Upon comparison with the "normal" conductivity (II.52) we have the Wiedemann-Franz law

$$\kappa_n/\sigma_n = \tfrac{1}{3}\pi^2 K_B{}^2 T/e^2. \tag{37}$$

Using (36) we write

$$\frac{\kappa}{\kappa_n} = \frac{3\beta^3\Gamma_{tr}}{2\pi^2}\int_{\omega_0}^{\infty} dx\, x^2 \operatorname{sech}^2\tfrac{1}{2}(\beta x)$$

$$\times \frac{h(x)}{2[\Delta\operatorname{Im}(u^2-1)^{1/2}-\Gamma]+2\Gamma'(1-h)+\Gamma_{tr}}. \tag{38}$$

In order to evaluate this expression asymptotically near $T=0$, we have to distinguish between the two cases whether the excitation spectrum of the system has a gap ($\omega_0 \neq 0$) or not. In the first case, i.e., for low impurity concentration ($\alpha = \Gamma/\Delta < 1$, see the preceding paper), we obtain, using the expressions (II.54) and (II.55) of the preceding paper, respectively,

$$\frac{\kappa}{\kappa_n} = \frac{4}{\pi^2}\frac{1-\alpha^{2/3}}{(2\Gamma/\Gamma_{tr})-\alpha^{2/3}}\beta\omega_0\exp(-\beta\omega_0),$$

$$T\gtrsim 0,\ \alpha = \Gamma/\Delta < 1. \tag{39}$$

Thus the thermal conductivity goes to zero exponentially as long as there is a gap in the excitation spectrum.

In the gapless region ($\alpha > 1$) we get at $T=0$, using (II.58) of the preceding paper and starting the integration in (38) at $\omega_0 = 0$,

$$\frac{\kappa}{\kappa_n} = \frac{1-\alpha^{-2}}{1+(2\Gamma'/\Gamma_{tr})\alpha^{-2}} < 1, \qquad \alpha = \Gamma/\Delta > 1. \tag{40}$$

Comparing with (II.59) we see that in the gapless region the ratio κ/κ_n is identical to the ratio σ/σ_n for the dc conductivity. Therefore the Wiedemann-Franz law holds, too.

Finally, we consider the transition-temperature region where the system is always gapless ($\alpha = \Gamma/\Delta > 1$ as $\Delta \to 0$). Expanding (38) in powers of Δ^2 we conclude in analogy to Eqs. (II.62) and (II.65) of the preceding paper that

$$\kappa/\kappa_n = 1 - \mathrm{const}\times(1-t), \qquad t = T/T_c \lesssim 1. \tag{41}$$

Numerical solutions for the superconductor case in the whole temperature range are reported in Ref. 6.

Magnetic Susceptibility of Single-Crystal Alpha-Uranium†

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(Received 26 June 1967)

The magnetic susceptibility of high-purity single-crystal α-uranium has been measured from 4 to 300°K. A different temperature dependence was observed in each of the three principal crystallographic axes, and changes in slope were also noted below 40°K. The results are discussed in terms of localization of $5f$ electrons, spin-density waves, or Brillouin-zone–Fermi-surface interplay.

INTRODUCTION

THE resistivity,[1] Hall effect,[2] thermoelectric power,[3] thermal conductivity,[4] specific heat,[5] and elastic constants[1] of α-uranium exhibit anomalous behavior around 40°K. X-ray and neutron diffraction[6] measurements show orthorhombic α-U to have a corrugated layer type of structure, and at 43°K, a minimum is noted in the amplitude of the corrugations and the atomic volume. Ho, Phillips, and Smith[7] have recently

shown that α-uranium is not a bulk superconductor at zero applied pressure but is one at 10 kbar. Geballe et al.[8] linked the behavior at 40°K with the absence of superconductivity at lower temperatures by assuming a localization of $5f$ electrons occurs at 40°K to the extent of 0.04 μ_B. Gardner and Smith[9] measured the susceptibility of polycrystalline α-uranium from 1 to 300°K and detected no temperature dependence within their experimental error. They concluded, partly from the pressure dependence of the superconducting transition temperature and partly by analogy with Cr, that a spin-density-wave system may exist in α-uranium below 40°K.

Measurements on polycrystalline samples, however, give only the average susceptibility over the principal crystallographic axes, and if any magnetic order exists, it is less likely to be detected when the magnetic moment is small. We have carried out detailed measure-

† This work was performed under the auspices of the U.S. Atomic Energy Commission.
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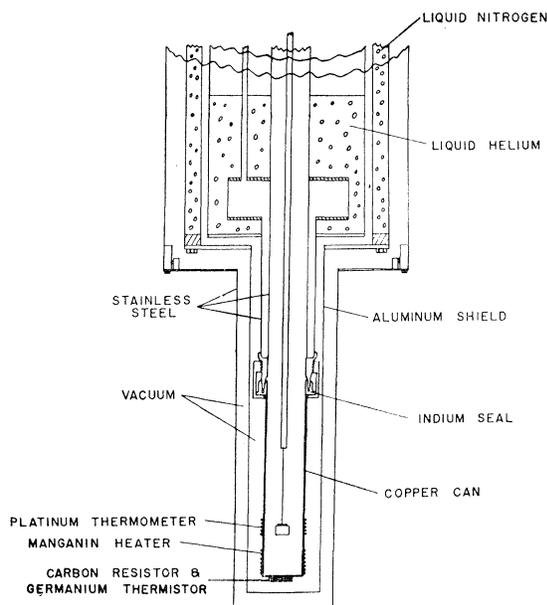[9] W. E. Gardner and T. F. Smith, Phys. Rev. 154, 309 (1967).

FIG. 1. Tail section of the helium cryostat showing the positions of the thermometers and sample.

ments on the magnetic susceptibility of four single crystals of α-uranium from 4.2 to 300°K.

EXPERIMENTAL

All the observations were made on single crystals made from uranium whose total impurity content was less than 80 parts per million (ppm) by weight. No individual metallic impurities (<10 ppm) were detected by spectrographic analysis. The crystals were grown by a grain coarsening method.[10]

The susceptibility of single-crystal α-uranium along the [100] axis was measured by the Faraday method. The force on the sample was recorded by an automatic weighing microbalance, the sample being suspended from the balance arm by a quartz rod and an aluminum chain. Correction factors for the susceptibility of the composite suspension were made at every temperature and magnetic field strength at which measurements of α-uranium were taken. As the susceptibility of α-uranium is not isotropic, the chain was so constructed that the sample could rotate freely in the magnetic field to ensure that the crystal axis with the greatest susceptibility was aligned parallel to the field. Consequently, only the susceptibility in the [100] direction could be observed by this method. The magnetic field and field gradient were measured by a rotating-coil gaussmeter previously calibrated by proton-resonance experiments. The reproducibility of the gaussmeter is ±3 Oe. The magnetic field strength was constant for all fields up to 10 kOe within the sensitivity of the gaussmeter. The field gradient was found to be constant for 2 cm above and below the specimen position. As

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the movement of the sample due to the motion of the balance arm was only 0.09 cm, the field and field gradient errors were less than 0.1%. Measurements of the susceptibility of high-purity Al, V, and Ta gave an absolute error of $\pm 10^{-8}$ emu g^{-1} compared with published results.[11] The error in reproducing the results and the relative susceptibility at various temperatures was only half this value.

The susceptibilities were measured at constant temperature, and the cryogenic arrangement is shown in Fig. 1. A calibrated germanium thermometer was used between 1.5 and 100°K, and a calibrated platinum thermomenter $(R4.2°K/R273°K = 4\times10^{-3})$ was used from 25–300°K. The overlapping temperature range for these two thermomenters was used to calibrate the internal consistency of the thermometers. The nature of the measurement precludes attaching the thermometers directly to the sample. The efficiency of the thermal link between the sample and the tail of the cryostat via the helium "exchange" gas was tested by noting the temperature difference between the cryostat thermometers and a calibrated thermometer suspended in the sample position. A supplementary calibration of the cryostat thermometers and an assessment of the reproducibility of the temperature measurements were made by repeated determinations of the susceptibility of a sample of cupric sulphate pentahydrate contained in a welded capsule. The susceptibility of this compound at various temperatures has been measured by Reekie.[12] The temperature uncertainty is 0.5°K between 4.2 and 200°K. Between 200°K and room temperature it is ±1°K.

Because the microbalance can only measure $\chi_{[100]}$, a self-compensating torque magnetometer was constructed to measure the susceptibility difference between orthogonal crystallographic axes. An orthorhombic crystal, mass m, in a uniform magnetic field H experiences a torque of $\frac{1}{2}mH^2 \sin2\theta(\chi_i-\chi_j)$, where i and $j = a$, b, and c, but $i\neq j$. θ is the angle between H
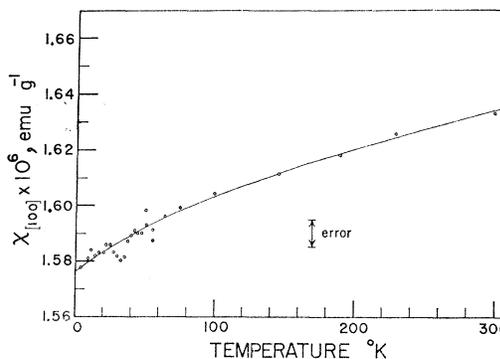

FIG. 2. The mass susceptibility in the [100] direction as a function of temperature.

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and the *i*th crystallographic direction. Measurement of the torque over 360° gives a sin2θ curve whose amplitude is directly proportional to the susceptibility difference $(\chi_i - \chi_j)$. The magnetometer was quite standard in design and has been described elsewhere.[13] Susceptibility differences to within $\pm 5 \times 10^{-10}$ emu g^{-1} were measured in fields of 20 kOe for a 0.75-g sample of α-uranium.

A cryogenic arrangement similar to the one described above was used in these measurements. The torque measurements were not as sensitive to vertical convection currents of the "exchange" gas around the sample as the microbalance determinations, and so higher gas pressures could be used. In the absolute measurements, only 20 μ of helium gas surrounded the sample while as much as 200 were used in the difference measurements. This ensured that below 77°K the sample was within ±0.2°K while above this temperature ±0.5°K difference was observed.

RESULTS

Measurements were made on four single-crystal samples. Three of the crystals had two parallel faces in the (100) planes, while the fourth crystal was a pseudo-unit-cell, i.e., each of its orthogonal faces was a (100) plane.

The values of $\chi_{[100]}$ for the pseudo-unit-cell are shown in Fig. 2. The error of $\pm 5 \times 10^{-9}$ emu g^{-1} is the scatter in the results over several runs. The absolute error on the ordinate, however, is $\pm 10^{-8}$ emu g^{-1}.

Figure 3 shows the results of the torque measurements on all four crystals. These values are calculated from the average amplitude of the sin2θ torque curve as the magnetic field is rotated 360° about the stationary crystal in both the clockwise and counterclockwise directions. An $H \sin\theta$ term was noted in the torque curves below 150°K, and this we attribute to very small amounts of single-crystal ferromagnetic uranium
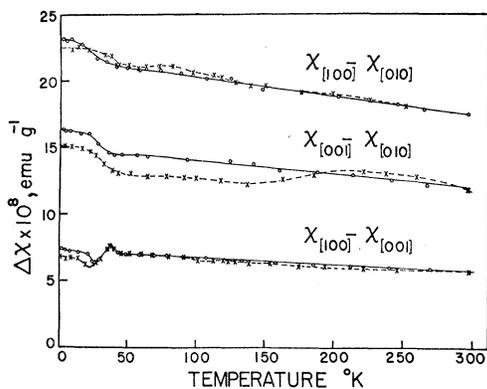
FIG. 3. The mass susceptibility difference between the three principal crystallographic axes. Circles, pseudo-unit-cell; crosses, three other crystals (see text).

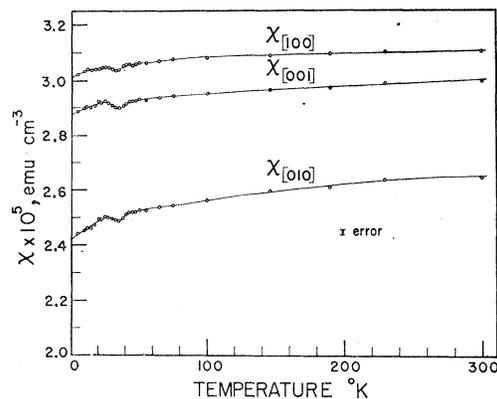[13] J. W. Ross, Argonne National Laboratory Report No. ANL-7155, 220, 1965 (unpublished).

FIG. 4. The volume susceptibility in the $\langle 100 \rangle$ directions.

hydride on the surface of the α-uranium crystals. In one of the first three single crystals, this term was as much as 30% of the $H^2 \sin 2\theta$ component and arose from 10 ppm hydride. In the pseudo-unit-cell, which was more carefully electropolished, only a 3% effect was noted. Averaging over 360°, rotation reduced the effect of impurity torque by approximately 80%. The most reliable results $(\pm \frac{1}{2}\%)$ are therefore for the pseudo-unit-cell.

No thermal hysteresis was noted in any of the measurements. Cooling the crystals in a magnetic field of 20 kOe through various temperature regions below 50°K had no measurable effect on the anisotropy of the crystals.

The anisotropy measurements can be combined with the values for $\chi_{[100]}$, and the susceptibility in all three principal crystallographic axes calculated. To eliminate the effect of volume changes on the susceptibility, we have used atomic-volume data of Barrett *et al.*[6] The susceptibility per cc in the principal directions is shown in Fig. 4.

DISCUSSION

In order to compare our results with those of polycrystalline samples, we have taken the average value over the three principal crystallographic directions. At room temperature $\chi_{\text{poly}} = 2.92 \times 10^{-5}$ emu cc^{-1} and at 4.2°K $\chi_{\text{poly}} = 2.78 \times 10^{-5}$ emu cc^{-1}. The room temperature value is 7% lower than that observed by Gardner and Smith[9] and 12% lower than that of Bates and Hughes.[14] Our samples are the purest uranium available at the present time.

Figure 4 shows a definite temperature dependence of χ in all three directions. The change of 1.4×10^{-6} emu cc^{-1} in χ_{poly} (5%) between 4.2 and 300°K is outside the error limits of Gardner and Smith[9] but is similar to that observed by Bates and Hughes[14] between room temperature and 600°K.

The present results do not substantiate Geballe's proposal of 0.04 μ_B localization of electrons if the mo-

[14] L. F. Bates and D. Hughes, Proc. Phys. Soc. (London) 67B, 28 (1954).

ments are randomly oriented. In this case, one would expect the susceptibility at 4°K to be 4×10^{-6} emu cc^{-1} greater than that at 40°K. Since no increase in χ_{poly} was observed below 40°K, the experimental accuracy of $\pm 10^{-7}$ emu cc^{-1} puts an upper limit of 0.005 μ_B on any localized magnetic moment on the uranium atoms. This value was obtained by assuming a random arrangement of moments and applying the formula $\Delta\chi\Delta T = \bar{\mu}^2/3R$, where $\Delta\chi$ = experimental error in emu mole^{-1}, ΔT = $40-4 = 36$°K, R is the gas constant, and $\bar{\mu}$ = average moment per uranium atom in Bohr magnetons. The observed susceptibility, however, cannot rule out a compensated spin arrangement of 0.04 μ_B below 40°K. Such a model would be indistinguishable, within the sensitivity of the experiment, from that proposed by Gardner and Smith, where a spin-density wave exists in α-uranium below 40°K. Orthorhombic α-uranium unlike bcc Cr has a large anisotropic paramagnetic component present in its susceptibility at all temperatures. One would not expect to see, therefore, effects similar to those observed in the torque measurements of Cr, particularly if in addition, the amplitude of the spin-density wave is smaller in α-uranium. Cooling in a 20-kOe field apparently is not sufficient to unbalance the domain structure.[15,16] Neutron diffraction data[6] on α-U do show some diffraction lines not present in the x-ray patterns, but these lines are present at all temperatures below 300°K.

The susceptibility of α-uranium can be separated into various contributions on a band model:

$$\chi_{poly} = \chi_p{}^s + \chi_p{}^{f,d} + \chi_{orb} + \chi_{dia} + \chi_L = 31.5 \times 10^{-6} \text{ emu } cc^{-1}.$$

The Pauli susceptibility $\chi_p{}^s$ of the s-like electrons is $1.86 \times 10^{-6} \times (\rho n_0/A)^{1/3}$. A is the atomic weight, ρ the density, n_0 the number of free electrons per atom. For α-uranium, $\chi_p{}^s = 1.0 \times 10^{-6}$ emu cc^{-1} if two s electrons are used. Friedel[17] gives -2.0×10^{-6} emu cc^{-1} for the diamagnetic susceptibility of the Radon core. No evidence exists which suggests that the effective mass of the conduction electrons is very different from the normal electronic mass, and so we replace the susceptibility due to the Landau diamagnetism χ_L by $-\frac{1}{3}\chi_p{}^s$. We conclude that the observed susceptibility comes almost exclusively from the Pauli susceptibility of the f-d band $\chi_p{}^{f,d}$ and the orbital paramagnetism χ_{orb}. The above term separation is only a rough approximation, however, as the large spin-orbit interactions in the actinides has been ignored.

It should be noted that the value of susceptibility difference between different crystallographic axes, although 15%, is small on an absolute scale $(4.8 \times 10^{-6}$ emu $cc^{-1})$. The total increase of about 5% in the volume susceptibilities with increasing temperature in the [100] and [001] directions and 10% increases in the [010] direction, may be due to changes in the relative positions of the Brillouin zones and the Fermi surface as the crystal contracts anisotropically and so affects the $\chi_p{}^{d,f}$ term.[18,19] Such a mechanism might also explain the temperature dependence of the susceptibilities below 40°K. Liftshitz[20] demonstrated that χ_p can behave in such a manner as pressure is applied when the Brillouin zone is close to the Fermi surface. In α-uranium, the large anisotropic contraction and expansion at temperatures below 300°K would have a similar effect to the variation of pressure. Alternatively, if the major contribution to the measure susceptibility is χ_{orb} our result would suggest that the band structure of α-uranium is anisotropic.[21]

The present results are the first to show the anomalous behavior of the susceptibility of α-uranium below 50°K. The size of the observed changes are small (2%), but well within the sensitivity of the measurements. The susceptibility results rule out a random arrangement of localized moments of 0.04 μ_B, but the measurements cannot differentiate between the other three mechanisms; ordered magnetic moments, spin-density waves, and temperature dependence of the band structure which we have discussed.

ACKNOWLEDGMENTS

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