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Critical-magnetic-field curve of lanthanum sesquicarbide

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The critical-magnetic-field curve of lanthanum sesquicarbide has been measured. The initial slope was extracted from these data and used, along with measured values of the upper and lower critical fields, to obtain the electronic coefficient of specific heat and the Ginzburg-Landau κ value. Experimental evidence indicates the absence of paramagnetic limitation. Values for the electron-phonon coupling constant and the band-structure density of states were also obtained after estimating the Debye temperature for this material.

I. INTRODUCTION

Lanthanum sesquicarbide belongs to the $D5_c$ crystal structure type as typified by Pu_2C_3. This is one of three structure types that favor high-temperature superconductivity, the other two being the $A15$ and $B1$ structures. Of these, the $D5_c$ sesquicarbides have been studied the least, probably because they are difficult to prepare and decompose rapidly in the presence of water vapor (air). While lanthanum sesquicarbide may be readily prepared with the $D5_c$ structure by arc melting, others such as yttrium-thorium sesquicarbide must be subsequently subjected simultaneously to high-pressure (10–20 kbar) and high-temperature (1200–1500°C) conditions to achieve the same structure.

The occurrence of superconductivity in the sesquicarbide and the variation of the zero-field transition temperature T_0 as a function of composition and preparation technique were first reported by scientists at Los Alamos Scientific Laboratory in 1969.[1–5] However, very little work has been reported with regards to measuring other superconducting parameters, such as critical magnetic fields, critical currents, etc., even though transition temperatures of the sesquicarbides compare favorably with those of other high-T_0 materials. Consequently, it was decided to examine the critical-magnetic-field curves of the sesquicarbides. These measurements permitted an estimation of the electronic coefficient of specific heat γ, and the Ginzburg-Landau κ value. Lanthanum sesquicarbide was selected for this initial study because the sesquicarbide phase is readily formed by arc melting the elements in an inert atmosphere.

II. SPECIMEN PREPARATION

Lanthanum sesquicarbide specimens were prepared using cleaned and weighed lanthanum metal ingots (99+%), and appropriate quantities of spectroscopic-grade graphite in a glove box freshly backfilled with titanium-gettered argon. The components were arc melted on a water-cooled hearth of the Reed design,[6] using a hand torch with flowing gettered argon. The buttons were repeatedly arc melted and inverted no less than six times after the disappearance of all graphite. Without exposure to air, the samples were embedded in Apiezon type-*N* grease, and sealed into a glass tube containing helium gas until measurements were performed.

Compounds with four nominal starting compositions were made in order to study the variation of superconducting parameters with composition. Two compositions, $LaC_{1.3}$ and $LaC_{1.6}$, were prepared individually, and two, $LaC_{1.4}$ and $LaC_{1.5}$, were prepared by mixing proper amounts of the initial compositions. Although Giorgi *et al.*[1] saw a variation in T_0 from 6.0 K for $LaC_{1.29}$ to 9.9 K for $LaC_{1.56}$, with a maximum of 11.0 K occurring for $LaC_{1.41}$, our samples showed no such variation. Rather, they all had transition temperatures of approximately 11.0 K, and the variations were less than 0.2 K. The simplest explanation seems to be that, in our method of preparation, the high-temperature composition is always present regardless of the starting composition. This hypothesis is compatible with the data, since the zero-field transitions were rather wide; 90% of the superconducting-to-normal transition occurred over a temperature span of 1.5 K, and the remaining 10% occurred in a tail which extended 3–4 K below the main transition. An attempt was made to determine the composition from lattice-parameter measurements, but this was unsuccessful because the diffuse nature of the x-ray diffraction pattern made it virtually impossible to extract accurate lattice parameters. Consequently, for the remainder of this paper, when lathanum sesquicarbide (or La_2C_3) is written, it refers to the high-transition-temperature composition ($T_0 = 11.0$ K).

The handling of these particular specimens was less difficult than first imagined, since it was found that the Apiezon N grease in which the samples were initially embedded also coated the samples, and ensured their preservation. Those samples which were coated with grease and left exposed on a laboratory table were found to remain intact for several months, while those which had the protective grease wiped off deteriorated with the characteristic carbide odor to a pile of dust in a matter of days.

III. EXPERIMENTAL TECHNIQUE

Measurements of the magnetic moment as a function of field showed the samples to be highly hysteretic type-II superconductors with large κ values. To improve the accuracy of these determinations, dc magnetization measurements were abandoned in favor of ac susceptibility measurements. The latter were carried out using a mutual inductance bridge at low frequencies (33–500 Hz) with a 1-G peak-to-peak amplitude driving field. This technique provides an accurate and sensitive method of determining H_{c2} in high-κ materials with irregular surface geometries.

Susceptibility measurements were made by balancing the bridge while the specimen was superconducting. Changes in the susceptibility of the specimen induced either by temperature or magnetic field variations produced an off-balance signal which was detected by a two-phase lock-in amplifier. In this way, both inductive and loss components were recorded. The criterion used to determine the superconducting transition temperature was the extrapolated onset of superconductivity, as shown in Figs. 1 and 2.

Slightly different experimental configurations

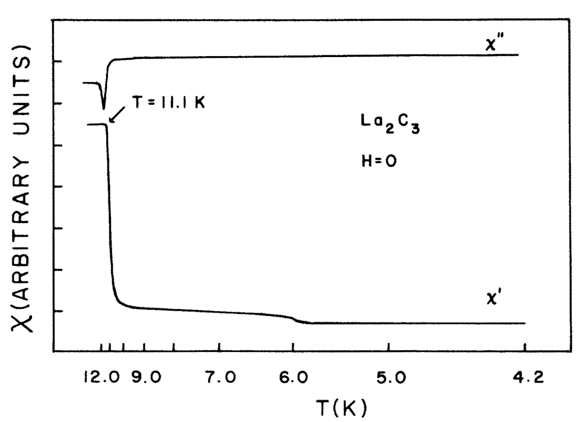

FIG. 1. Typical recorder trace of ac susceptibility (arbitrary units) versus temperature at constant field, showing both inductive χ' and resistive χ'' components. The inductive component reveals the presence of a second phase at 6.0 K. The arrow denotes the extrapolated onset of superconductivity.

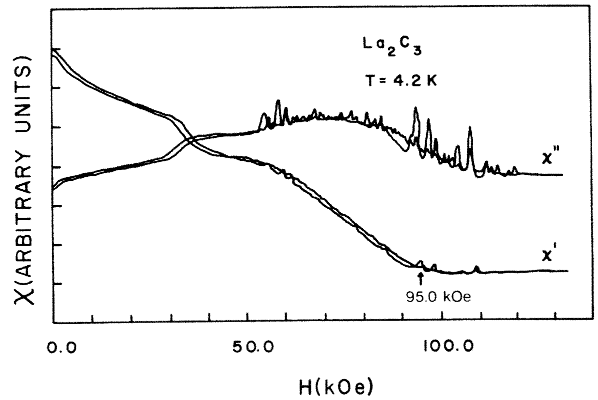

FIG. 2. Typical recorder trace of ac susceptibility (arbitrary units) versus field at constant temperature, showing both inductive χ' and resistive χ'' components. The arrow denotes the extrapolated onset of superconductivity. This curve was taken for both increasing and decreasing fields. The presence of noise reflects the higher gain settings used for the resistive component.

were employed for these susceptibility measurements, depending upon whether the experiment was performed above or below helium temperature.

At temperatures above 4.2 K, the sample was enclosed in a vacuum can with a heater. Constant magnetic fields were applied by a superconducting solenoid, while susceptibility was measured as a function of temperature. The temperature was measured by a germanium resistor which was later corrected for magneto resistance characteristics, as described by Neuringer *et al.*[7] A typical trace is shown in Fig. 1. Below 4.2 K, the sample was directly immersed in liquid helium, and temperature was held constant while susceptibility was measured as a function of applied field. High fields above 70 kOe used in this study were supplied by an NRL Bitter-type solenoid.

IV. RESULTS AND DISCUSSION

A. Determination of upper and lower critical fields

Measurements of the upper and lower critical fields were made by means of an ac susceptibility technique, as described in Sec. III. A typical trace of the susceptibility χ vs externally applied magnetic field H is shown in Fig. 2. The upper critical field H_{cu} was defined as that point where the susceptibility completely returned to its normal-state value.

Specimens measured in swept dc fields by ac techniques can show superconductivity above H_{c2} if the sweep rate of the dc field is less than the frequency of the ac measuring field.[8] Consequently, it was necessary to determine whether the upper critical field H_{cu} was the bulk critical field

H_{c2}, or the critical field of a superconducting surface sheath H_{c3}. In order to answer this question, some high-quality V_3Ga specimens in the form of right circular cylinders were measured in the same experimental configuration used to measure the lanthanum sesquicarbide. Measurements of χ vs H were made both before and after coating with a layer of nickel, which would suppress surface superconductivity. For this experiment, the layer of nickel was 10 μm thick. We saw no difference in the transitions, and thus concluded that there was no observable surface sheath superconductivity in this specimen.

If surface superconductivity were present, it would be more readily apparent in the V_3Ga test sample than in our La_2C_3 sample because of its more regular shape and smoother almost mirror-like surface. The lanthanum sesquicarbide sample, on the other hand, was broken into several irregularly shaped fragments with sharp edges, which would tend to suppress a surface sheath. In addition, the surfaces of the sesquicarbide were of a gritty almost granular appearance and exhibited a rapid surface deterioration which has been a problem in the ESCA studies.[9] Consequently, we identify H_{cu} as the bulk upper critical field H_{c2}.

The lower critical field H_{c1} was estimated for the lanthanum sesquicarbide sample by measuring the field where flux first began to penetrate the specimen.[10] After suitable correction for demagnetization factors,[11] the value of H_{c1} was 22 ± 4 Oe, where the error limits are imposed by the difficulty in selecting the precise point where the flux began to penetrate the sample.

B. Positive curvature of critical-field curve

The results of the critical-magnetic-field determinations are shown in Fig. 3. The horizontal bars indicate an uncertainty in temperature because of uncertainty in the magnetoresistance corrections applied to the germanium thermometer. Our measurements show that the critical-magnetic-field curve of lanthanum sesquicarbide exhibits an unusual positive curvature extending to fields as high as 20 kOe. This positive curvature has been observed in other materials, but to a lesser extent.[12] In our earlier work,[9] we did not fully appreciate the extent of this tail and consequently arrived at values for the initial slope of the critical-field curve which were almost eight times lower than the value reported here. The simplest explanation for this region of positive curvature is that although great care was exercised in sample preparation, compositional variations existed in the bulk of the material. The crossing at lower fields of different critical-field

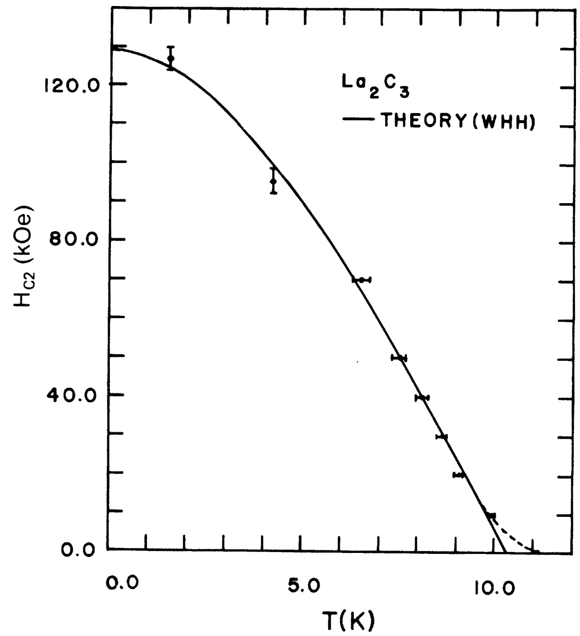

FIG. 3. Critical-magnetic-field curve of lanthanum sesquicarbide. The positive curvature portion of this curve at low fields (dashed portion of curve) is well documented (see Ref. 9). The smooth line is a theoretical curve.

curves corresponding to different compositions within the sample would produce a tail. This is reasonable in view of the very broad measured transitions, which in some instances clearly indicate the presence of a second phase. A point that bears repeating is that extreme caution must be exercised when interpreting critical-magnetic-field data near T_0, since meaningful parameters extracted by analysis can only be obtained from data which does not fall within this tail region.

In order to make a comparison with theory, we need values of the initial slope of the critical-field curve and the transition temperature at zero field. Owing to the curvature in the low-field portion of the critical-magnetic-field curve, we have analyzed the data as follows. It was found that good agreement with theory could be obtained by extrapolating the linear portion of the critical-field curve above 20 kOe back toward the temperature axis. The point where this line intersects the temperature axis we call the extrapolated zero-field transition temperature T_0^*, and the slope of this extrapolated line, the initial slope of the critical-field curve $dH_{c2}/dT|_{T=T_0^*}$. (Here we reserve T_0 for the measured zero field transition temperature.) When this procedure was carried out, the following values were obtained: $T_0^* = 10.4$ K, and $dH_{c2}/dT|_{T=T_0^*} = 1.8 \times 10^4$ Oe/K.

C. Absence of paramagnetic limitation

In very high magnetic fields, Pauli paramagnetism becomes an important consideration in determining the value of H_{c2}. It was recognized independently by Clogston[13] and Chandrasekhar[14] that since conduction electrons in a metal give rise to a paramagnetic susceptibility, a magnetic field would result in a lowering of the free energy of the normal state towards the lower free energy of the superconducting state. Consequently, the transition from the superconducting to the normal state would occur at a lower field value than if the paramagnetic contribution did not exist. Werthamer, Helfand, and Hohenberg[15] (WHH) describe this situation in terms of two parameters, α, the paramagnetic limitation parameter, and λ_{so}, a spin-orbit scattering parameter which tends to reduce the effects of Pauli paramagnetism. α may be obtained from the value of the initial slope of the critical-magnetic-field curve through use of the following equation[15]:

$$\alpha = 5.28 \times 10^{-5} \left.\frac{-dH_{c2}}{dT}\right|_{T=T_0^*} , \tag{1}$$

where the slope is given in Oe/K. Values for λ_{so} were obtained from published curves[16] which were generated by computer solution of the equation by WHH[15] for the critical-magnetic-field curve.

The data of Fig. 3 may be replotted in terms of reduced variables for comparison with WHH by use of the following definitions:

$$t = T/T_0^* , \tag{2}$$

$$h^* = H_{c2}\left(T_0^* \left.\frac{-dH_{c2}}{dT}\right|_{T=T_0^*}\right)^{-1} . \tag{3}$$

Replotted data are shown in Fig. 4, along with the theoretical curve for $\alpha = 0.95$ and $\lambda_{so} \geqslant 16$. The actual values of α and λ_{so} are of less importance than the fact that the data show no indication of paramagnetic limitation, since this would have significantly depressed the high-field portion of the curve.

D. Electronic coefficient of specific heat

Our data for the initial slope of the critical-field curve of lanthanum sesquicarbide allows us to calculate other parameters of this material which are of interest. If we combine the BCS[17] expression,

$$\left.\left(\frac{dH_c}{dT}\right)^2\right|_{T=T_0^*} = 19.4\gamma_v , \tag{4}$$

where T_0^* has been substituted for T_0, with

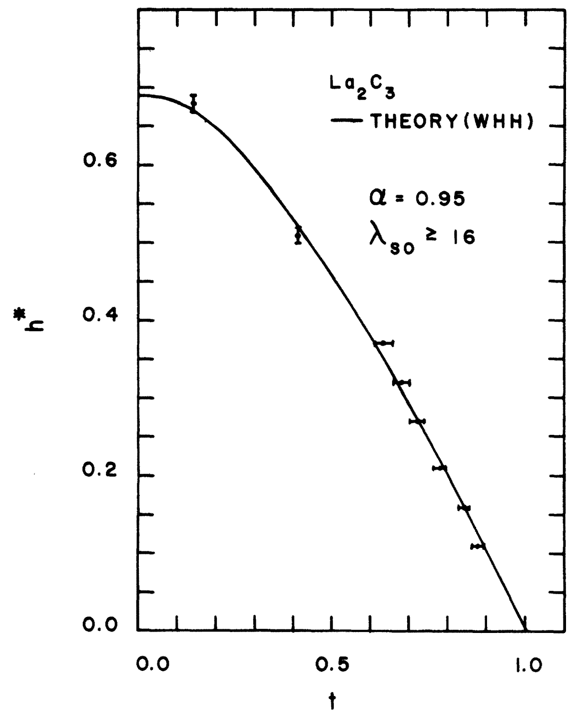

FIG. 4. Critical-magnetic-field curve of lanthanum sesquicarbide normalized according to Ref. 15.

$$H_{c2} = \sqrt{2}\,\kappa H_c , \tag{5}$$

we obtain the following expression for the electronic coefficient of specific heat γ_v:

$$\gamma_v = \frac{1}{38.8\kappa^2}\left.\left(\frac{dH_{c2}}{dT}\right)^2\right|_{T=T_0^*} . \tag{6}$$

The value of κ was obtained from the determination of H_{c1} and H_{c2} at 4.2 K as follows. From the two equations[18]

$$H_{c1}(t) = \frac{\ln\kappa_3(t)}{\sqrt{2}\,\kappa_3(t)} H_c(t) \tag{7}$$

and

$$H_{c2}(t) = \sqrt{2}\,\kappa_1(t) H_c(t) , \tag{8}$$

we may obtain

$$\frac{H_{c1}(t)}{H_{c2}(t)} = \frac{\ln\kappa_3(t)}{2\kappa_1(t)\kappa_3(t)} , \tag{9}$$

where $t = T/T_0^*$. In the dirty limit ($l \ll \xi_0$), $\kappa_3 = 1.31\kappa$ and $\kappa_1 = 1.11\kappa$. Equation (9) then becomes

$$\frac{H_{c1}}{H_{c2}} = \frac{\ln(1.31\kappa)}{2.91\kappa^2} . \tag{10}$$

The solution of (10) gives a value of $\kappa = 84 \pm 9$. The initial slope of the critical-magnetic-field curve has already been discussed in Sec. IV B and found to be -1.8×10^4 Oe/K. Substituting these values

TABLE I. Material parameters of lanthanum sesquicarbide.

T_0	11.1 K
T_0^*	10.4 K
$\left.\frac{dH_{c2}}{dT}\right\|_{T=T_0^*}$	-1.8×10^4 Oe/K
α	0.95
λ_{so}	≥ 16
$H_{c1}(4.2\text{ K})$	22 ± 4 Oe
$H_{c2}(4.2\text{ K})$	95 kOe
κ	84 ± 9
γ_v	1190 ± 260 erg $\text{K}^{-2}\,\text{cm}^{-3}$
V_m	51.47 $\text{cm}^3\,\text{mole}^{-1}$
γ_m	6.10 ± 1.3 mJ $\text{mole}^{-1}\,\text{K}^{-2}$
Θ_D	300 K [a]
μ^*	0.13 [a]
λ	0.84
$N_{bs}(0)$	0.70 ± 0.16

[a] Values estimated from similar T_0 materials.

into Eq. (6), we find γ_v to be 1190 ± 260 ergK^{-2} cm^{-3}.

E. Estimate of other superconducting parameters

McMillan[19] derived a general equation for the superconducting transition temperature,

$$T_c = \frac{\Theta_D}{1.45}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right] . \qquad (11)$$

In Eq. (11), Θ_D is the Debye temperature, T_c is the transition temperature, μ^* is the Coulomb coupling constant, and λ is the electron-phonon coupling constant. By making use of this equation along with some reasonable estimates for Θ_D and μ^*, it is possible to obtain an empirical value of the electron-phonon coupling constant λ. For the transition temperature T_c we use our value of T_0^*, namely, 10.4 K; for Θ_D and μ^* we select 300 K and 0.13 as being typical of superconductors with this transition temperature. Using these parameters, a value of $\lambda=0.84$ is obtained. The band-structure density of states at the Fermi energy can now be calculated through the use of

$$N_{bs}(0) = 3\gamma_m(1+\lambda)^{-1}/2\pi^2K_B^2 , \qquad (12)$$

where K_B is Boltzmann's constant and γ_m is the molar electronic specific-heat coefficient.[19] If we express γ_m in units of mJ mole^{-1}, Eq. (10) reduces in our case to

$$N_{bs}(0) = 0.212\gamma_m/(1+\lambda) , \qquad (13)$$

where $N_{bs}(0)$ is in units of states/eV atom. The molar volume V_m of La_2C_3 is calculated from the lattice parameter $a=8.8095$ Å published by Giorgi *et al.*[1] These values are also listed in Table I.

In conclusion, we have measured the critical-magnetic-field curve of lanthanum sesquicarbide. These measurements indicate an absence of paramagnetic limitation at high fields and a positive curvature at low fields. In order to obtain values of the zero-field transition temperature and initial slope that were consistent with the remainder of the critical-magnetic-field curve, it was necessary to ignore the low-field portion in favor of a linear extrapolation of the intermediate portion of the curve. Subsequently, we were able to extract values of the electronic coefficient of specific heat and, by applying the McMillan equation, values for the electron-phonon coupling constant and the band structure density of states. Specific-heat measurements on this material would be useful to provide an accurate determination of the Debye temperature and to corroborate our measured value of the electronic coefficient of specific heat.

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