Heat Capacity of MgB$_2$: Evidence for Moderately Strong Coupling Behavior

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Abstract

We characterize the superconducting state of phase pure polycrystalline samples of the new layered superconductor MgB$_2$ by specific heat measurements in magnetic fields up to 9 T. The characteristic jump at the superconducting transition is observed and compared with the predictions of weak coupling BCS-theory and the $\alpha$-model. Our analysis shows excellent agreement with the predictions for $2\Delta/k_B T_C = 4.2(2)$ with a Sommerfeld term $\gamma_{\text{exp}}$ of 3.1(1) mJ/molK$^2$ indicating that MgB$_2$ is a superconductor in the moderately strong electron-phonon coupling regime.

74.25B, 74.80Dm, 74.72.-h
Recently, Akimitsu and co-workers reported superconductivity at $T_C \approx 39\,\text{K}$ in the layered diboride MgB$_2$ \cite{1}. This discovery on the one hand again focuses attention on the borides as possible candidates for high-$T_C$ superconductivity. On the other hand, $T_C$ of MgB$_2$ exceeds the generally agreed theoretical limit for phonon mediated superconductivity and raises the question as to another possible coupling mechanism \cite{2}. However, first measurements of the thermodynamic properties and in particular of a sizeable partial $^{11}$B isotope effect by Bud’ko et al. strongly hint at the importance of phonons for superconductivity in MgB$_2$ \cite{3}. Kortus and co-workers, based on electronic band structure calculations conclude that the metallic character is due to covalent B-B bonding and that $T_C$ particularly benefits from strong electron-phonon coupling in concert with high frequency vibrations associated with the light mass of the boron atoms \cite{4}. Evidence for strong-coupling $s$-wave superconductivity was indeed found from $^{11}$B nuclear spin lattice relaxation measurements from which a rather large gap ratio of $2\Delta/k_B T_C \approx 5$ was derived \cite{4}. Strong electron-lattice coupling also seems to be able to explain Al doping experiments carried out by Slusky et al. that show a decrease of $T_C$ with increasing Al content and finally a loss of bulk superconductivity at $\approx 10\%$ Al doping \cite{6}. These experiments, in particular, reveal MgB$_2$ to be close to a structural instability involving a boron interlayer alternation rather than bond alternation in the B layers. All presently available tunneling spectroscopy experiments consistently fit very well to an $s$-wave BCS quasi-particle density of states and consistently exclude $d$-wave symmetry of the order parameter. However, the gap values resulting from these studies span a wide range and currently leave a somewhat inconclusive situation. The very first experiments by Rubio-Bollinger et al. gave a surprisingly small value of 2 meV (weak-coupling BCS value is 5.9 meV) \cite{7}. More recent work by Schmidt et al. \cite{8} ($\Delta=4.3$ meV) and Sharoni et al. \cite{9} ($\Delta=5 - 7$ meV) put $\Delta$ closer to the weak-coupling value or even into an intermediate coupling regime. This wide range of gap values seems to result from defects or minor non-superconducting impurity phases, or chemical reactions at the surface of the polycrystalline specimen.

In this Letter, we report a heat capacity study in zero field and a magnetic field of 9 T of
phase pure samples of MgB$_2$. In the zero-field measurements we observe the characteristic jump in $c_P$ at the superconducting transition temperature $T_C=38.5$ K associated with the formation of the superconducting condensate. Our $\Delta c_P(T_C)$ is in good agreement with the finding of Bud’ko et al. [3]. However, a more detailed analysis of the anomaly was not carried out in their work. The detailed temperature dependence of the heat capacity anomaly fits very well to model calculations assuming a BCS-like temperature dependence of the gap and a gap ratio $2\Delta(0)/k_B T_C \approx 4.2(2)$. This value is significantly increased over the BCS ratio of $2\Delta(0)/k_B T_C=3.52$. From the low temperature data taken at 9 T we extract a Sommerfeld coefficient $\gamma_{exp} = 3.1(1)$ mJ/mol K$^2$. Comparing this value with the results of band structure calculations we derive an electron-phonon coupling parameter $\lambda_{el-ph} \approx 0.8$ in good agreement with theoretical estimates from linear-response electronic structure calculations [10].

Our findings for $\gamma_{exp}$ and $\Delta c_P(T_C)$ imply a ratio $\Delta c_P(T_C)/\gamma_{exp}T_C \approx 0.7$ which is significantly lower than e.g. for the weak coupling BCS value of 1.43.

Polycrystalline samples of MgB$_2$ were prepared from stoichiometric mixtures according to the procedure described in ref. [1]. Phase purity was confirmed with a STOE powder diffractometer. The superconducting transition temperatures $T_C$ were determined with a Quantum Design MPMS7 magnetometer and conventional 4-point resistivity measurements and amounted to $\approx 38.5$ K. For the heat capacity measurements pellets of $\approx 3$ mm diameter and $\approx 15$ mg were pressed, sealed in Ta tubes under Ar atmosphere, and sintered at 950 oC (sample 1) and 850 oC (sample 2) for 10 h. The heat capacity was measured with a Quantum Design PPMS relaxation calorimeter in the temperature range 1.8 to 100 K in fields up to 9 T. Particular care was taken to determine the addenda and thermal relaxation parameters of the platform and the suspension wires at each magnetic field individually [11].

Fig. 1 displays the zero-field heat capacity of MgB$_2$ in comparison with the data taken within an external field of 9 T. An anomaly centered at $\approx 38$ K is visible in the zero-field data which is suppressed by a magnetic field of 9 T. The maximum of the anomaly amounts to $\Delta c_P(T_C)/T_C \approx 2$ mJ/mol K$^2$. The difference of the zero-field and the heat capacity at 9 T is shown in Fig. 2 together with a theoretical curve (solid line in Fig. 2). The theoretical
calculations were carried out within the framework of the ‘α-model’ proposed by Padamsee et al. [12]. This model assumes a BCS-type gap but allows a variable ratio \( \alpha \equiv \Delta(0)/k_B T_C \); in the case of weak-coupling BCS theory \( \alpha = 1.76 \). This simplistic approach was initially used to model the specific heat jumps of elemental superconductors like In, Sn and Zn, Pb - In alloys, and more recently also of layered organic superconductors as well as of the layered rare earth carbide halides [12-14].

To calculate the heat capacity we used a polynomial representation of the temperature dependence of the BCS gap as tabulated by Mühlschlegel for \( T \leq T_C \) [15]. Following Padamsee et al. \( \Delta c_P(T) \) was obtained according to

\[
\Delta c_P/(\gamma_{fit} T_C) = C_{es}(t)/(\gamma_{fit} T_C) - t = d/dt (S_{es}/\gamma_{fit} T_C) - t
\]

with \( t \equiv T/T_C \) and the entropy \( S_{es} \) as defined in eq. (2) in ref. [12]. Subtraction of high-field data from zero-field heat capacities to correct for the lattice heat capacity contributions also implies a subtraction of the normal state linear heat capacity term which is accounted for by the \(-t\) term in eq. (1). With \( \Delta(T) \equiv 0 \), for \( T > T_C \) eq. (1) leads to

\[
\Delta c_P/T_C \equiv 0.
\]

Fitting eq. (1) to the experimental results therefore provides \( \gamma_{fit} \) merely from the magnitude of the anomaly. The detailed temperature dependent shape of the anomaly is determined by \( \alpha \). To fit the experimental data we varied as adjustable parameters \( \alpha, \gamma_{fit}, T_C, \) and a parameter that simulated a Gaussian broadening of \( T_C \) [14]. In addition, we allowed for a small shift of the baseline which never exceeded 2 mJ/mol K.

The fits of the experimental results of the two independent samples converge rapidly to \( \alpha = 2.1(1) \) with \( T_C = 38.67(5) \) K and \( \delta T_C = 0.55(5) \) K (sample 1) and with \( T_C = 37.84(5) \) K and \( \delta T_C = 0.56(5) \) K (sample 2). \( \delta T_C \) corresponds to \( \sigma \) in a Gaussian distribution of \( T_C \) and indicates a smearing of \( T_C \) of less than 1.5 % emphasizing good homogeneity of both samples. The fits consistently converged to \( \gamma_{fit} = 1.1(1) \) mJ/mol K\(^2\) for both samples.

A reliable independent determination of the Sommerfeld coefficient e.g. from low temperature heat capacity data turned out to be difficult since a field of 9 T is not sufficient to
suppress superconductivity completely \[14,17\]. \( H_{c2} \) measurements indicate a critical temperature of \( \approx 15K \) at 9 T. In a plot \( c_p/T \) versus \( T^2 \) we observe a good linear correlation already above 10K and marked deviations only below \( \approx 5K \) (see Fig. 3).

A fit of the 9 T data using \( c_p/T = \gamma_{\text{exp}} + \beta \cdot T^2 \) yields \( \gamma_{\text{exp}}=3.1(1) \) mJ/mol K\(^2\) and \( \beta=1.24(6) \times 10^{-5} \) J/mol K\(^4\) corresponding to a low temperature Debye temperature \( \Theta_D(0) \) of \( \approx 776(14)K \) in good agreement with the results of the early heat capacity study by Swift and White and recently by Bud’ko et al. \[18,3\].

From a comparison with the results of various band structure calculations, which consistently predict a Sommerfeld term \( \gamma_{\text{BS}} \approx 1.7 \) mJ/mol K\(^2\) \[4,10,19\], an electron phonon coupling parameter \( \lambda_{\text{el-ph}} \) is derived to

\[
\lambda_{\text{el-ph}} = \frac{\gamma_{\text{exp}}}{\gamma_{\text{BS}}} - 1 \approx 0.82(6) \tag{3}
\]

which is in very good agreement with theoretical predictions \[14,20,21\].

Our results clearly substantiate the scenario of MgB\(_2\) being in the ‘intermediate or moderately strong’ coupling regime as conjectured from tunneling spectroscopy experiments by Sharoni et al. \[9\] and more recently by Raman spectroscopy \[22\] and full-potential LMTO density-functional calculations \[11\]. The heat capacity measurements do not suffer from the inherent problems of tunneling or optical techniques, namely surface defects or deterioration and our results indicate a gap value of 7.0(3) meV for MgB\(_2\). The ratio \((T_C/\Theta_D)^2\) amounts to \(2.3 \times 10^{-3}\) and is close to classical elemental strongly-coupled superconductors. From McMillans’s expression using a typical value \(\mu^* \approx 0.15\) for the Coulomb pseudopotential we estimate an empirical electron-phonon coupling constant \( \lambda_{\text{el-ph}} \approx 1 \) which is somewhat larger than the value obtained from the linear heat capacity term.

Since initial submission of this paper two more heat capacity studies have been reported, both carried out on commercial samples with 98% nominal purity \[23,24\]. Both papers find somewhat decreased \(T_C\)’s but within error limits identical \( \Delta c_p(T_C) \)’s of \( \approx 80 \) mJ/mol K\(^2\). The work by Wang et al. reliably derives \( \gamma_{\text{exp}}=2.67 \) mJ/mol K\(^2\) from measurements in magnetic fields up to 16 T which is close to our findings. From a subtraction of a theoretically
estimated lattice heat capacity from zero-field data Wälti et al. find an increased $\gamma_{\text{exp}}$ of 5.5 mJ/mol K$^2$. As in our work these investigations observe as well the striking difference between $\gamma_{\text{exp}}$ and $\gamma_{\text{fit}}$ which now appears to have become a robust result. Wang et al. assign this discrepancy to possible non-BCS behavior resulting from gap anisotropy and only partial condensation of the electrons at $T_C$. Liu et al. propose multigap superconductivity and an impurity-sensitive specific-heat jump at $T_C$ as a possible explanation [21].

In summary, we present and analyze heat capacity measurements which show that the new superconductor MgB$_2$ is a BCS superconductor in the intermediate or 'moderately' strong electron-phonon coupling regime. From fits of the heat capacity jump we conclude $2\Delta(0)/k_BT_C=4.2(2)$ corresponding to a gap of 7.0(3) meV at $T=0$K.

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FIG. 1. Heat capacity $C_P/T$ of a polycrystalline sample of MgB$_2$ determined in zero field and with an applied magnetic field of 9 T (sample 2).

FIG. 2. Heat capacity difference $\Delta c_P$ obtained as described in the text. The full line represents the results of fits assuming $\alpha=\Delta(0)/k_B T_C=2.1$ and a Sommerfeld coefficient of $\gamma_{\text{fit}} = 1.1$ mJ/mol K$^2$. The dashed curve indicates a fit with the weak coupling BCS heat capacity ($\alpha_{\text{BCS}}=1.76$). Both fits allowed for a slight temperature independent shift of the background ($< 2$ mJ/mol K) as described in the text.
FIG. 3. Heat capacity $c_P/T$ versus $T^2$ together with a linear approximation for temperatures $T > 5\, \text{K}$ (solid line). A Sommerfeld coefficient $\gamma_{\exp}$ of 3.1(1) mJ/molK$^2$ is obtained from the intersection with the ordinate.