Magnetic Susceptibility of High-Purity Thorium†

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The magnetic susceptibility of thorium has been measured between 18 and 328 °K. The thorium samples had been refined by the electrotransport process and had electrical resistivity ratios ranging between 790 and 1300. Linear extrapolation of the data to 0 °K yields a value of $+0.383\times10^{-6}$ emu/g. This susceptibility increases nearly linearly with increasing temperature to $(+0.412\pm0.001)\times10^{-6}$ emu/g at 300 °K. This behavior is qualitatively consistent with the behavior of a number of other physical properties and implies a temperature-dependent electronic distribution in thorium metal.

INTRODUCTION

In the course of surveying the physical properties of thorium, it became evident that the temperature dependence of a number of physical parameters contained implications of a temperature-dependent electronic distribution in this metal. For instance, Clusius and Franzosini[1] noted that heat-capacity data contained a temperature-dependent contribution which was presumed to be electronic in origin. Subsequent heat-capacity measurements by Wallace[2] showed this extra contribution to persist and to increase up to at least 1300 °K. Further, measurements[3] of the elastic constant $C_{12}-C_{44}$, which in the nearly-free-electron limit is associated with the bulk modulus of the electron gas,[4] change monotonically from negative values at low temperatures to positive values at temperatures above 253 °K. In addition, it has been found by Peterson *et al.*[5] that the temperature dependence of the electrical resistivity does not follow a simple theory. Below 80 °K, the experimental resistivity data are well fitted by the Bloch-Grüneisen equation with a Debye temperature of 135 °K, but above 80 °K, the experimental values lie above the Bloch-Grüneisen values with the magnitude of the discrepancy increasing with increasing temperature. Finally, a recent study[6] of the thermal conductivity of high-purity thorium has shown that the Lorentz ratio of the metal extrapolates to very nearly the theoretical value at very low temperatures where impurity scattering dominates. At intermediate temperatures, the occurrence of inelastic phonon-electron scattering invalidates the theoretical value of the Lorentz ratio and experimental values lie well below this value. But at high temperatures where nearly elastic phonon-electron scattering dominates, the Lorentz ratio might be expected to return to the theoretical value. In fact, the Lorentz ratio for thorium in the high-temperature region was found to be 20–30% larger than the theoretical value.

In view of these observations, it would seem that the magnetic susceptibility of thorium should show some temperature dependence. Early measurements of thorium susceptibility by Honda,[7] Owen,[8] and Klemm[9] are not in good agreement but may be discounted because of the questionable purity of the metal which was available to them. More recent measurements by Leach,[10] McClelland,[11] and Smith and Greiner[12] show good agreement for the magnetic susceptibility of thorium at room temperature with respective values of +0.422, +0.403, and +0.410 for an average of $+0.412\pm0.005$, all in units of 10^{-6} emu/g. Leach apparently did not make measurements as a function of temperature, and Smith and Greiner examined only the limited temperature range 130–300 °K where no significant temperature dependence was detected. McClelland reported negligible temperature dependence from room temperature down to about 160 °K but found below 160 °K a slow decrease to $+0.373\times10^{-6}$ emu/g at 77 °K, which was his lowest temperature of measurement. McClelland qualified his report by stating that his apparatus was new and not yet exhaustively tested so that the observed temperature variation might not be real. On the basis of this information and because high-purity thorium was available, it was decided to reexamine the magnetic susceptibility of thorium over an extensive temperature range below room temperature.

PROCEDURE AND RESULTS

The thorium which was used in this investigation was prepared by magnesium reduction of thorium tetrachloride.[13] This thorium was further refined by the electrotransport technique.[14] Four samples, each of about 0.5 g, were selected for magnetic susceptibility measurements. These samples were electropolished to clean and passivate the surfaces. High purity was evidenced by the electrical resistivity ratios, $\rho_{300}/\rho_{4.2}$, which ranged between 790 and 1300 for the four samples.

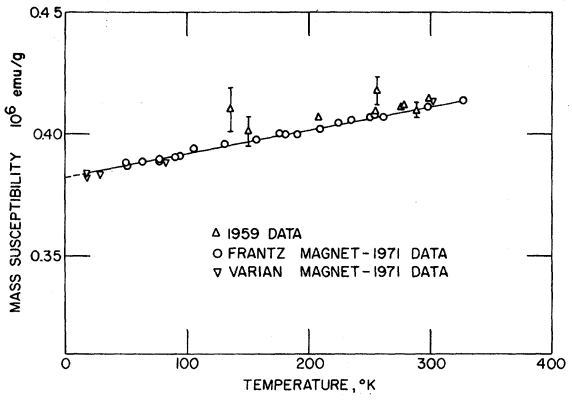

FIG. 1. Magnetic susceptibility of high-purity thorium as a function of temperature.

Magnetic susceptibilities were measured independently with two separate pieces of apparatus, both utilizing the Faraday technique.[15] The first of these used a Frantz magnet and could accommodate larger samples to yield higher precisions but was limited to the temperature range 50–330 °K. The second used a Varian magnet and with smaller samples could be cooled to 18 °K. Verification that these two pieces of apparatus yielded comparable values is shown by room-temperature measurements. With the Varian magnet a total of eight measurements, two with different specimen orientations for each of the four samples, yielded an average value of $(+0.413 \pm 0.006) \times 10^{-6}$ emu/g for the room-temperature susceptibility of thorium. With the Frantz magnet the four samples were combined into one test specimen weighing 2.02 g, and the room-temperature susceptibility of this composite was measured as $(+0.412 \pm 0.001) \times 10^{-6}$ emu/g. No field dependence was detected between 6.2 and 11.1 kOe in these or in subsequent measurements, and thence there was no indication of the presence of ferromagnetic impurities.

Experimental values are plotted as a function of temperature in Fig. 1. Symbols distinguish data taken with the Frantz magnet from data taken with the Varian magnet, and data from the 1959 experiments[12] are included for comparison. In the plot, precisions which are not delineated with error bars are of the order of the size of the plotted points. Because only one of the original four samples was measured as a function of temperature in the Varian magnet, the smaller mass with weaker force resulted in lesser precision ($\sim \pm 0.002 \times 10^{-6}$ emu/g) than was obtained with the composite of four samples in the Frantz magnet ($\sim \pm 0.001 \times 10^{-6}$ emu/g). Temperatures in the range 50–330 °K were measured with copper vs constantan thermocouples, while temperatures below 50 °K were measured with a gold–0.07% iron vs copper thermocouple. Uncertainties in temperature values were of the order of ±2°, but temperature variation during any given measurement was limited to ±0.1°. On the basis of the field calibrations the accuracy of the measurements is estimated as ±2%. Linear extrapolation of the temperature trend yields a value of $+0.383 \times 10^{-6}$ emu/g for the magnetic susceptibility of thorium at 0 °K.

Two unsuccessful attempts were made to measure the magnetic susceptibility of thorium at temperatures below 18 °K through use of ac inductance techniques. The failure of these attempts is attributable to the extreme purity of the thorium with an attendant low-electrical resistivity which allows large eddy-current effects to complicate ac measurements. Even though these attempts did not yield values for the susceptibility, the superconducting transition near 1.39 °K was clearly evident.

DISCUSSION

It can be seen from Fig. 1 that the comparatively large uncertainties in the 1959 data[12] when combined with the limited temperature range of measurement masked the weak temperature dependence which is present in the magnetic susceptibility of thorium metal. The present measurements show that the magnetic susceptibility of thorium increases about 8% in a nearly linear manner as the temperature rises from 0 to 328 °K. The behavior of the magnetic susceptibility is thus qualitatively consistent with the behavior of a number of other physical properties which were mentioned in the Introduction.

If diamagnetic contributions and electron-phonon coupling are neglected, the extrapolated value of the susceptibility at 0 °K corresponds to a density of electronic states at the Fermi surface of 18.7 states/Ry atom per spin. In view of the neglected terms, this is in acceptable accord with values of 14.6 states/Ry atom from the theoretical calculations of Gupta and Loucks[16,17] and of 12.6 states/Ry atom from electronic-specific-heat coefficients.[18,19]

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[1]K. Clusius and P. Franzosini, Z. Naturforsch. 11A, 957 (1956).
[2]D. C. Wallace, Phys. Rev. 120, 84 (1960).
[3]P. E. Armstrong, O. N. Carlson, and J. F. Smith,

J. Appl. Phys. 30, 36 (1959).
[4]J. de Launay, Solid State Phys. 2, 276 (1956).
[5]D. T. Peterson, D. F. Page, R. B. Rump, and D. K. Finnemore, Phys. Rev. 153, 701 (1967).
[6]H. G. Schettler, J. J. Martin, F. A. Schmidt, and G. C. Danielson, Phys. Rev. 187, 801 (1969).
[7]K. Honda, Ann. Physik 32, 1027 (1910).
[8]M. Owen, Ann. Physik 37, 657 (1912).
[9]L. Klemm, Z. Elektrochem. 45, 354 (1939).
[10]S. J. Leach, thesis (University of Nottingham, 1955) (unpublished), quoted by L. F. Bates and M. M. Newmann, Proc. Phys. Soc. (London) 72, 345 (1958).
[11]J. D. McClelland, U. S. AEC Report No. NAA-SR-1286, 1954, pp. 31–32 (unpublished).
[12]J. F. Smith and J. D. Greiner, Phys. Rev. 115, 884 (1959).
[13]D. T. Peterson, W. E. Krupp, and F. A. Schmidt, J. Less-Common Metals 7, 288 (1964).
[14]D. T. Peterson and F. A. Schmidt, J. Less-Common Metals 24, 223 (1971).
[15]P. W. Selwood, *Magnetochemistry* (Interscience, New York, 1956), p. 11.
[16]W. R. Decker and D. K. Finnemore, Phys. Rev. 172, 430 (1968).
[17]J. E. Gordon, H. Montgomery, R. J. Noer, G. R. Pickett, and R. Tobon, Phys. Rev. 152, 432 (1966).
[18]R. P. Gupta and T. L. Loucks, Phys. Rev. Letters 22, 458 (1969).
[19]R. P. Gupta and T. L. Loucks, Phys. Rev. B 3, 1834 (1971).

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Effective-Mass Parameters for Electronic Energy Bands*

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The continuation of electronic energy bands in the neighborhood of symmetry points is discussed in terms of explicit expressions derived within the Green's-function method. The accuracy and convenience of these formulas are demonstrated in the calculations of specific band parameters at various symmetry points of the Brillouin zone for degenerate as well as nondegenerate states in both nonrelativistic and relativistic problems. Applications of this approach are briefly discussed.

Methods of continuing the band structure $E_n(\vec{k})$ in the neighborhood of a point $\vec{k}_0$ at which $E_n(\vec{k}_0)$ is known are of considerable interest both in theoretical and semiempirical contexts. Standard $\vec{k}\cdot\vec{p}$ perturbation theory gives a straightforward expansion for a nondegenerate Bloch state of band index n and wave vector $\vec{k}_0$ in terms of the momentum matrix elements, $\vec{p}_{nn'}(\vec{k}_0)$, and the inverse effective-mass tensor, which is given by the well-known f-sum rule[1]

$$\left(\frac{m}{m^*}\right)^{(n)}_{ij} = \delta_{ij} + \left(\frac{2}{m}\right) \mathrm{Re} \sum_{n'}{}' \frac{p_{i,nn'}(\vec{k}_0)\, p_{j,n'n}(\vec{k}_0)}{E_n(\vec{k}_0) - E_{n'}(\vec{k}_0)} \,. \quad (1)$$

This result and the corresponding formulas for degenerate band parameters are quite general and they have been useful in many aspects of solid-state theory. Nevertheless, they do not provide a practical means for accurately calculating the band parameters since the evaluation of the sum over excited states in (1) requires, in general, an appreciable number of energy eigenvalues and a large number of interband momentum matrix elements which are generally unavailable.

A more tractable result for the effective mass at the center of the Brillouin zone was obtained by Bardeen[2] within the spherical approximation. Bardeen's formula is accurate and simple since it involves only the logarithmic derivatives of the s and p radial functions evaluated on the equivalent sphere at the energy of the lowest Γ_1 state. The spherical approximation, however, used in this approach is inapplicable to states other than the s-like Γ_1 state of monatomic cubic crystals. In contrast, the generalization of Bardeen's formula given by Cohen and Ham[3] applies to any symmetry state; however, the evaluation of the surface integral, which appears in their formula to replace the sum over excited states in (1), appears to be a difficult computational task and to our knowledge it has not been carried out for any specific calculations.

In this paper we present and evaluate explicit expressions for the effective-mass parameters at various symmetry points in the Brillouin zone for degenerate as well as nondegenerate bands in both nonrelativistic and relativistic problems. These results, which are derived within the framework of the Green's-function method[4] (GFM), are both very accurate and very convenient to evaluate and, we believe, will be quite useful. That the GFM should be useful in this connection is not surprising in view of its unsurpassed effectiveness in determining $E(\vec{k})$ for crystal potentials which can be approximated by the muffin-tin form.

The GFM dispersion relation is given by