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Effect of Pressure on the Curie Temperature of $ZrZn_2$†

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The initial pressure derivative of the Curie temperature of $ZrZn_2$ has been measured under hydrostatic conditions, yielding a value of $-(1.95\pm0.1)$°K kbar^{-1} for a sample with a Curie temperature of (21.5 ± 0.5)°K. This is in good agreement with the values of -1.8 and -2.4°K kbar^{-1} predicted by Wohlfarth using the model of a very weak itinerant ferromagnet and two different methods of calculation. The present measurement allows an estimate of the effective degeneracy temperature for $ZrZn_2$ of 300°K and an estimate for the initial differential susceptibility of 6.2×10^{-5} emu g^{-1} Oe^{-1}.

I. INTRODUCTION

THE very weak itinerant ferromagnets (VWFMs) are characterized as materials which have very small splitting energies between the energy bands comprised of those electrons with spins aligned parallel to a magnetic field and those aligned antiparallel. Consequently, the relative magnetization at zero field and temperature, $M(0,0)$, is much less than 1 μ_B per unpaired electron.[1] Some examples of VWFMs are the fcc alloys of Fe with Ni, Pd, and Pt. Wohlfarth has suggested that $ZrZn_2$ is also a VWFM, but there has been some controversy as to whether $ZrZn_2$ is intrinsically a ferromagnet. Foner *et al.*[2] suggested that the weak ferromagnetism observed in $ZrZn_2$ is due to transition-metal impurities. However, recently Blythe[3] has shown by doping high-purity $ZrZn_2$ with widely differing concentrations of Fe that similar values of magnetization at 4.2°K, and Curie temperatures are observed regardless of the amount of Fe, and concluded that $ZrZn_2$ is intrinsically ferromagnetic.

An explicit expression for the volume or pressure dependence of T_C (the Curie temperature) for the VWFMs has been obtained by Wohlfarth[4] and has been applied to the fcc alloys of Fe with Ni, Pd, and Pt and to $ZrZn_2$. The effect of pressure on T_C for the fcc Fe alloys has been measured[5] and is consistent with the theory[6] which predicts that $-\partial T_C/\partial P$ is proportional to T_C^{-1}. From the fcc Fe-alloy data, Wohlfarth predicts an approximate value of $-\partial T_C/\partial P = 1.8$°K kbar^{-1} for $ZrZn_2$. This is very close to his earlier estimate of 2.4°K kbar^{-1} obtained from forced magnetostriction data.[4] Such a correlation between $ZrZn_2$ and the fcc alloys would be remarkable considering that the constituents of $ZrZn_2$ are nonmagnetic *and* that its Curie temperature ($\simeq$20°K) is over an order of magnitude lower than those for the Fe alloys ($\simeq$300–700°K). An experimental determination of $-\partial T_C/\partial P$ for $ZrZn_2$ was thus seen to be desirable and has been carried out in this work.

II. EXPERIMENTAL PROCEDURE

A. Sample Preparation

Samples for hydrostatic-pressure studies should ideally be solid ingots (assuming good single crystals are not available). However, several attempts to obtain good quality ingots by holding the mixture of Zr and Zn at 1225°C for 1–5 days failed because of the reactivity of the alloy with the container (quartz or tantalum). It was discerned that the Zn vapor pressure is not a problem, if the temperature is increased slowly ($\sim$1 day) from 900 to 1225°C. A quartz tube retained its integrity for several hours *after* the temperature had been increased slowly to 1225°C, but then failed. On such a time scale, complete alloying did not occur. Well-reacted samples were obtained, however, by sintering pressed pellets in vacuum for 5 days at 910°C. The pellets were then pulverized, repressed, and homogenized for 3 days at 910°C. Attempts to melt the reacted pellets to form solid ingots were successful to a degree, but voids appeared inside the ingot. In the interest of assuring isotropic compression of the sample, such ingots with pores could not be used. Thus, the sample used for the present measurements was made of compacted powder from the homogenized pellet. The density of the compact was sufficiently low ($\sim$80% of theoretical density), assuring complete permeation of the sample by the pressure-transmitting medium (helium), thus effecting truly hydrostatic conditions.

A chemical analysis of the sample used indicated that it was slightly off stoichiometry with an actual composition of $ZrZn_{1.9}$. While the exact composition of the sample affects the Curie temperature and the magnitude of the magnetization, within this range the presence of VWFM is not affected.[7] Contribution from impurities was kept to a low level, with the major metalic impurities being Fe at 30 ppm and Hf at 40 ppm.

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B. Measurement of $\partial T_C/\partial P$

An accurate measure of the pressure-induced change in T_C was made using the self-inductance technique.[8] This technique consists of determining the self-inductance of a coil containing the sample as a function of temperature at a fixed pressure. The inductance was measured to a precision of $\pm 0.02\%$.

Since this experiment was conducted below 40°K and with pressures up to 3 kbar, helium had to be used as the pressure-transmitting medium to insure hydrostatic pressures. For some of the measurements, the He inside the pressure bomb and in the lower portion of the high-pressure tubing solidifies. Therefore, the He inside the pressure bomb will essentially be isolated (i.e., at constant volume) and the sample pressure will decrease with decreasing temperature[9] after the solidification occurs. Thus, the data had to be corrected to constant pressure using the known He isochore data of Dugdale.[10] Details of the sample holder and pressure bomb are shown in Fig. 1, and the system used to compress the He gas up to 3 kbar, is similar to the one described by Schirber.[11]

Coarse temperature control was effected by positioning the pressure bomb in the He vapor just above the liquid-He bath and fine control was accomplished with a Cryogenics Research Model TC101 controller. Temperatures were stable to and measured to within ± 0.1°K using Cu-versus-AuFe thermocouples calibrated against a germanium resistance standard. Thermocouple 1 (Fig. 1) was used to measure sample temperature directly, while thermocouple 2 was used at 4.0°K to make pressure corrections to thermocouple 1. Thermocouple 3 was used to insure freezing of the He from the bottom of the bomb upward to minimize pressure gradients.

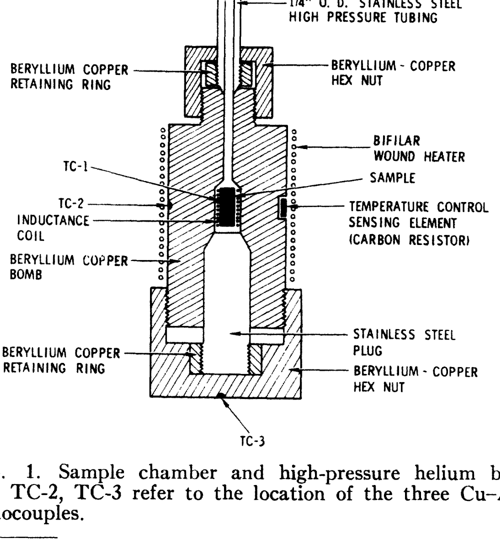

FIG. 1. Sample chamber and high-pressure helium bomb. TC-1, TC-2, TC-3 refer to the location of the three Cu–AuFe thermocouples.

C. Measurement of T_C

The absolute value of the Curie temperature was determined from magnetization measurements as a function of magnetic field H. The magnetization was determined by measuring the change in flux through a coil wound around the sample during magnetic field reversal. Integration of the voltage from the coil was accomplished using a high-impedance integrating digital voltmeter. Wohlfarth[1] has shown for VWFMs that

$$[M(H,T)]^2=[M(0,0)]^2(1-T/T_C)^2 + 2\chi_0 H/M(H,T)\,, \quad (1)$$

where $M(H,T)$ is the magnetization, H is the magnetic field, and χ_0 is the zero-field differential susceptibility. This relation is valid over a relatively large temperature range for the VWFMs (for ZrZn$_2$ over $0<T<2T_C$). As can be seen from Eq. (1), T_C is determined as the temperature, where a plot of $[M(H,T)]^2$ versus $H/M(H,T)$ intersects the origin.

III. RESULTS AND DISCUSSION

The results of the determination of T_C is shown in Fig. 2 in the form of an M^2-versus-H/M plot. From this plot, a Curie temperature of (21.5 ± 0.5)°K is estimated, which is in agreement with Blythe.[3] In Fig. 3 the reduced inductance is plotted versus temperature at various constant pressures. The reduced inductance is defined as

$$(L-L_\infty)/(L_0-L_\infty)\,,$$

where, for each pressure, L is the inductance measured at some temperature T, L_∞ is the inductance for $T>35$°K, and L_0 is the inductance at $T=0$°K. While there is a small change in the general shape of the inductance curve at the higher pressures, this change is

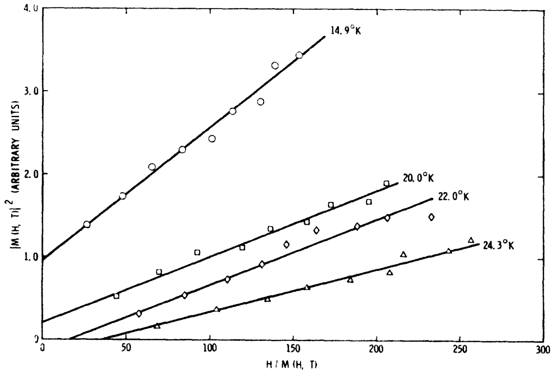

FIG. 2. Value of T_C is determined as the temperature for which the data as plotted above have a zero intercept.

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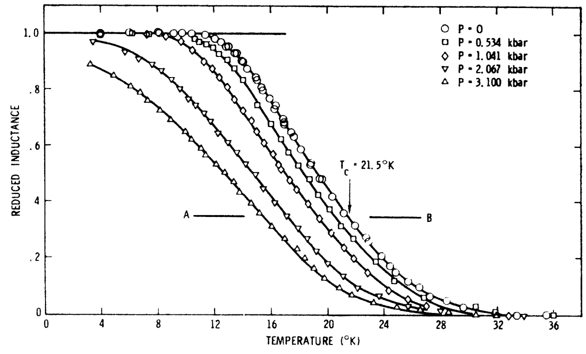

FIG. 3. Reduced inductance versus temperature isobars.

not apparent at the temperatures in the range of T_C. Thus, the pressure dependence of the Curie temperature can be measured along line AB, as shown in Fig. 3 with the result being plotted in Fig. 4. Within experimental error, the Curie temperature is a linear function of pressure up to 3 kbar, yielding $-\partial T_C/\partial P = (1.95 \pm 0.1)$°K kbar^{-1}. This result is in good agreement with Wohlfarth's earlier predictions of 1.8 and 2.4°K kbar^{-1}.

Following the notation of Wohlfarth,[4]

$$-\partial T_C/\partial P = 2\kappa CNN(\epsilon_F)\mu_B{}^2 T_F{}^2/T_C\,, \qquad (2)$$

where κ is the compressibility, N is the number of atoms per unit volume, $N(\epsilon_F)$ is the density of states per atom at the Fermi surface, T_F is the effective degeneracy temperature, and C is a constant related to the magnetostriction. From the measured value of $(\partial T_C/\partial P)T_C \approx 1800$ for the fcc Fe alloy VWFMs near 36% Ni[5] and a previous estimate of $T_F = 2000$°K for a 36% Ni–Fe alloy,[12] we are able to estimate $T_F = 300$°K for $ZrZn_2$. This estimate uses the assumption (following Wohlfarth) that the quantity $\kappa CNN(\epsilon_F)$ is reasonably constant. Our value of 300°K for T_F is in good agreement with the estimate of 260°K made from specific-heat data.[1] Further, we can estimate from forced magnetostriction data[4,13] and the measured values of $(\partial T_C/\partial P)T_C{}^{-1}$ that the initial differential susceptibility χ_0 of $ZrZn_2$ is 6.2×10^{-5} emu g^{-1} Oe^{-1}. This is a reasonable value in that it falls about halfway between the previously measured values.[1]

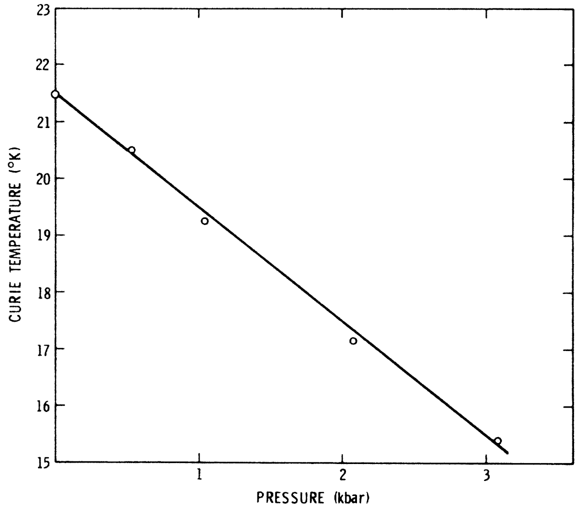

FIG. 4. Determination of $\partial T_C/\partial P$ from the values of T_C at various pressures as shown in Fig. 3.

In conclusion, the agreement of the pressure derivative of T_C in $ZrZn_2$ with the predictions of the theory of very weak itinerant ferromagnetism is striking, giving support to the correctness of the theory. $ZrZn_2$ provides a fruitful area for further examination in regard to this theory, since Blythe[14] and Ogawa[15] have shown that T_C can be varied over a wide range by alloying with a few percent of Ti or Hf. Thus, the relation giving $-\partial T_C/\partial P$ proportional to $T_C{}^{-1}$ can be tested over a wide range of T_C, as in the fcc Fe alloys. A measurement of the pressure derivative of the magnetic moment at 0°K is also needed for comparison to the fcc Fe alloys.

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