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Conventional s -wave pairing in the presence of spin fluctuations in superconducting Mo_3Sb_7 from specific heat measurements

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The superconducting properties of the spin fluctuation-superconductor Mo_3Sb_7 have been investigated by specific heat measurements down to 0.5 K and under magnetic fields of up to 2 T. The obtained temperature and magnetic field dependences of the electronic specific heat strongly suggest a conventional s -wave pairing, while possible $(s+g)$ -wave pairing symmetry has been proposed earlier. In addition, the temperature dependence of the upper critical field H_{c2} is fully consistent with the Werthamer–Helfand–Hohenberg theory predicting its behavior for a conventional phonon-mediated type II superconductor.

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Since the discovery of unconventional superconductors exemplified by cuprates, superconductivity has been one of the most revitalized subjects of condensed-matter physics. Both strong theoretical and experimental efforts have been devoted to clarify the pairing symmetry in such compounds. While a growing consensus has emerged about the d -wave pairing in cuprates, other fruitful developments have been proposed to deal with the puzzling superconducting properties of some exotic superconductors. It is worth mentioning the two-gap superconductivity in MgB_2 ,^{1,2} possible p -wave superconductivity in Sr_2RuO_4 ,^{3,4} the either $(s+g)$ -wave pairing or two-gap superconductivity in $\text{YNi}_2\text{B}_2\text{C}$,^{5,6} and the presence of both A and B phases in the filled skutterudite $\text{PrOs}_4\text{Sb}_{12}$.⁷⁻⁹

Among all the experimental techniques providing evidence for these previous schemes, specific heat measurements have become one of the most powerful tools to investigate the superconducting properties. Since the specific heat probes the quasiparticle excitations across the superconducting gap, both its temperature and magnetic field dependences can reveal the nature of the superconducting state. Actually, while the electronic specific heat in the superconducting state, C_{es} , should exponentially vanish at low temperature in conventional s -wave superconductors,¹⁰ it is expected to be proportional to T^2 in d -wave superconductors.¹¹ Furthermore, under magnetic fields, C_{es} can be expressed as $C_{es} = \gamma(H)T$, where $\gamma(H)$ is the Sommerfeld coefficient under magnetic fields. $\gamma(H)$ is expected to be proportional to the applied magnetic field H for a gapped superconductor due to the confinement of the quasiparticle excitations in the vortex cores.¹² Contrarily, if the delocalized quasiparticles play a significant role, $\gamma(H)$ follows a $H^{1/2}$ dependence underlying nodal superconductivity such as in $\text{YNi}_2\text{B}_2\text{C}$ (Ref. 6) or in cuprates.^{13,14}

Recently, the Mo_3Sb_7 compound, which crystallizes in the Ir_3Ge_7 -type structure (space group $Im\bar{3}m$), was found to dis-

play both spin fluctuations and a superconducting transition at ~ 2.3 K.¹⁵ Moreover, a possible $(s+g)$ -wave pairing symmetry has been suggested by Dmitriev *et al.* based on the results obtained by the Andreev reflexion method.¹⁶ As spin fluctuations have been proposed as a possible origin of exotic pairing symmetry,¹⁷ such intriguing results have brought us to carry out a thorough study of the specific heat under magnetic field of the Mo_3Sb_7 compound.

In this Brief Report, we report on the temperature and magnetic field dependences of the specific heat of Mo_3Sb_7 down to 0.5 K. Rather than suggesting an exotic behavior, our data unequivocally show the fully gapped nature of the Mo_3Sb_7 compound, i.e., s -wave pairing symmetry.

The Mo_3Sb_7 polycrystalline sample has been prepared via a metallurgical route described in detail elsewhere.¹⁵ Heat capacity measurements, realized by the relaxation method, have been performed on a square shaped sample of ~ 50 mg from 0.5 up to 4 K and under magnetic fields of up to 2 T using a heat capacity and a He^3 physical property measurement system option (Quantum Design).

Figures 1(a) and 1(b) show the temperature dependences of the heat capacity $C_p(T, H)$ of the Mo_3Sb_7 compound depicted as C_p/T vs T^2 for different magnetic fields H , varying from 0 up to 2 T. The critical temperature T_c at zero field is near 2.3 K, in very good agreement with our recent investigation.¹⁵ Moreover, the extrapolation of the data to 0 K points to an intercept which is very close to zero testifying to the good quality of the sample and to the full superconducting volume [Fig. 1(a)]. As can be clearly observed in Fig. 1(a), superconductivity is gradually suppressed and the quasiparticle contribution increases with increasing the magnetic field. The superconducting anomaly can no longer be observed for fields higher than ~ 1.7 T, therefore standing for the upper critical field H_{c2} . This value is in good agreement with the value derived from the Andreev reflexion method.¹⁸

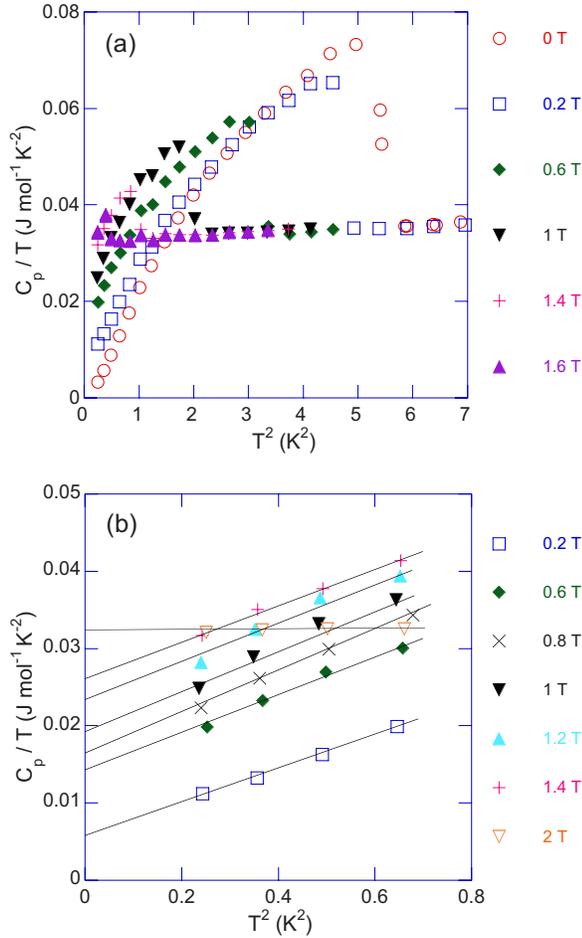


FIG. 1. (Color online) (a) Temperature dependence of C_p/T for different magnetic fields as a function of T^2 (for sake of clarity, the data for $H=0.8, 1.2, 1.7,$ and 2 T are not displayed). (b) Low temperature dependence of C_p/T as a function of T^2 (for sake of clarity, the data for $H=1.6$ and 1.7 T are not shown). The solid lines stand for the best fit to the data highlighting the estimation of $\gamma(H)$ for $T \rightarrow 0$ K.

To shed some light on the superconducting properties and to provide information on the gap structure require a detailed analysis of the quasiparticle excitations in the vortex state. The analysis of the zero field specific heat data in the normal state, $C_n(T)$, has been described in detail elsewhere.¹⁵ To summarize, it was found that $C_n(T)$ can be expressed as

$$C_n(T) = \gamma_n T + C_{\text{lattice}}(T), \quad (1)$$

where $\gamma_n T$ is the electronic term due to free charge carriers and $C_{\text{lattice}}(T) = \beta T^3 + \alpha T^5$ is the phonon contribution and including a T^5 term to account for the anharmonicity of the lattice. A fit of the present data based on relation (1) leads to $\gamma_n \approx 33.5 \text{ mJ mol}^{-1} \text{K}^{-1}$, in very good agreement with the value obtained in Ref. 15. Moreover, the ratio $\Delta C / \gamma_n T_c$ can be inferred from the specific heat measurement at null magnetic field leading to the value of 1.04 in perfect agreement with that previously reported.¹⁵ Assuming that $C_{\text{lattice}}(T)$ is independent of the magnetic field, the electronic specific heat in the superconducting state, C_{es} , is then given by $C_{\text{es}}(T, 0)$

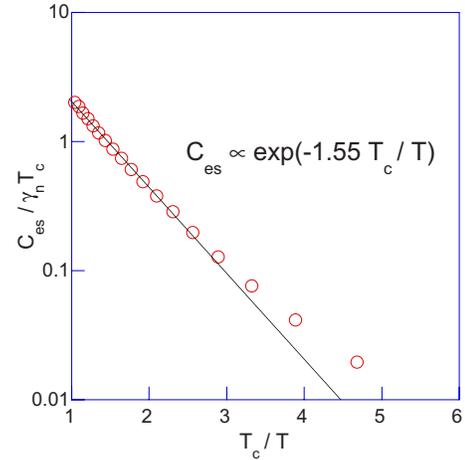


FIG. 2. (Color online) Logarithmic $C_{\text{es}} / \gamma_n T_c$ vs T_c / T of Mo_3Sb_7 . The solid line represents the best exponential fit to the data for $1 < T_c / T < 3.5$.

$= C_p(T, 0) - C_{\text{lattice}}(T)$. The logarithmic plot of $C_{\text{es}}(T, 0) / \gamma_n T_c$ as a function of T_c / T is shown in Fig. 2. For $T > 0.7$ K, $C_{\text{es}}(T, 0)$ exponentially vanishes revealing the absence of gap nodes in the superconducting order parameter. Small deviations from linearity can only be observed at very low temperatures and have also been noticed in other superconductors.^{1,19} The fit from 0.7 to 2.2 K leads to $C_{\text{es}}(T, 0) \propto \exp(-1.55 T_c / T)$ close to the weak-coupling BCS formula $C_{\text{es}}(T, 0) \propto \exp(-1.44 T_c / T)$.¹⁰ Hence, this analysis gives first clear evidence of the BCS nature of the Mo_3Sb_7 type II superconductor. If this assumption is valid, this would be in contrast to the results, based on the Andreev reflexion method, reported on a single crystal by Dmitriev *et al.*¹⁶ where a $(s+g)$ -wave pairing symmetry has been called for.

To try to elucidate this paradox, the magnetic field dependence of γ , displayed in Fig. 3, could provide further information. $\gamma(H)$ has been determined from the linear fit in the range $0.5 \text{ K} \leq T \leq 1.5 \text{ K}$ for $T \rightarrow 0$ K [see Fig. 1(b)]. As shown in Fig. 3, $\gamma(H)$ linearly increases with H for fields of up to 1.7 T. This behavior is strongly adverse to the

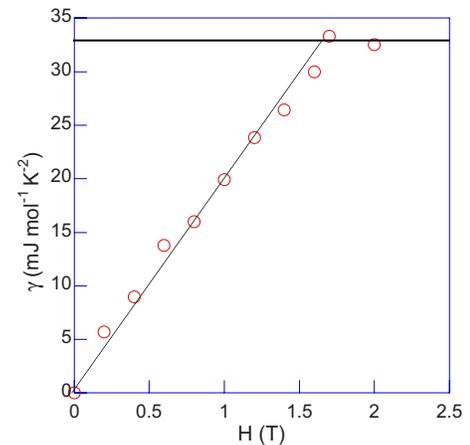


FIG. 3. (Color online) Magnetic field dependence of γ . The horizontal solid line highlights the normal state value γ_n . The solid line is the best fit to the data suggesting $\gamma(H) \propto H$ up to 1.7 T.

$\gamma(H) \propto H^{1/2}$ dependence expected for nodal superconductivity²⁰ or to that obtained for two-band superconductivity.¹ In addition, no low-field curvature is revealed as in the case of the *s*-wave superconductors NbSe₂ and CeRu₂.^{21–23} For *s*-wave superconductors, $\gamma(H)$ can be expressed as $\gamma(H) \approx \gamma_n H/H_{c2}$, provided H is much higher than the lower critical field H_{c1} .¹² In the present case, this hypothesis is valid since H_{c1} has been estimated to be close to 1 mT.²⁴ Using the experimental γ_n and H_{c2} values, we get $\gamma_n/H_{c2} \approx 19.7 \text{ mJ mol}^{-1} \text{ K}^{-2} \text{ T}^{-1}$ close to the value of $20.2 \text{ mJ mol}^{-1} \text{ K}^{-2} \text{ T}^{-1}$ determined from the linear fit (see Fig. 3). Thus, the magnetic field dependence of γ strongly indicates that the present superconductor has a conventional *s*-wave pairing symmetry.

The temperature dependence of the upper critical field H_{c2} , determined by considering the midpoint over the C_p anomaly, is plotted in Fig. 4. No positive curvature near T_c can be observed as is the case in MgB₂, YNi₂B₂C, or PrOs₄Sb₁₂ and proposed as an intrinsic property of two-gap superconductivity.^{6,25,26} In addition, the value of $H_{c2}(0)$ has been estimated from the Werthamer–Helfand–Hohenberg (WHH) formula expressed as²⁷

$$H_{c2}(0) = -0.69T_c \left. \frac{dH_{c2}}{dT} \right|_{T_c}, \quad (2)$$

where $dH_{c2}/dT|_{T_c}$ is the upper critical field slope determined near T_c . From this formula, we get $H_{c2}(0) \approx 2T_c$, with $dH_{c2}/dT|_{T_c} \approx -1.24 \text{ T K}^{-1}$. This slope is in good agreement with that obtained on a single crystal by Bukowski *et al.*²⁴ The value of $H_{c2}(0)$ also confirms the typical type II superconductivity in Mo₃Sb₇ since $H_{c2}(0)$ satisfies the relation $H_{c2}(0) \leq H_p(0)$, where $H_p(0)$ (in T) is the Pauli limiting field expressed as $H_p(0) = 1.84T_c$.²⁸ Using the critical field slope and the critical temperature T_c , the theoretical temperature dependence of H_{c2} vs T/T_c can be determined with the WHH theory²⁷ assuming negligible spin-paramagnetic and spin-orbital effect. The results are depicted in Fig. 4 coupled with

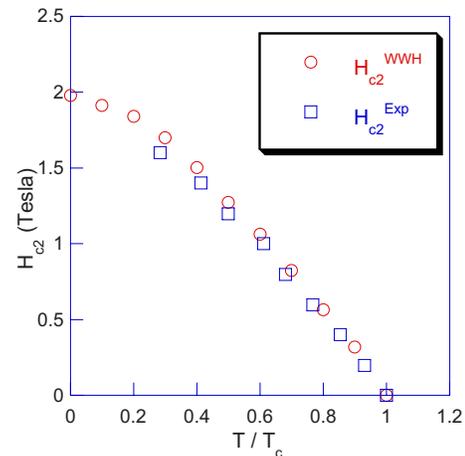


FIG. 4. (Color online) Upper critical field H_{c2} derived from the experimental data and from the WHH theory as a function of the reduced variable T/T_c .

the experimental ones. We can note an excellent agreement with the simplified WHH theory, indicative of conventional pairing mechanism.

In conclusion, specific heat measurements under magnetic field down to 0.5 K have been performed on a high-quality polycrystalline Mo₃Sb₇ sample. All the results strongly support that the spin fluctuation Mo₃Sb₇ compound exhibits a conventional *s*-wave pairing symmetry.

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