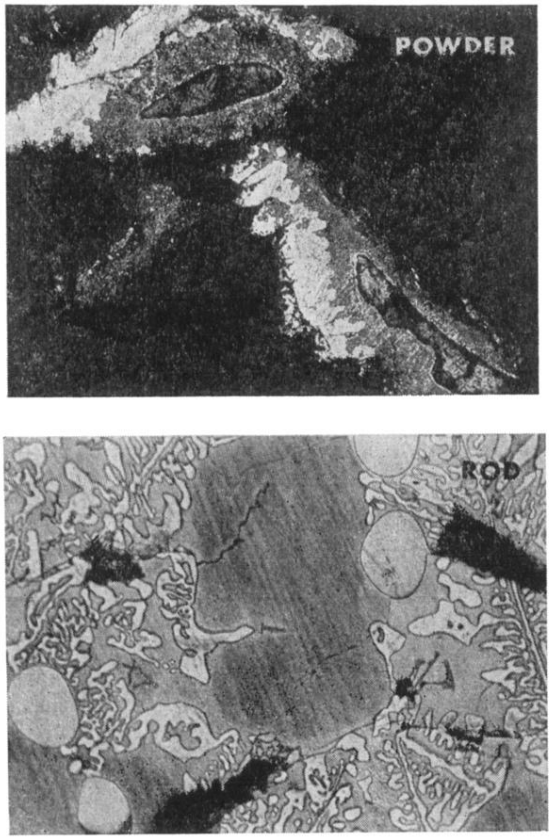

FIG. 1. Metallographs of the powder and the rod samples. Each picture covers an area of 300×400 μ. The powder grains are shown imbedded in an epoxy resin which is the dark structureless area surrounding the grains.

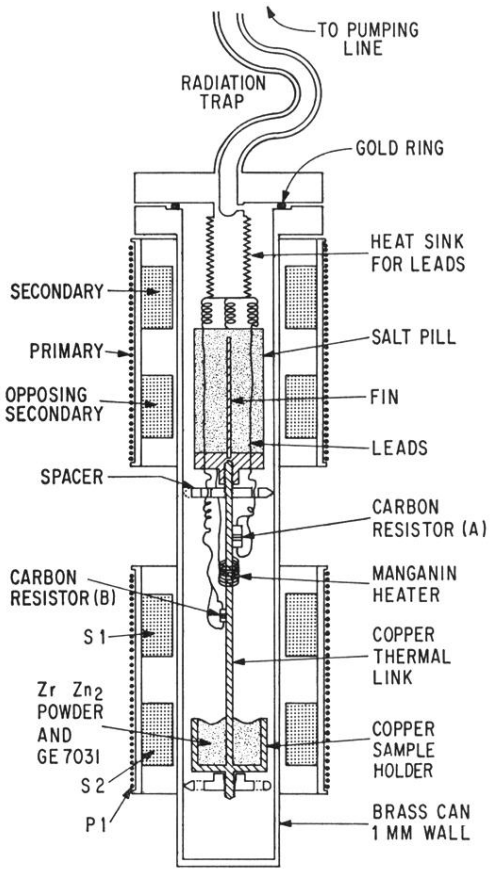

FIG. 2. A schematic of the apparatus employed in the measurement of $\Delta M/\Delta H$ over the temperature range 120 to 0.1°K.