Deriving the Ginzburg-Landau parameter from heat-capacity data on magnetic superconductors with Schottky anomalies

Nigel R. Leigh and Damian P. Hampshire
Department of Physics, University of Durham, South Road, Durham DH1 3LE, United Kingdom
(Received 15 May 2003; published 7 November 2003)

The specific heat of the Chevrel phase (CP) magnetic superconductors $(Sn_{0.65}Eu_{0.35})Mo_6S_8$ and $(Sn_{0.50}Eu_{0.50})Mo_6S_8$ have been measured in high magnetic fields. The Schottky contributions, including self-field and exchange terms, were calculated and then subtracted to improve determination of the Ginzburg-Landau parameter. Two approximate high-field specific-heat equations are presented which are used to find the free-ion ground state of these CP compounds and the doublet ground-state properties in some rare-earth high-temperature superconductors without advanced computation. The approximate equations allow simple calculation of the degeneracy and moments of the ground-state multiplet and the ordering temperature.

DOI: 10.1103/PhysRevB.68.174508 PACS number(s): 74.25.Ha, 74.70.Ad

I. INTRODUCTION

In Ginzburg's original paper in 1957 on ferromagnetic superconductors, he considered the possibility of superconductivity in gadolinium produced by outer conduction electrons coexisting with magnetism produced by the inner $4f$ electrons.[1] The relationship between superconductivity and magnetism has been a long-standing issue that has produced intensive research into a wide range of complex materials from those in which the electrons responsible for the magnetism become the superelectrons[2,3] to those where, even on the scale of the unit cell, the magnetic ordering is almost completely spatially separated from the superelectrons.[4] Susceptibility measurements are widely made to investigate the magnetic properties in the normal state and the Curie-Weiss law used to interpret the data and provide equivalent free-ion ground-state properties.[5] Magnetization measurements are often used to find the superconducting parameters.[6] Nevertheless, specific-heat measurements on magnetic superconductors are sometimes preferred to susceptibility and magnetic measurements because they can provide information about both the magnetic contribution and the superconducting state and are less susceptible to errors associated with granularity and surface or bulk flux pinning. We report here the results of specific-heat measurements in magnetic fields up to 15 T on Chevrel phase (CP) magnetic superconductors in the series $(Sn_{1-x}Eu_x)Mo_6S_8$. These materials show large Schottky magnetic contributions to the specific heat due to the Eu^{2+} ions. Two approximate equations are presented for interpreting specific-heat data that facilitate simple calculation of the degenerate ground-state properties (and the Curie temperature and Curie constant) without advanced computation. The magnetic contribution to the total heat capacity of the CP materials is calculated and subtracted so that the size and magnetic-field dependence of the superconducting specific-heat jump (Δc) at the superconducting-normal phase boundary can be accurately determined. The two independent parameters of the Ginzburg-Landau (GL) theory [i.e., the upper critical field (B_{c2}) and the Ginzburg-Landau parameter (κ)][7] are then obtained from Δc for a superconducting material coexisting with strong magnetism.

II. FABRICATION AND EXPERIMENTAL RESULTS

Chevrel phase superconductors (MMo_6X_8, where M is a metal atom and X a chalcogen) have a crystal structure that is almost isotropic, with the M ion lying in the center of a unit cell of comparatively large volume ($\sim$278 Å^3). This crystal structure ensures that the M ions are well separated from the conduction electrons and each other, consistent with electronic band-structure calculations.[4] It leads to magnetic ordering below 10 K, effective Bohr magneton values close to the free ion values and interesting properties such as the coexistence of magnetism and superconductivity at the unit-cell level. Samples of the series $(Sn_{1-x}Eu_x)Mo_6S_8$ with $x=0.00$, 0.35, and 0.50 were fabricated under argon at temperatures up to 1450 °C and sintered using a hot isostatic press operating at 800 °C and 2000 bars.[8] The specific heat of these samples was then measured from 3 to 30 K and in magnetic fields up to 15 T. Figure 1 shows the specific-heat data (c) for the two magnetic samples. Accurate determina-

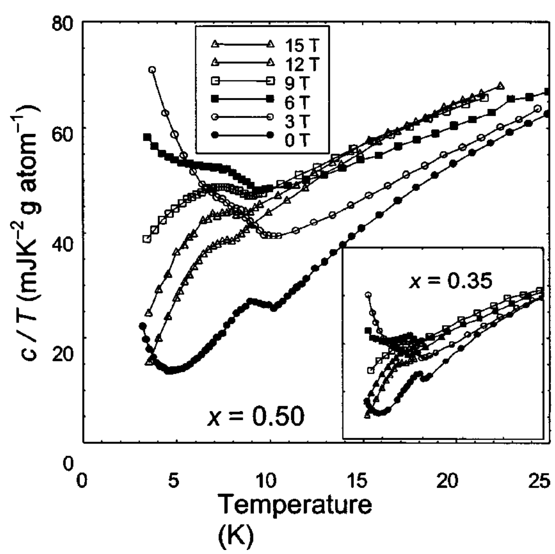

FIG. 1. c/T as a function of temperature and applied field for the Chevrel phase superconductor $(Sn_{0.50}Eu_{0.50})Mo_6S_8$. Inset: c/T as a function of temperature and applied field for $(Sn_{0.65}Eu_{0.35})Mo_6S_8$; the inset axes and symbols are the same as in the main figure.

tion of the size of the jump in the specific heat in high magnetic fields is not possible directly from the raw data because of the strong magnetic background.

III. ANALYSIS AND DISCUSSION

For an antiferromagnetic material with different moments on two sublattices A and B, the magnetization for sublattice A, M_A, is given in the mean-field approximation by

$$M_A = n_V g_J J \mu_B B_J(J, y_A), \tag{1}$$

where

$$y_A = g_J J \mu_B \mu_0 [H_{ext} + D(M_A + M_B) + \lambda M_B], \tag{2}$$

n_v is the density of magnetic ions on one sublattice, g_J is the Landé g factor, J is the total angular momentum quantum number, μ_B is the Bohr magneton, B_J is the Brillouin function, $\mu_0 H_{ext}$ is the externally applied field. In Eq. (2), both self-field and exchange terms are included using the factor D and the Weiss constant λ. In general, D is dependent on crystal structure. For example, if the structure includes dense columns of ions that are well separated or alternatively dense sheets of ions that are well separated, D will tend to be large and positive or large and negative, respectively. The classical Lorentz field gives $D = 1/3$. To simplify the analysis we have set $D = 1$. Equivalent expressions give the magnetization for sublattice B, M_B, by swapping the A and B indices. The ordering temperature is $T_M^A = -\lambda C/2$, where C is the Curie constant, given by $C = n_V g_J^2 J(J+1) \mu_B^2 \mu_0 / 3k_B$. For ferromagnetic materials, sublattices A and B are equivalent and the ordering temperature is $T_M^F = (1+\lambda)C$. Standard thermodynamic considerations show that the magnetic contribution to the specific heat c_m is given by

$$c_m(H_{ext}, T) = c_m(0,T) - \frac{T}{\rho} \frac{\partial^2}{\partial T^2} \left[-\int_0^{H_{ext}} \mu_0 M \, dH_{ext} \right]_T, \tag{3}$$

where ρ can be taken as either the mass or molar density.[9] Figure 2 shows the numerically calculated values of c_m as a function of temperature and applied field for the antiferromagnetic material $EuMo_6S_8$ with the Eu ions in the 2+ valence state and the parameters: $J = 3.5$, $g_J = 2.0$, $n_v = 3.64 \times 10^{27}\ m^{-3}$ and the ordering temperature T_M^A arbitrarily fixed to be 1.5 K. Above the ordering temperature, the magnitude of the Schottky anomaly increases and then saturates even up to very high magnetic fields.

Figure 3 shows the superconducting and magnetic contribution for $(Sn_{0.50}Eu_{0.50})Mo_6S_8$ as a function of both temperature and field, together with the calculated magnetic contribution (solid lines). The zero-field contribution $c(0,T)$ was obtained by extrapolating by eye the specific heat from the critical temperature (T_c) down to $T = 0$ K and then subtracted from the total specific heat. This extrapolation only affects the values of B_{c2} and κ obtained at the highest field measured. At all lower fields, the extrapolation is constrained in the region of the jump by measurements of the normal-state properties measured in higher fields (cf. Fig. 4). The

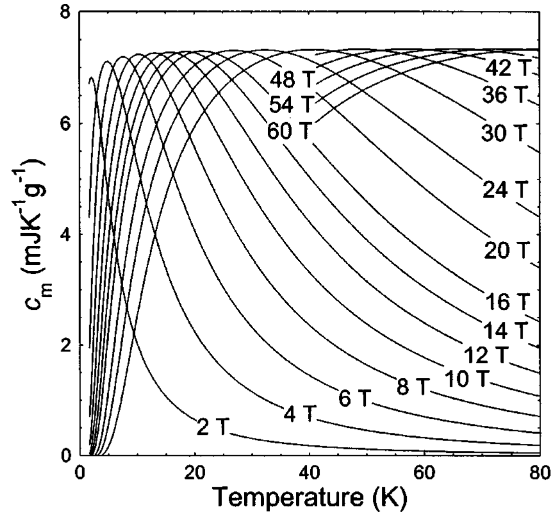

FIG. 2. c_m as a function of temperature and applied field, calculated for antiferromagnetic $EuMo_6S_8$ with $T_M^A = 1.5$ K, $J = 3.5$, $g_J = 2.0$, and $n_v = 3.64 \times 10^{27}\ m^{-3}$.

calculated values were obtained using the free ion values of J and g_J (i.e., 3.5 and 2, respectively), a value of n_v within 3% of the nominal composition (consistent with x-ray data showing almost single-phase material), and a value of $T_M^A = 0.35 \pm 0.5$ K. This value for the ordering temperature is consistent with the range 0.2–0.6 K for $EuMo_6S_8$ cited in the literature.[10] The agreement between calculations and experiment above ~10 K confirms that the Eu^{2+} ions are essentially free ions. Figure 4 shows the specific heat after the magnetic contribution has been subtracted for the $(Sn_{0.65}Eu_{0.35})Mo_6S_8$ and $(Sn_{0.50}Eu_{0.50})Mo_6S_8$ samples. Both samples show a field-independent specific heat above ~10 K, characteristic of nonmagnetic superconductors including $SnMo_6S_8$.[11] The size of the specific-heat jump (Δc)

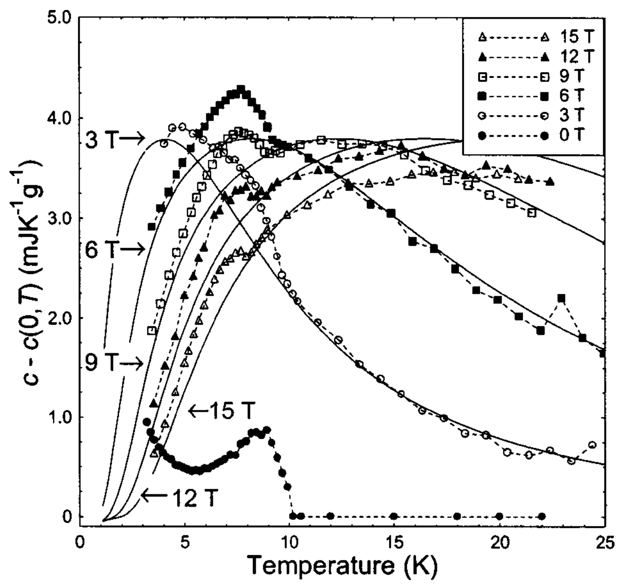

FIG. 3. $c - c(0,T)$ as a function of temperature and applied field for $(Sn_{0.50}Eu_{0.50})Mo_6S_8$; symbols are the experimental data and solid lines are the calculated values.

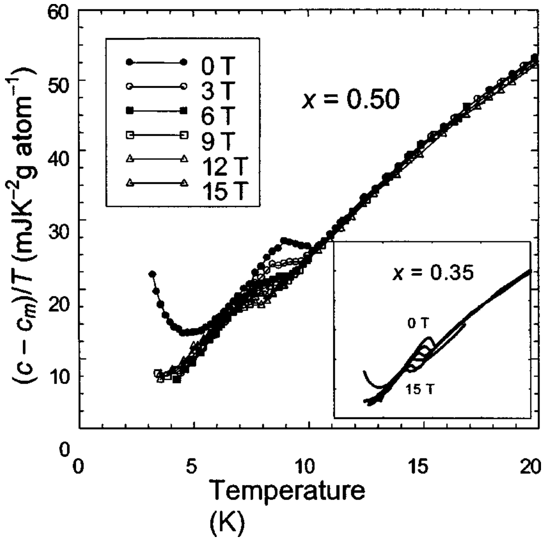

FIG. 4. $(c-c_m)/T$ as a function of temperature and applied field for $(Sn_{0.50}Eu_{0.50})Mo_6S_8$. Inset: $(c-c_m)/T$ as a function of temperature and applied field for $(Sn_{0.65}Eu_{0.35})Mo_6S_8$; the applied fields in the inset and the inset axes and are the same as in the main figure.

can be equated to the upper critical field (B_{c2}) and the Ginzburg-Landau parameter (κ) using[12]

$$\left.\frac{\Delta c}{T_c}\right|_B = \frac{\left(\frac{dB_{c2}}{dT}\right)^2}{1.16\mu_0[2\kappa^2(T)-1]}. \tag{4}$$

Using the data in Fig. 4, the specific-heat jump at each field is analyzed using a standard procedure that considers an idealized sharp jump that conserves entropy and from which Δc and B_{c2} are then obtained.[11] The temperature dependence of κ is then determined using Eq. (4) and the results are presented in Fig. 5 (including data obtained on $SnMo_6S_8$). The average values of $\kappa(T)$ and the normal-state resistivity increase systematically as the doping level is increased consistent with an expected increase in the conduction electron scattering rate. The marked improvement in analysis, achieved by accurate subtraction of the magnetic background, shows that κ increases as T decreases for both magnetic samples, which is similar to metallic superconductors.[13] The data also confirm the very high (technologically important) values of dB_{c2}/dT for these Eu-doped compounds (-6.1 T K^{-1} for $x=0.35$ and -5.5 T K^{-1} for $x=0.50$) that are both larger than the undoped sample (-3.9 T K^{-1}).

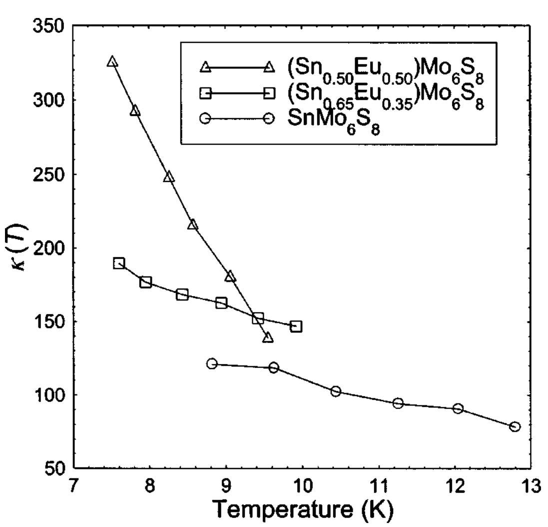

FIG. 5. κ as a function of temperature for $(Sn_{1-x}Eu_x)Mo_6S_8$ with $x=0.00$, 0.35, and 0.50.

The calculations of c_m are computationally demanding, particularly if the free parameters J, g_J, n_v, and T_M are completely unknown. For antiferromagnetic materials, simultaneous transcendental equations must be solved numerically at an accuracy sufficient to find the integrals and double derivatives in Eq. (3). We have compared the behavior of the Schottky anomalies predicted from the numerical solutions with the heat capacity that follows from a simple approximate form for the magnetization M given by

$$M = M_s \tanh\left(\frac{CH_{ext}}{M_s(T-\theta)}\right) = M_s \tanh\left(\frac{g_J(J+1)\mu_B\mu_0 H_{ext}}{3k_B(T-\theta)}\right), \tag{5}$$

where J now represents the degeneracy of the ground state, M_s the saturation magnetization (where $M_s = n_{cell} g_J \mu_B J$ and n_{cell} is the number of magnetic ions per unit cell), and θ is the Curie-Weiss constant (where $\theta = T_M^F$ in the ferromagnetic case and $\theta = C - T_M^A$ in the antiferromagnetic case). Above T_M the results from both the approximate form and those calculated using the full functional form for M (Fig. 2) have the same general features. At low fields, the magnitude of the peak of the anomaly either increases or decreases with increasing field for the antiferromagnetic or ferromagnetic case, respectively. Hence there is a significant difference from the standard analysis of Schottky anomalies that does not consider interacting ions, since this work provides a simple direct interpretation of the increase/decrease in the magnitude of the peak in the anomaly just above the ordering temperature. This intrinsic behavior for the Schottky anomaly above the ordering temperature is not found from simple partition function calculations that consider noninteracting ions. In high fields, a saturation in the peak value of the Schottky anomaly is found. From Eq. (5) analytic forms for the field-temperature dependence (i.e., $\mu_0 H_{ext}^{peak}$ vs T^{peak}) and for the saturation value (c_m^{sat}) of the peak can be calculated of the form

$$\mu_0 H_{ext}^{peak} = \frac{6.54}{g_J(J+1)}(T^{peak} - \theta), \tag{6}$$

$$c_m^{sat} = 1.12\frac{n_{cell}RJ}{(J+1)}, \tag{7}$$

where R is the molar gas constant. The prefactors, 6.54 and 1.12, were chosen to ensure that Eqs. (6) and (7) are consistent with the rigorous calculation for Eu^{2+} and should only be considered approximate across the rare-earth series. The equations can be used to calculate the Curie temperature and Curie constant of single-phase materials or the quantity of

TABLE I. Values of c_m^{sat} and $\partial(\mu_0 H_{ext})/\partial T_{peak}$ determined from the specific-heat data of Meulen *et al.* (Ref. 14) for 1-2-3 high-temperature superconductors. Values of J and $g_J(J+1)$ are estimated from these results using Eqs. (6) and (7). Shown in square brackets are the theoretical values of J and $g_J(J+1)$ for the free ions.

Material	c_m^{peak} ($J\,K^{-1}mole^{-1}$)	J	$\partial(\mu_0 H_{ext})/\partial T_{peak}$ ($T\,K^{-1}$)	$g_J(J+1)$
$ErBa_2Cu_3O_7$	3.5	0.6 [7.5]	0.6	10.9 [10.2]
$YbBa_2Cu_3O_7$	3.5	0.6 [3.5]	1.0	6.5 [5.1]
$DyBa_2Cu_3O_7$	2.5	0.4 [7.5]	0.4	16.4 [11.3]

second-phase materials of known magnetic properties without advanced computation. We have successfully used this approach to model the specific heat above 3 K of a $(Pb,Gd)Mo_6S_8$ superconductor ($T_M^A \leqslant 1$ K) with $\sim$6% Gd_2S_3 magnetic second phase ($T_M^A = 5.5$ K).[11]

We have analyzed the Schottky anomalies in the literature for the 1-2-3 high-temperature superconductors $YbBa_2Cu_3O_7$, $ErBa_2Cu_3O_7$, and $DyBa_2Cu_3O_7$ (Ref. 14) using Eqs. (6) and (7), and derived the values of $g_J(J+1)$ and J shown in Table I. The values of $g_J(J+1)$ are in reasonable agreement with free ion values. The magnitude of the peak value of the heat capacity at the Schottky anomaly for these materials increases with increasing field (above the ordering temperature) indicating antiferromagnetic ordering at low temperatures. The calculated values of J are all close to 0.5, indicative of the ground state of the rare-earth ions in these compounds being a doublet state. These observations are consistent with neutron-diffraction measurements on $ErBa_2Cu_3O_7$ that show a two-dimensional antiferromagnetic doublet ground state.[14]

IV. CONCLUSION

We conclude that the ground-state properties of a magnetic system can be deduced from specific-heat data using the two approximate equations provided [Eqs. (6) and (7)] and that the increasing or decreasing magnitude of the Schottky anomaly above the ordering temperature used to indicate antiferromagnetic or ferromagnetic ordering, respectively. Hence the magnetic contribution can be calculated for both single and multiphase compounds, which is necessary for accurately determining B_{c2} and κ in strongly magnetic superconductors.

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