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Nuclear Specific Heat of Holmium*

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The specific heat of holmium has been measured between 0.95° and 4.2°K. The magnetic hyperfine interaction in holmium is so large that over this entire temperature range the nuclear hyperfine term represents the predominant contribution to the specific heat. Below 1.5°K the specific heat appears to be that of an ideal paramagnetic gas of spin $\frac{7}{2}$. At 1°K the specific heat has the extremely large value of $0.37R$.

PARAMAGNETIC resonance[1,2] and nuclear alignment experiments[3] on holmium indicate a very large magnetic hyperfine interaction in that rare earth. This interaction is, in fact, so large that the nuclear contribution to the holmium specific heat was expected to be easily discernible above 1°K. We have measured the specific heat of holmium between 0.95° and 4.2°K and have found that over this entire temperature range the predominant contribution to the specific heat comes from the hyperfine term.

The measurements were made in a conventional low-temperature calorimeter. The holmium samples used were cut from a specimen which was reported by the manufacturer (Michigan Chemical Corporation) to contain the following impurities: Cu and Ni, 0.01% each; Ta, 0.26%; O_2, 0.14%; Ca, 0.1%; Y, 0.05%; Er, 0.2–0.5%.

Figure 1 shows the data plotted as a function of T^{-2}. The open circles represent measurements taken on a 181-g sample, the black circles are the points obtained using a 14.8-g sample. The low-temperature specific heat of holmium is so large that we encountered difficulty in attaining thermal equilibrium between the larger sample and the helium bath during the calibration of the carbon resistor which was used for measuring sample temperatures. For this reason the open circles at the lowest temperatures are less reliable than the other points. We believe the uncertainty of the majority of data points to be less than ±3%.

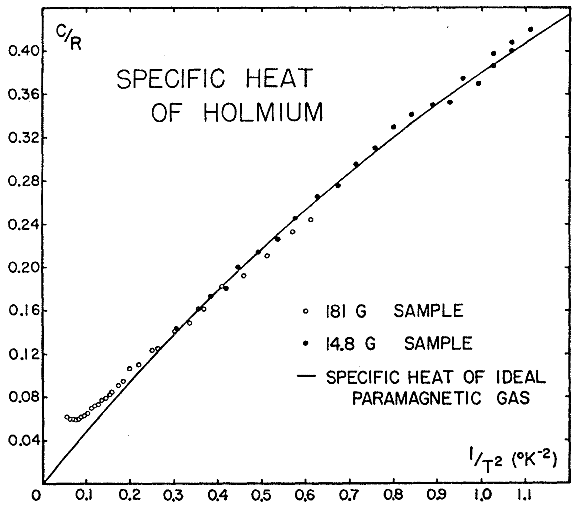

FIG. 1. Specific heat of holmium as a function of (temperature)$^{-2}$. The curve represents the specific heat of a spin-$\frac{7}{2}$ ideal paramagnetic gas for which the ratio $\mu H/Ik$ has been chosen to be 0.309 deg.

It is of interest to note that the hyperfine interaction in holmium is so strong that its contribution to the specific heat cannot be regarded as being proportional to T^{-2} even at temperatures as high as 1.5°K. The data, however, appear to be consistent with the view that the nuclei may be described as an ideal paramagnetic gas. The specific heat of such a gas is given by

$$C/R = -(x^2/4)\{(2I+1)^2 \operatorname{csch}^2[(2I+1)x/2] - \operatorname{csch}^2[x/2]\}, \quad (1)$$

where $x = \mu H/IkT$, (μ = magnetic moment of the gas particles, I = angular momentum of the gas particles, and H = magnetic field in which the gas is situated).

For small x,

$$C/R \approx (x^2/3)\{I(I+1) - (x^2/80)[(2I+1)^4 - 1]\}. \quad (2)$$

In order to obtain the best fit of Eq. (1) to our data we have chosen x to be equal to $0.309T^{-1}$. This value for $\mu H/Ik$ indicates that the internal magnetic field in holmium is 8.9×10^6 oe. (I, the nuclear spin quantum number of holmium, is $\frac{7}{2}$. μ, the nuclear magnetic moment, is assumed to be 3.3 nuclear magnetons.)

A comparison of our specific heat measurements with the paramagnetic resonance measurements of Baker and Bleaney[1,2] on 1% holmium ethyl sulfate in yttrium ethyl sulfate indicates that the hyperfine coupling is roughly 30% larger in the metal than in the salt. Though the major contribution to the field probably comes from the $4f$ electrons, the above result suggests that there is an additional contribution to the coupling in the metal. This additional coupling presumably arises from the polarization of the conduction electrons. This result is to be contrasted with that obtained by Kurti and Safrata.[4,5] They found the hyperfine inter-

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[1] J. M. Baker and B. Bleaney, Proc. Phys. Soc. (London) **A68**, 1090 (1955).

[2] J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A245**, 156 (1958).

[3] H. Postma and W. J. Huiskamp, *Proceedings of the Seventh International Conference on Low-Temperature Physics, 1960* (University of Toronto Press, Toronto, 1961), p. 180.

[4] N. Kurti and R. S. Safrata, Phil. Mag. **3**, 780 (1958).

[5] N. Kurti, J. Appl. Phys. **30**, 215S (1959).

action in terbium metal to be of almost the same size as the interaction in terbium ethyl sulfate.[6]

In Fig. 2 the experimental results and the hyperfine specific heat as calculated from Eq. (1) are plotted as a function of T. Above 1.5°K the hyperfine term, though dominant, no longer represents the only significant contribution to the specific heat. We hope to measure the specific heat of holmium between 4 and 15°K in the near future. Any detailed discussion of our present measurements above 1.5°K will be more meaningful when the higher temperature data are available. On the basis of the present results, however, we conclude that the data cannot be represented as the sum of hyperfine, lattice, electronic, and spin-wave terms, at least so long as the spin-wave contribution is assumed to have a simple $T^{\frac{3}{2}}$ dependence. This conclusion is not surprising in view of the fact that the data of Gerstein *et al.*,[7] on the specific heat of holmium above 12°K indicate a magnetic transition at the relatively low temperature of 19.4°K.

We also plan to make measurements between 0.95°K and 15°K on a second sample of holmium. The sharp disagreement between the measurements of Stanton *et al.*,[8] and Kurti and Safrata on terbium,[4,5] and between the measurements of Dash *et al.*,[9] and Lounasmaa and Guenther[10] on dysprosium suggests that oxygen or other impurities in rare earth samples may seriously affect specific heat measurements. The nuclear contribution to the specific heat of holmium is so large that possible impurity effects probably are not noticeable below 1.5°K. However, such impurity effects, if present, could be comparable to, or larger than, the lattice, electronic, and spin-wave contributions to the specific heat in the helium region. Thus measurements on more than one sample are advisable before making any evaluation of the non-nuclear contributions to the holmium specific heat.

We should like to point out that the very large specific heat of holmium at 1°K and below makes this metal more useful than cobalt as an isothermal reservoir for such applications as a magnetic refrigerator.[11]

Note added in proof A. We have recently made specific heat measurements between 1.25° and 4.2°K on a second holmium sample. Information provided by the supplier (Nuclear Corporation of America, Research Chemical Division) indicates that this second sample has a different, and slightly smaller, impurity content than our first specimen. Nevertheless, the gram-atomic specific heats of the two specimens are the same, within experimental error, over the 1.25°–4.2°K region. Thus any contribution from impurity effects to the holmium specific heat must be relatively small.

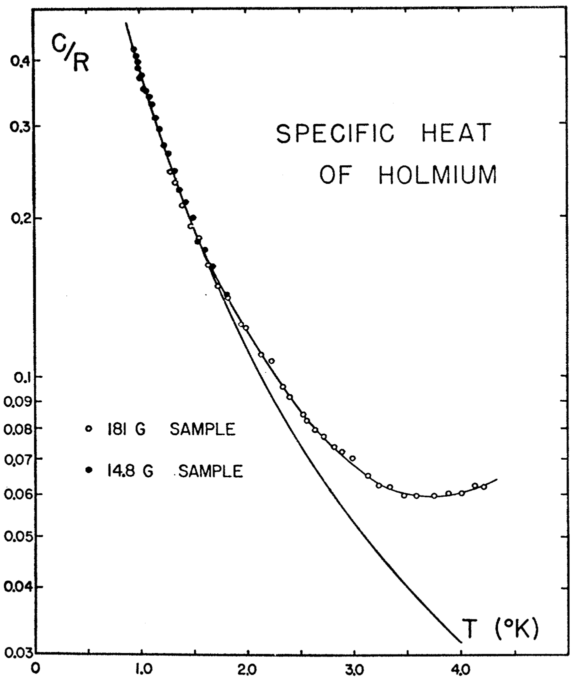

Fig. 2. Specific heat of holmium as a function of temperature. A smooth line has been drawn through the data points. The lower curve is identical to that in Fig. 1.

Note added in proof B. The parameter x introduced above can be written as $x = a't^{-1}$. Here a' is a constant which measures the strength of the hyperfine interaction. As stated above, we find that a' has the value 0.309° for holmium metal. Professor B. Bleaney of Oxford has recently examined the question of the size of the hyperfine structure constants of the rare-earth metals. Using data from the trivalent rare-earth ions in dilute paramagnetic salts, his calculations indicate that the constant a' should have the value 0.312° for holmium metal. On the basis of this very close (and perhaps fortuitous) agreement between the experimental and calculated values of a', we now conclude that any contribution of the conduction electrons to the hyperfine coupling in holmium metal is negligible. We are grateful to Dr. O. V. Lounasmaa and Dr. R. Parks for informing us of Professor Bleaney's work, which was reported at the Kyoto conference on magnetism (1961).

ACKNOWLEDGMENT

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[6] J. M. Baker and B. Bleaney, Proc. Phys. Soc. (London) **A68**, 257 (1955).

[7] B. C. Gerstein, M. Griffel, L. D. Jennings, R. E. Miller, R. E. Skochdopole, and F. H. Spedding, J. Chem. Phys. **27**, 394 (1957).

[8] R. M. Stanton, L. D. Jennings, and F. H. Spedding, J. Chem. Phys. **32**, 630 (1960).

[9] J. G. Dash, R. D. Taylor, and P. P. Craig, *Proceedings of the Seventh International Conference on Low-Temperature Physics, 1960* (University of Toronto Press, Toronto, 1961), p. 705.

[10] O. V. Lounasmaa and R. A. Guenther (unpublished results). We are grateful to Dr. Lounasmaa for informing us of his results prior to their publication.

[11] C. V. Heer and R. A. Erickson, Rev. Sci. Instr. **29**, 440 (1958).