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Heat Capacity of Ferromagnetic Superconductors*

NORMAN E. PHILLIPS
Department of Chemistry and Lawrence Radiation Laboratory, University of California, Berkeley, California

AND

B. T. MATTHIAS
Bell Telephone Laboratories, Murray Hill, New Jersey

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Heat capacity measurements on two samples from each of the systems $La_{1-x}Gd_x$ and $Y_{1-x}Gd_xOs_2$ show features which are correlated with the reported existence of both ferromagnetic and superconducting transitions. For one sample the measurements cover a wide enough temperature range to show that the entropy associated with the ordering of the gadolinium spins is the $xR\ln 8$ expected for complete order. The heat capacities of the other samples are consistent with complete ordering. Superconducting transitions have been observed both above and below the maximum in the heat capacity associated with the spin ordering. The entropy differences between the normal and superconducting states show that superconductivity is not confined to small volume elements but probably extends throughout the sample.

RECENTLY, solid solutions of elements and intermetallic compounds have been discovered in which superconductivity and ferromagnetism appear to coexist.[1–3] A question of central interest which cannot be answered by magnetic susceptibility measurements is whether the whole sample is both superconducting and ferromagnetic or whether, for example, superconductivity is confined to small regions of the sample.[4] This note presents results of some preliminary calorimetric measurements which show both a superconducting transition in a ferromagnet and a spin alignment taking place in a superconductor. The measurements also indicate that superconductivity and ferromagnetism exist simultaneously throughout the whole sample.

Figure 1 shows the heat capacity of two samples belonging to the system $Y_{1-x}Gd_xOs_2$, between 1.1° and 4.2°K. In this range it is considerably in excess of that to be expected for the lattice and conduction electrons alone. The observed entropy is in each case only 50% of the $xR\ln 8$ that would be expected for the complete ordering of the gadolinium spins but the shape of the curves is consistent with an entropy of that amount being associated with the total heat capacity anomaly. Susceptibility measurements on similar samples[3] show that the ferromagnetic curie point, T_c, for the $Gd_{0.075}$ sample is 3.1°K. For the $Gd_{0.04}$ sample the presence of superconductivity makes the measurement of T_c by that technique difficult but an extrapolation from higher gadolinium concentrations gives 1.4°K. The heat capacity maxima are, respectively, 2.5°K and below 1.1°K. This correlation must be considered satisfactory in view of the width of the transition and the different nature of the two measurements. At temperatures above the Curie point both samples have a heat capacity which increases with increasing magnetic field, as expected for paramagnetic materials. The one exception occurs for the $Gd_{0.04}$ sample near 3.6°K, which is the superconducting transition temperature observed in the susceptibility measurements. Here the heat capacity decreases in small fields in the way expected for a superconductor just below its transition temperature, but then starts to increase in larger fields. The maximum decrease with field, 8 millijoules/mole deg, gives a lower limit for the difference in heat capacity between the normal and superconducting states. For a pure metal with electronic heat capacity γT this difference is about $1.4\gamma T_s$ at the superconducting transition temperature, T_s. In the present case the transition is spread over a 10% range of temperature in the way typical of solid solutions and, while the maximum difference depends to a certain extent on the shape of the distribution, it can be expected to be approximately γT_s. The assumption that the whole sample becomes superconducting leads then to a minimum value for γ of 2.3 millijoules/mole deg^2, which is of the usual order of magnitude. For example, pure Os has a γ of 1.1 millijoules/mole-deg^2.[5]

For the $Gd_{0.075}$ sample the superconducting transition occurs *below* the ferromagnetic Curie point. In this case there is a bump of about 2% in the zero field heat capacity relative to that in fields of 150 and 300 gauss. The heat capacity seems to approach a constant value as the field is increased and the apparent value of γ is 4.0 millijoules/mole deg^2. This result shows that superconductivity is not confined to a small fraction of the sample, as seemed possible from the susceptibility measurements,[4] but probably occupies the whole volume.

It is interesting that external fields of a few hundred gauss can destroy superconductivity in a ferromagnet for which the field associated with the saturation moment is several times greater. This observation is con-

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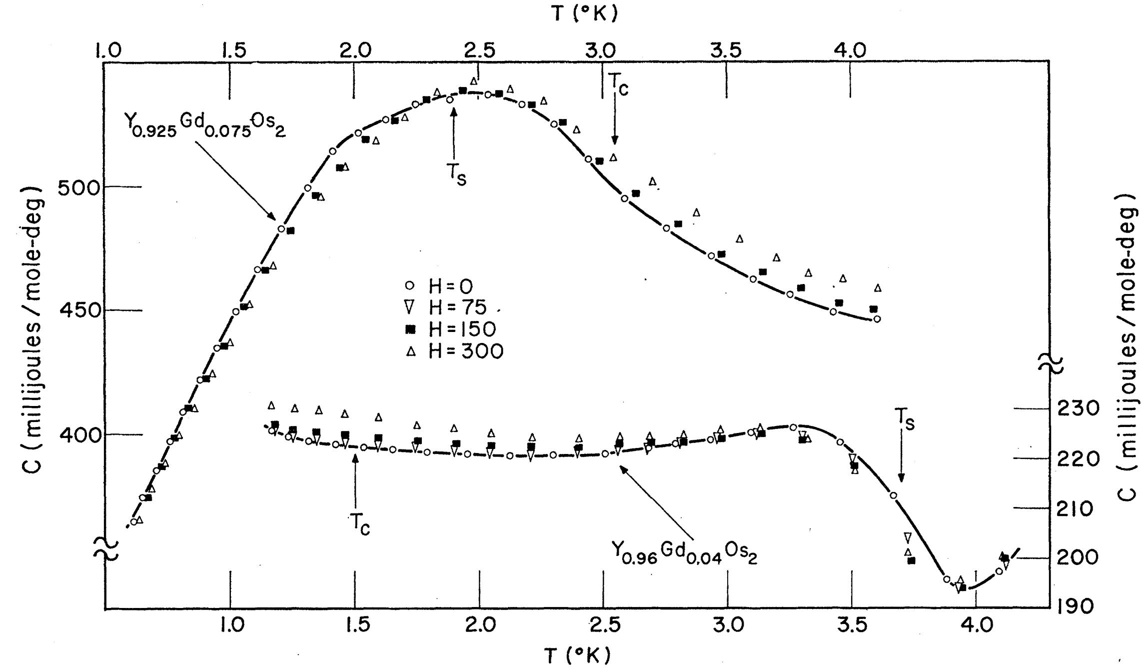

FIG. 1. Heat capacity of solid solutions of $GdOs_2$ in YOs_2. T_c and T_s are, respectively, the ferromagnetic Curie point and superconducting transition temperature obtained by magnetic susceptibility measurements (see reference 3).

sistent with the fact that the energy of interaction of the saturation moment with the external field is greater than the superconducting energy and with the result of Anderson and Suhl[6] that the range of ferromagnetic ordering in a superconductor must be small compared to the coherence length.

Figure 2 shows the heat capacity of two solid solutions of gadolinium in lathanum. The measurements below 1.1°K were made in an adiabatic demagnetization calorimeter.[7] The behavior of the 0.7% gadolinium sample at temperatures between 0.3 and 1.1° is complicated by thermal hysteresis and a spontaneous evolution of heat following some of the heating periods and lasting for several minutes. In some cases the temperature of the sample suddenly jumped by several tenths of a degree. We believe that these effects are all associated with the exposure of the sample to a magnetic field during cooling: no such effects were observed above 1.1°K. Between 0.6° and 1.1°K it was possible to make measurements without having exposed the sample to the field of the main magnet and results obtained this way are generally higher, show no spontaneous heating,

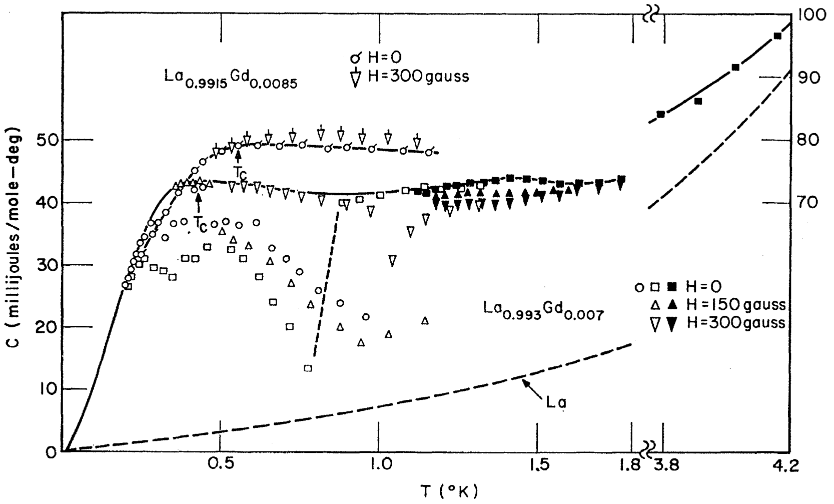

FIG. 2. Heat capacity of solid solutions of gadolinium in lanthanum. Magnetic susceptibility measurements indicate a superconducting transition in the 0.7% gadolinium sample at about 2.1°K and ferromagnetic Curie points at temperatures indicated by T_c (see references 1 and 2). Each symbol designates a single series of consecutive measurements: the open symbols represent points obtained in the adiabatic demagnetization calorimeter.

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and are the only ones which join the measurements at higher temperatures. On the assumption that the correct heat capacity between 0.3 and 1.1°K is that obtained when no spontaneous heating was evident the heat capacity is very similar to that for $Y_{0.96}Gd_{0.04}Os_2$. With the extrapolation to $T=0$ shown in the figure the entropy in excess of that for pure lathanum at 4.2°K is 95% of the expected 0.007 $R\ln 8$. The superconducting transition is spread out between 1.4° and 1.8°K. The maximum decrease in heat capacity on application of a magnetic field is 8 millijoules/mole deg and is consistent with the value 6.7 millijoules/mole deg^2 for γ for pure lanthanum.[8] For each of the lanthanum-gadolinium samples the heat capacity maximum is in good agreement with an extrapolation of the T_c vs composition curve from above the point at which it crosses the T_s curve. Both samples are known to be superconducting at and below the maxima.[2]

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Magnetic Field Dependence of Energy Gap in Superconductors*

K. K. Gupta† and V. S. Mathur
The Enrico Fermi Institute for Nuclear Studies and the Department of Physics,
The University of Chicago, Chicago, Illinois

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The dependence of energy gap in superconductors on static magnetic fields has been derived in a gauge-invariant way from the theory of Bardeen, Cooper, and Schrieffer. It has been shown that the gap width decreases with magnetic field approaching the critical value. Optimum conditions have been discussed for the observation of such an effect. The decrease in gap width has been calculated for two supreconductors, Al and Sn, and it has been shown that for film thickness between 10^{-4} to 10^{-5} cm, the effect can be large enough to be observable.

1. INTRODUCTION

MUCH progress has been made in recent years in the theory of superconductivity proposed by Bardeen, Cooper, and Schrieffer.[1] Whereas the existence of an energy gap and the related thermal properties have been explained quite satisfactorily, the treatment of the electromagnetic properties of superconductors has not been quite unambiguous, mainly because of the question of gauge invariance.[2] A lot of work has appeared in the literature on the problem of gauge invariance,[3–6] especially with a view to deriving the Meissner effect and the Pippard equation.[7]

In the present paper we consider another aspect of the magnetic behavior of a superconductor—the dependence of the energy gap on a static magnetic field. Since superconductivity is destroyed at a critical value of the magnetic field, one may expect that the energy gap would decrease with magnetic fields approaching the critical field. The purpose of the present paper is to study this possibility, and to explore the conditions under which the gap decrease might be large enough to be observable.

Some experimental attempts have been made to study the effect of magnetic field on penetration depth and the gap width. Notable are the experiments of Pippard,[8] and of Spiewak,[9] and the more recent attempt of Ginsberg and Tinkham.[10] Studying the behavior in a microwave field, Pippard found that for tin, in presence of a static magnetic field close to the critical field, the penetration depth increased by less than 3%. Spiewak's experiment also performed with tin wires (thickness $\sim 60\mu$) at a lower microwave frequency again indicated a very small effect for both longitudinal and transverse magnetic fields. Ginsberg and Tinkham, in contrast with the above experiments, used very thin superconducting films (thickness 12 A), and with the technique of transmission of far infrared radiation through such specimens, found a very small effect again. One of the purposes of the present investigation is to understand these negative results on the BCS model of superconductivity. We shall see that according to our calculations, these experiments have been performed with films either too thick or too thin, while the optimum thickness for maximum effect lies somewhere in between the two.

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† Present address: Tata Institute for Fundamental Research, Bombay, India.

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