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Specific heat of $Mg(B_{1-x}C_x)_2$, $x = 0.05$, 0.1

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ABSTRACT

We report measurements of the specific heat of two samples of carbon-doped MgB_2, $Mg(B_{1-x}C_x)_2$, $x = 0.05$ and 0.1, in magnetic fields to $\mu_0 H = 9$ T and at temperatures from ~1 K to somewhat above the critical temperature for superconductivity for each sample. The carbon doping reduced the critical temperature from 39 K for MgB_2 to 31.4 K and 19.7 K for the $x = 0.05$ and 0.1 samples, respectively. The results give the electron–phonon coupling and the electron density of states, including the individual contributions of the π and σ bands. These quantities are compared with theoretical calculations. The results also give the energy gaps on the π and σ bands, which are compared with other experimental determinations, and also with theoretical calculations that include predictions of the "merging" of the two gaps as a consequence of the band filling and increased interband scattering associated with doping.

1. Introduction

The initial interest in the discovery of superconductivity in MgB_2 [1] was focused on the remarkably high critical temperature, $T_c \sim 39$ K, which seemed to be inconsistent with the BCS phonon-mediated electron pairing, Although calculations soon showed that the BCS mechanism did account for the high T_c, the superconductivity is still of special interest for another reason: MgB_2 is an example of multi-band, multi-gap superconductivity, *with substantially different energy gaps on different sheets of the Fermi surface*. The possibility of multi-band superconductivity had been recognized theoretically much earlier [2,3], and general relations for the thermodynamic properties, including relations between the gaps and details of the specific heat, had been derived [4]. However, MgB_2 was the first example in which the thermodynamic properties clearly show the presence of significantly different energy gaps on the different electron bands. The difference in the gaps makes possible the experimental separation of the contributions of the different bands to the thermodynamic properties. Specific-heat measurements [5,6] gave the first experimental evidence of two gaps, and their analysis with the α model [7], as extended to a two-band superconductor [8], gave values of the relevant parameters consistent with other experiments and theoretical calculations [9]. Measurements of the specific heat have a special role in such investigations for several reasons: they give information about the electron density of states (EDOS) that is not readily obtained from other measurements; whereas most other measurements that give information about the energy gaps are sensitive to surface properties, the specific heat is a bulk property. Doped samples of MgB_2 present a unique opportunity to study the effects of band filling, interband coupling, and interband scattering in a well understood two-band superconductor. As in the case of MgB_2 itself, specific-heat measurements can be expected to make a useful contribution to research on the doped materials.

In this paper measurements of the specific heat of two carbon-doped MgB_2 samples are reported, and parameters that characterize the electron contributions are compared with other experimental results and theoretical predictions. (Different values of those parameters, derived in a preliminary analysis of the data, were given in a conference report [10]. The preliminary analysis was based on the assumption that the zero-field, "residual" density of states was associated with non-superconducting regions of the $Mg(B_{1-x}C_x)_2$. Subsequent X-ray measurements showed that the impurity phase was MgB_2C_2, which would have a different lattice specific heat. The differences between the parameters reported here and those in the conference report are a consequence of corrections for the contribution of MgB_2C_2 to the measured specific heat, and a more rigorous separation of the lattice and electron contributions, which is described in Section 4.2. Miscommunication

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over notation led to an error, by a factor two, in the carbon content of the samples in the conference report.) Following an outline of some of the theoretical considerations in the remainder of this section, brief descriptions of the samples and the measurements are given in Sections 2 and 3. The relations used in the analysis of the data are summarized in Section 4.1. The presence of a nonsuperconducting impurity, MgB_2C_2, required a three-step process to obtain the contributions of the two bands to the electron specific heat: the lattice and electron contributions to the specific heat of the samples as measured were separated, and the electron specific heat corrected for the contribution of the MgB_2C_2, as described in Section 4.2; the superconducting-state electron specific heat of the $Mg(B_{1-x}C_x)_2$ was then analyzed to separate the contributions of the two bands, as described in Section 4.3. The results of the measurements and their analysis are compared with theoretical calculations and other experimental results in Sections 5.1 and 5.2, and summarized in Section 6.

MgB_2 comprises graphite-like hexagonal layers of B atoms separated by layers of Mg ions that are lined up with the centers of the boron hexagons. Because only s and p electrons are involved, band-structure calculations are straightforward and the results are relatively reliable. There is general agreement among the theoretical results, and also good agreement between theory and experiment. The Fermi surface consists of two tubular networks, the π bands, derived from the three-dimensional boron p_z orbitals, and two concentric cylindrical elements, the σ bands, derived from the quasi two-dimensional boron $p_{x,y}$ orbitals [11–15]. Both σ bands are hole like; one of the π bands is hole like and the other electron like. Although there are four distinct sheets of the Fermi surface, the superconducting-state energy gaps on each pair of bands are similar [15], and for the purpose of comparing theoretical predictions with thermodynamic properties MgB_2 can be regarded as a two-band superconductor. The E_{2g} phonon mode, which involves stretching of the bonds in the boron planes, couples strongly with the σ bands. It produces the larger of the two gaps, on the σ bands, and plays a major role [11,12,14,16] in producing the high T_c. The phonons couple weakly with the π bands, and relatively weak interband coupling also contributes to the smaller π-band gap. First principles calculations of the specific heat [15,17] show evidence of the major two-gap features observed experimentally [9].

The only widely studied dopants are Al on the Mg sites, and C on the B sites. In both cases electrons are added to the Fermi sea, and T_c decreases with increasing concentration of dopant. The band filling associated with doping, particularly in the σ band, can be expected to be important in determining the nature of the superconductivity. One suggestion [18] is that the decrease in T_c with doping is mainly a band-filling effect. For a multiband superconductor nonmagnetic scattering centers can be pair breaking and can also have an effect on the nature of the superconducting condensate on different sheets of the Fermi surface [19]. Interband scattering in a two-gap superconductor is also expected to reduce T_c, and to equalize the two gaps [20,21]. Mazin et al. [22] suggested that in the absence of observed correlations of T_c with resistivity in MgB_2 samples the case for two-gap superconductivity was not settled, but explained this apparent paradox on the basis of weak interband scattering. In any case, interband scattering can be expected to be stronger in the doped samples.

2. Samples

The samples were made by heating Mg turnings and B_4C powder, an approach that was first used by Mickelson et al. [23]. X-ray diffraction studies show that the C-doped samples produced by this method consist of two phases, a distorted MgB_2 structure and MgB_2C_2, which is nonsuperconducting [23,24]. The presence of substantial amounts of MgB_2C_2 seems to be a common feature of samples produced by this method [23–25]. Neutron diffraction measurements showed the presence of 7% MgB_2C_2 in another $x = 0.1$ sample [26]. For the samples studied in this work, powder X-ray diffraction measurements gave estimates of ∼6% and ∼10% for the MgB_2C_2 in the $x = 0.05$ and 0.1 samples, respectively. The presence of MgB_2C_2 in the samples also manifests itself as a normal-state-like contribution to the zero-field specific heat. The specific-heat measurements show the presence of paramagnetic impurities at the level of several tenths mol%. Straight-line, entropy-conserving constructions on the specific-heat anomalies at the transitions gave $T_c = 31.4$ K and 19.7 K for the $x = 0.05$ and 0.1 samples, respectively. For a sample with $T_c \sim 31$ K, essentially the same as that of the $x = 0.05$ sample, the lattice parameter is contracted from the 3.087 A for MgB_2 to 3.055 A, with no change in the b and c parameters [23]. Other properties of similar samples prepared by this method are reported elsewhere [23,24].

3. Specific-heat measurements

The specific-heat measurements were made in the same apparatus as those reported earlier for MgB_2 [6,9]. They were based on a heat-pulse technique with a mechanical heat switch to make and break thermal contact between the sample and a temperature-controlled heat shield. The measurements extend from ∼1 K to somewhat above T_c for each sample. They include measurements of the specific heat in magnetic fields, $C(H)$, in fields to $\mu_0 H = 9$ T. The results are shown as $[C(H) - C(9)]/T$ vs T. in Fig. 1. This figure gives an overview of the resolution of the H dependence of the "raw" data that would not be apparent in a plot of $C(H)/T$. Fig. 1b also permits a comparison with the specific heat of the only other sample on which such measurements have been reported, a sample with a similar T_c, for which the results were presented only in that form [25]. Comparisons of the data in different fields suggest that the 9-T data are low relative to the data in other fields by an amount that is estimated to be of the order of 1%. In the vicinity of T_c the discrepancy between the data in 9 T and the data in other fields can be seen in Fig. 1, where $[C(H) - C(9)]/T$ is consistently non-zero, and also in Fig. 2, where the 9-T data are consistently low. The H dependence of the entropy at a temperature slightly above T_c provides a measure of the consistency of the measurements in different fields: For the $x = 0.05$ sample at 35.0 K, for all H other than 9 T the entropies are within +0.3/−0.4% of their average; for 9 T the entropy is −1.1% relative to that average. For the $x = 0.1$ sample at 21.5 K, the comparable numbers are ±0.4% and −0.7%. Because of the discrepancy between the 9-T data and the data in other fields, the 9-T data have been omitted from all quantitative analyses, but they are included in the figures for the information they give on the 9-T transitions to the vortex state.

4. Analysis of specific-heat data

4.1. Relations used in fitting and interpreting the data

The analysis of the data is based on the usual assumption that $C(H)$ is the sum of an H-dependent electron component, $C_e(H)$, and an H-independent lattice component, C_{lat}. In addition, $C_e(H)$, which is designated C_{es} in the superconducting state and $C_{ev}(H)$ in the vortex state, is taken to be $C_{en} = \gamma T$ in the normal state. With the commonly used polynomial expression for C_{lat},

$$C_{lat} = B_3 T^3 + B_5 T^5 + B_7 T^7 + \cdots, \tag{1}$$

$$C(H) = C_e(H) + B_3 T^3 + B_5 T^5 + B_7 T^7 + \cdots,$$

and, in the normal state,