Specific Heat of an Icosahedral Superconductor, $Mg_3Zn_3Al_2$

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Specific-heat measurements are reported for cubic (c), icosahedral (i), and amorphous (a) phases of $Mg_3Zn_3Al_2$ in the temperature range 0.04–5 K. All three phases are superconducting, with $T_c = 0.32$, 0.41, and 0.75 K, respectively. The electronic density of states $N(0)$ is comparable to that expected in the free-electron model for all three phases. Compared to the c phase, significant lattice softening is observed in the i phase and, especially, in the a phase, indicating an increase in the electron-phonon coupling parameter λ with decreasing order.

Solids with icosahedral point-group symmetry have attracted much attention since their discovery several years ago.[1] A great deal of effort has been aimed at understanding the structure and its stability. As the sample quality improves, other properties are being investigated with probes such as electrical[2] and thermal[3] resistivity, magnetization,[4] NMR,[5] Mössbauer effect,[6] extended x-ray-absorption fine structure,[7] and electron-energy-loss spectroscopy.[8] So far, no thermodynamic measurements have appeared.[9]

In this Letter, we present measurements of the specific heat of Frank-Kasper cubic[10] (c) icosahedral[11] (i), and amorphous (a) phases of $Mg_3Zn_3Al_2$. This system is particularly interesting for a number of reasons. First, it contains no transition elements, which distinguishes it from most icosahedral systems investigated previously. Without the complication of magnetic effects, it should be possible to study the influence of icosahedral symmetry on electron and phonon properties. Second, high-quality, single-phase samples of icosahedral[12] as well as crystalline $Mg_3Zn_3Al_2$ are available. Third, we have found that the material is superconducting in all three phases, and this allows us to determine not only the electron and phonon densities of states but also the electron-phonon interaction strength and its dependence on structure. The results show that the superconducting state in the icosahedral phase is remarkably similar to that in the cubic phase,[13] which is a well-behaved, weakly coupled BCS superconductor. In all respects the specific-heat results show that the i-phase properties lie between the c phase and a phase but much closer to the c phase. This is in contrast to other measurements cited above, in which the icosahedral phase generally resembles much more closely the amorphous phase. The linear term in the specific heat above T_c does not show an anomalously high density of electronic states, as has been predicted by two calculations.[14] It is close to the free-electron value, supporting a more recent calculation.[15] Also, an upper limit can be placed on any linear contribution below T_c that might be due to, for instance, structural defects associated with lines of disclinations.[16]

The cubic, Frank-Kasper phase was prepared by us by melting in a closed quartz tube and cooling slowly. From the same boule, the icosahedral phase was prepared in the form of a 0.8-mm × 15-μm ribbon by spin quenching in an inert atmosphere. Both were single phase according to x-ray studies. The grain size was ~1 μm in the i phase and ~10 μm in the c phase. The amorphous sample was sputtered in Ar from a $Mg_3Zn_3Al_2$ target onto Al_2O_3 substrates held at 77 K. The low substrate temperature and a low sputtering power (1 W for 80 h) were necessary to prevent formation of microcrystalline peaks in the x-ray diffraction pattern. Calorimetric detection of ortho-para conversion of molecular hydrogen in the sample at low temperatures[17] showed the presence of 0.4 at.% clustered H_2. The H_2 is undoubtedly located in microvoids and is thought to have no significant effect on the properties measured here.

Standard four-probe resistivity measurements were performed on the as-prepared samples from 0.015–300 K. The specific heat was measured with a relaxation calorimeter described previously.[17] The c-phase sample, 650 mg, was placed on the Al_2O_3 plate of the calorimeter with ~1 mg Apiezon N grease for thermal contact. The i-phase sample, 82 mg, was gently broken and mixed with 22 mg N grease for thermal contact. The same procedure was used for the 80-mg a-phase sample after scraping the 25-μm-thick film from the substrate.

The specific-heat data for the three phases are shown in Figs. 1–3, after subtraction of the heat capacity of the addenda (grease plus empty). Each material shows a jump in the specific heat at approximately (see below) the temperature at which the resistance goes to zero (Table I) followed at lower temperatures by a steep, roughly exponential decrease. This indicates that the superconductivity is indeed a bulk effect. The transition is considerably broader for the sputtered sample than for the c- or i-phase samples. The scatter in the data is least for the large, solid crystalline sample and greatest for the 80-mg a-phase sample. This is due to the small sample size and also to the fact that thermal equilibrium of the
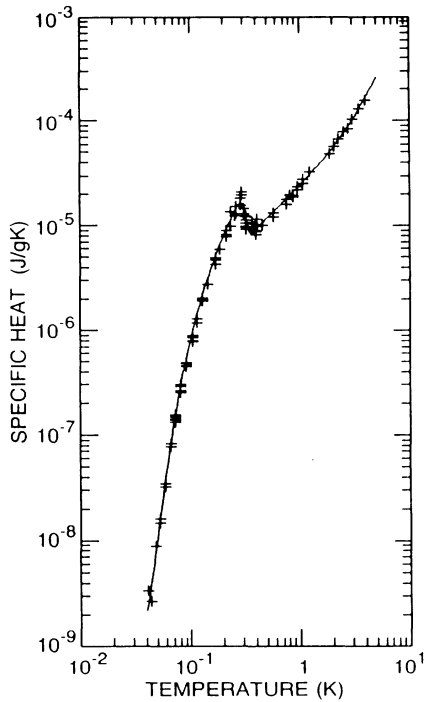
FIG. 1. Specific heat of cubic (Frank-Kasper) Mg₃Zn₃Al₂.

sample and calorimeter is more difficult to achieve with both powder-grease samples, complicating the data reduction.

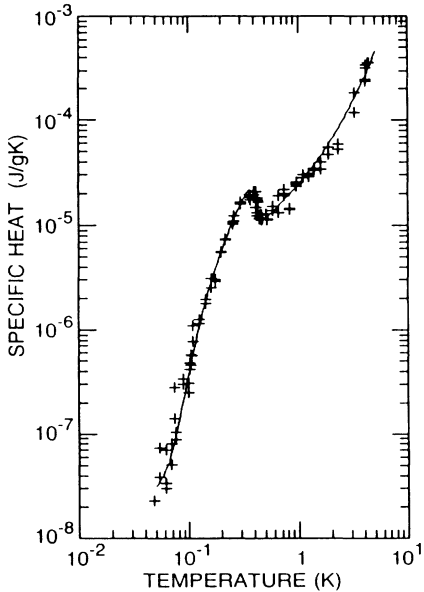To analyze the data, we assume that the specific heat in the normal state is the sum of an electronic linear con-
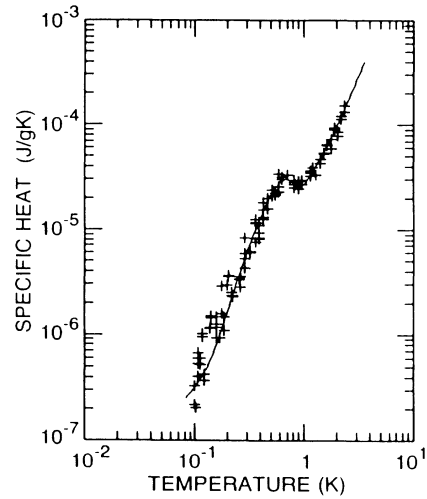

FIG. 2. Specific heat of icosahedral Mg₃Zn₃Al₂.

FIG. 3. Specific heat of amorphous Mg₃Zn₃Al₂.

tribution and a cubic term due to phonons,

$$C_n = \gamma T + \beta T^3, \tag{1}$$

and that below T_c it contains three contributions,

$$C_s = \alpha T + \beta T^3 + \eta \exp(-1.764 T_c/T) R(T/T_c). \tag{2}$$

The same phonon term appears below T_c, but the electronic contribution falls approximately exponentially as a result of the gap associated with superconductivity. $R(T/T_c)$ is the ratio of the Mühlschlegel numerical calculation,[18] based on the BCS theory, to the exponential

TABLE I. Numerical results for resistivity ρ, specific-heat fitting parameters γ, β, α, η, T_c, and ΔT_c in Eqs. (1) and (2), the electronic specific-heat ratio C_{es}/C_{en} at T_c, and derived quantities Θ_D (Debye temperature), v (sound velocity), λ (electron-phonon coupling parameter), and $N(0)$ (unrenormalized density of electronic state). $N(0)$ is in units of states/eV atom.

	Cubic	Icosahedral	Amorphous
$\rho_{300\,K}$ ($\mu\Omega$ cm)	90	79	380
$\rho_{4.2\,K}$	71	77	400
T_c(resistivity) (K)	0.330	0.442	1.25
ΔT_c(resistivity)	0.015	0.020	0.15
γ (10^{-5} J/g K²)	2.3 ± 0.2	2.2 ± 0.3	1.9 ± 0.3
β (10^{-6} J/g K⁴)	1.12 ± 0.04	2.75 ± 0.3	7.5 ± 0.6
α (10^{-5} J/g K²)	0.003	0.06	0.3
η (10^{-5} J/g K)	0.86 ± 0.15	1.20 ± 0.2	1.8 ± 0.4
T_c(specific heat) (K)	0.315 ± 0.01	0.410 ± 0.01	0.754 ± 0.03
ΔT_c(specific heat) (K)	0.026	0.050	0.18
$C_{es}/C_{en}(T_c)$	2.9 ± 0.6	3.0 ± 0.8	3.1 ± 0.8
Θ_D (K)	348	258	185
v (10^5 cm/sec)	3.10	2.28	1.6
λ	0.36	0.39	0.45
$N(0)$	0.15	0.14	0.11

in Eq. (2). $R(T/T_c)$ is a slowly varying function with values between 14 and 100 for our range of temperatures and is expressed as a power series for computational convenience. To account for the width of the transition, the sample is assumed to be inhomogeneous with different volumes of the sample having different values of T_c. The distribution of effective transition temperatures T_c' is chosen to be Gaussian, so that the specific heat contributed by a portion of the sample with T_c' is weighted by the volume factor $\exp\{[-(T_c'-T_c)/\Delta T_c]^2\}$ suitably normalized. The total specific heat is obtained by our summing the contributions over a range $T_c - 2\Delta T_c < T_c' < T_c + 2\Delta T_c$. A nonlinear least-squares-fitting routine is then used to determine the six parameters: γ, β, α, η, T_c, and ΔT_c. The results are given in Table I and they describe the solid lines in Figs. 1–3.

It is interesting to compare the parameters in order of decreasing structural order, c to i to a. T_c increases monotonically through the series, with an especially large jump between the i and a phases. This trend cannot be attributed to the electron density of states (proportional to γ), since γ only *decreases* in the series. However, a dramatic softening is indicated by β, which increases by a factor of 7 from c to a; the corresponding Debye temperature Θ_D and the average sound velocity v (Table I) both decrease by a factor of 1.9. According to McMillan's equation,[19] such a change results in an increasing value of the electron-phonon coupling parameter λ, determined by Θ_D, T_c, and the electron Coulomb repulsion parameter μ^* which we set equal to the typical value of 1.2 for polyvalent metals.[19] The values deduced for λ (Table I) span a range which includes the value for both Al and Zn ($\lambda = 0.38$), indicating that all three phases are in the weak-coupling limit. This is consistent with the low values of $T_c/\Theta_D \ll 1$. The jump in the electronic heat capacity at the transition is expected to be $C_{es}/C_{en} = 2.43$ in the BCS model. Within the uncertainties, the measured quantity C_{es}/C_{en} ($=2.43\eta/\gamma T_c$) agrees with the theoretical value.

The values of γ and λ can be used to calculate $N(0)$, the electronic density of states without phonon enhancement,[19]

$$N(0) = 3\gamma/2\pi^2 k_B^2(1+\lambda), \tag{3}$$

where γ is expressed in molar units by the taking of an average molar weight of 40.4 g. The values of $N(0)$ listed in Table I are typical for polyvalent metals and are close to the free-electron-model value[19] of $3/4(Z/E_F) \approx 0.18$, where Z and E_F are the valence and Fermi energy averaged over the three elements. This similarity conflicts with the predictions[14] of an anomalously high $N(0)$, but supports a more recent calculation.[15]

The electrical resistivities of the c and i phases are similar and correspond to a mean free path of ∼8 Å in the free-electron model. This represents a lower limit for the intrinsic mean free path, as the conductivity may be limited by scattering at grain boundaries and microcracks in these very brittle materials. The resistivity of the i phase of $Mg_3Zn_3Al_2$ is considerably lower than typical icosahedral systems involving transition elements. Resistivity data are well known to be difficult to interpret unambiguously, but the low resistivity of the present i phase supports the suggestion[20] that s-d scattering dominates the resistivity in icosahedral systems containing transition elements. The resistivity in the amorphous sample, however, is much higher than in the c or i phases; it is typical of other amorphous metals where the conductivity is limited by extremely short intrinsic mean free paths. The value of T_c determined via resistivity (Table I) is generally near the upper end of the range defined by ΔT_c from the specific heat. This is consistent with a percolation path of superconductivity in an inhomogeneous sample and demonstrates the problems inherent in attempting to determine T_c from resistance measurements alone.

The linear term αT included for $T < T_c$ is not suggested clearly by the data but is included to set a conservative upper limit to any contribution from a volume of normal metal or a linear term because of a constant density of glasslike defect states. The fractional volume of normal metal is limited by α in Table I to 0.1% of the c phase, 3% of the i phase, and 15% of the a phase. Alternatively interpreting α in terms of defect states, which in the metallic glass $Zr_{70}Pd_{30}$ contribute $\alpha_0 T = 1.1 \times 10^{-6}$ J/gK to the specific heat,[21] we can place upper limits of $0.03\alpha_0$ for the c phase, $0.5\alpha_0$ for the i phase, and $3\alpha_0$ for the a phase. The result for the i phase is particularly significant as it places an upper limit on any future proposals of structural defect states in this icosahedral material.[22] The large α for the a phase is not due to the trapped H_2, since such a large contribution does not appear for similarly trapped H_2 in plasma-deposited films[17] of a-Si:H. It is more likely due to a non-Gaussian distribution of T_c.

We conclude that icosahedral $Mg_3Zn_3Al_2$ is a well-behaved, weakly coupled superconductor with an electron density of states close to the free-electron model and a Debye temperature which is close to that of the cubic phase. In all respects it falls closer to the crystalline Frank-Kasper phase than to the amorphous phase. This is in contrast to other measurements on icosahedral systems, most of which are sensitive to point properties. The difference may be due to the higher degree of icosahedral perfection of the present samples.

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