Spin Fluctuations and Superconductivity in Mo_3Sb_7

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(Received 15 February 2007; published 20 July 2007)

Temperature dependences of the magnetic susceptibility, specific heat, and electrical resistivity have been measured for the Mo_3Sb_7 compound in the 0.6–350 K range. This compound exhibits bulk superconductivity occurring at 2.25 K and follows the Kadowaki-Woods relation, $A/\gamma^2 = 1.0 \times 10^{-5}\ \mu\Omega \cdot \mathrm{cm}(\mathrm{K} \cdot \mathrm{mol/mJ})^2$, as a heavy-fermion system does. We show, from experimental evidence and theoretical argument, that Mo_3Sb_7 can be classified as a coexistent superconductor-spin fluctuation system. The McMillan equation including paramagnon effects was found to give an accurate estimation of the transition temperature.

DOI: 10.1103/PhysRevLett.99.037006 PACS numbers: 74.70.Ad, 74.20.Mn, 74.25.Bt

Over the past 20 years, both theoretical and experimental efforts were made on materials which not only undergo superconducting transition but also exhibit rather unconventional properties in their normal and superconducting states. Among them, it is worth mentioning Chevrel phases containing rare-earth ions or the heavy-fermion $CeCu_2Si_2$ compound which display an intimate interplay of superconductivity and magnetism [1–3] and intermetallic actinides such as UPt_3 or UCo_2 with spin fluctuation behavior [4,5]. Only a few materials without any actinide element exhibit both superconductivity and spin fluctuation behavior [6].

Quite recently, great attention has been focused on the intermetallic perovskite superconductor $MgCNi_3$ [7] where strong ferromagnetic spin fluctuations have been observed by NMR measurements [8]. These fluctuations could either suppress superconductivity or induce an exotic pairing mechanism [9]. More precisely, spin fluctuation effects usually manifest themselves at low temperature as a T^2 term in the electrical resistivity, a paraboliclike temperature dependence of the magnetic susceptibility and for some compounds, in an upturn of the specific-heat temperature dependence [5].

Recently, a new type II superconductor, namely Mo_3Sb_7, which crystallizes with a Ir_3Ge_7 type structure (space group $Im3m$), was identified as being a Pauli paramagnet with a superconducting transition temperature, T_c, of 2.1 K and an upper critical field of 17 kOe [10]. In another study [11], the maximum energy gap value as well as the critical temperature have been derived from the Andreev reflection method and turned out to be, respectively, 0.32 meV (close to the expected BCS value of 0.35 meV), and 2.2 K, value which is in good agreement with that found by Bukowski *et al.* [10].

In this Letter, we report on electrical resistivity, magnetic susceptibility, and, for the first time, heat capacity measurements on a Mo_3Sb_7 polycrystalline sample. The results suggest that Mo_3Sb_7 could be classified as a coexistent superconductor-spin fluctuation system.

The Mo_3Sb_7 compound has been prepared via a metallurgical route. Stoichiometric amounts of high purity Sb shots (5*N*) and Mo powders (5*N*) were loaded into a quartz ampoule which was heated up to 750 °C and left at this temperature for 10 days. The product was then powdered and finally densified by hot pressing at 600 °C for 2 h under 51 MPa using graphite dies. The obtained sample has been characterized by x-ray, neutron diffraction, and by electron probe microanalysis (EPMA). The x-ray diffraction pattern as well as the neutron and EPMA studies have only revealed the presence of the cubic phase, of Ir_3Ge_7 structure type.

Electrical resistivity measurements have been performed on a parallelepipedic shaped sample (typical dimensions of $2 \times 2 \times 10\ \mathrm{mm}^3$) with an ac transport measurement system option (PPMS-Quantum Design) between 1.9–350 K. Magnetization curves were measured from 5 to 300 K under a magnetic field up to 7 T (MPMS-Quantum Design) and heat capacity measurements from 300 K down to 600 mK using a heat capacity and a He^3 PPMS option.

The low temperature heat capacity and electrical resistivity dependences of Mo_3Sb_7 are shown in Figs. 1, 2(a),

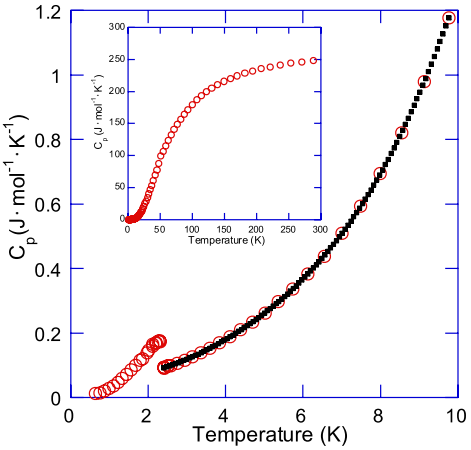

FIG. 1 (color online). Temperature dependence of the specific heat C_p of Mo_3Sb_7 at low temperature highlighting the specific-heat jump at the transition temperature. The dashed line stands for the best fit to the data according to Eq. (1). Inset: temperature dependence of the specific heat up to 300 K.

and 2(b), respectively. The sharp specific-heat discontinuity ΔC occurring at 2.3 K (Fig. 1) strongly suggests that this compound undergoes a superconducting transition. This observation is corroborated by the electrical resistivity curve which shows a drop to zero resistance at about 2.25 K with a transition width of ~0.1 K [Fig. 2(b)]. Both results are in good agreement with previous studies [10,11] and indicate that the superconducting state is not due to the presence of any secondary phase but is clearly a bulk property.

Strong evidences have been found indicating that Mo_3Sb_7 is also a spin fluctuation system. First of all, an intriguing feature is the dependence of the electrical resistivity, ρ, at low temperature ($T < 50$ K), which can be fitted by a $\rho(T) = \rho_0 + AT^2$ law [Fig. 2(a)]. The fit based on this relation using ρ_0 and A as fitting parameters gave $\rho_0 = 104\ \mu\Omega \cdot \mathrm{cm}$ and $A = 6.5 \times 10^{-3}\ \mu\Omega \cdot \mathrm{cm} \cdot \mathrm{K}^{-2}$. This typical quadratic dependence, associated with both a large increase and a saturation tendency of the electrical resistivity in going up to room temperature [Fig. 2(a)], is often attributed to spin fluctuations [5,12].

Another piece of evidence indicating that Mo_3Sb_7 is a spin fluctuation system is the temperature dependence of the magnetic susceptibility plotted in Fig. 3. The susceptibility displays a parabolic dependence at low temperature, then increases with temperature, and at higher temperatures becomes maximum around 180 K and obeys a Curie-Weiss law. It must be noted that the magnetization curves clearly show the absence of any ferromagnetic impurities (see inset in Fig. 3). The parabolic dependence of the magnetic susceptibility at low temperature, which was also noticed in the UAl_2 compound [13], is consistent with the theoretical predictions made by Béal-Monod *et al.* [14] on the spin fluctuation contribution to the low temperature dependence of the magnetic susceptibility.

Another striking feature is observed in analyzing the values of the magnetic susceptibility. Supposing Mo_3Sb_7

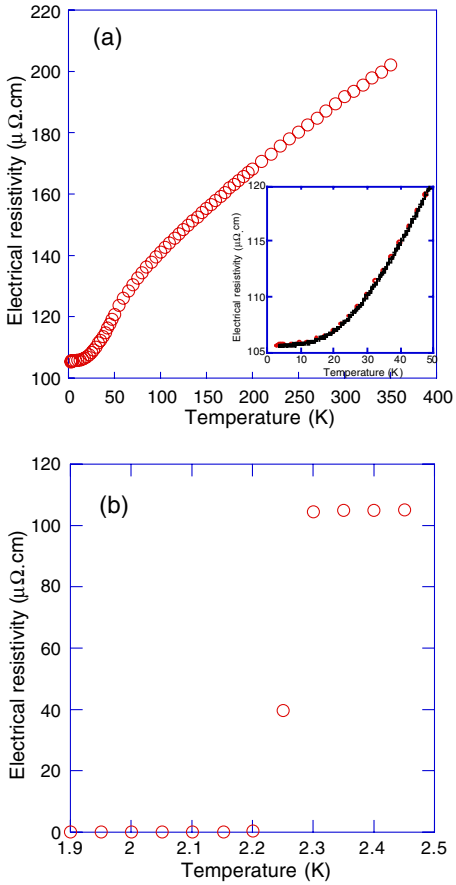

FIG. 2 (color online). (a) Electrical resistivity as a function of the temperature. Inset: parabolic dependence of the electrical resistivity at low temperature. (b) Superconducting transition of Mo_3Sb_7. The transition temperature is determined by the average of the onset and end point temperatures.

to be a Pauli paramagnet solely, the values of the susceptibility are anomalously high. At room temperature, it amounts to 522×10^{-6} EMU · mol^{-1}. This is in good agreement with that measured by Hulliger [15], but it is more than 2 times higher than the value reported on a Mo_3Sb_7 single crystal [10]. Such high values of the magnetic susceptibility have also been observed in the $Y(Co_{1-x}Al_x)_2$ system [16], considered as a strongly exchange-enhanced paramagnet.

To go further, we have performed a fit of the normal state heat capacity data, C_n, up to 10 K (see inset, Fig. 1) using an expression of the form

$$C_n = \gamma_n T + \beta_n T^3 + \alpha_n T^5, \qquad (1)$$

where γ_n and β_n are the electronic and lattice specific-heat coefficients, respectively, α_n a term to account for the anharmonicity of the lattice and T the absolute temperature. No additional $T^3 \ln(T/T_{sf})$ term due to spin fluctuations [17–20] (T_{sf} being the spin fluctuation temperature) was added as no characteristic anomaly in the specific heat could be detected in the normal state. Though such low temperature anomaly is often regarded as the most reliable

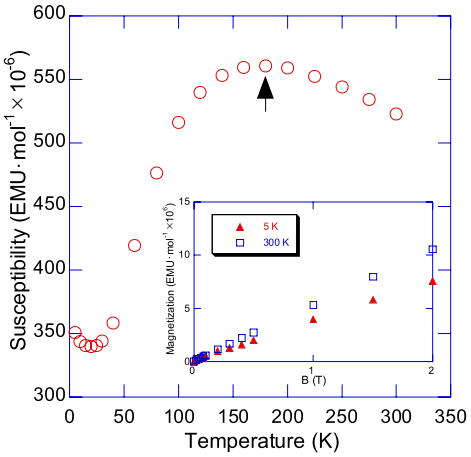

FIG. 3 (color online). Magnetic susceptibility as a function of the temperature in Mo_3Sb_7. The arrow indicates the position of the maximum. Inset: low field magnetization curves for the two extreme temperatures investigated (5 and 300 K).

indication for spin fluctuation behavior, some other spin fluctuation systems did not show this type of dependence such as, for example, $LuCo_2$ and Pd [21,22]. This striking outcome could be explained by a high spin fluctuation temperature. A rough estimation of this characteristic temperature based on the magnetic susceptibility leads to $T_{\mathrm{sf}} \sim 180$ K (Fig. 3) [23]. This value is of the same order of magnitude as that estimated in pure palladium, where $T_{\mathrm{sf}} \sim 250$ K [13]. The low temperature anomaly due to the $T^3 \ln(T/T_{\mathrm{sf}})$ term could then be spread out so that it could not be possible to separate it from the lattice and electronic contributions.

The obtained coefficients from the fit are 34.2 mJ/mol · K^2, 0.65 mJ/mol · K^4, and 2.6×10^{-3} mJ/mol · K^6 for γ_n, β_n, and α_n, respectively. From these results, we can have a deeper insight into the superconducting properties of the Mo_3Sb_7 compound through estimating the $\Delta C/\gamma_n T_c$ ratio which yields 1.04 with $\Delta C = 80$ mJ/mol · K and $T_c = 2.25$ K (Fig. 1). This value is much lower than the well-known BCS value of 1.43 [24]. Moreover, the ratio A/γ_n^2 is equal to 0.55×10^{-5} $\mu\Omega \cdot \mathrm{cm}(\mathrm{K} \cdot \mathrm{mol/mJ})^2$ which is in fairly good agreement with the Kadowaki-Woods relation $A/\gamma_n^2 = 1.0 \times 10^{-5}$ $\mu\Omega \cdot \mathrm{cm}(\mathrm{K} \cdot \mathrm{mol/mJ})^2$ satisfied by heavy-fermion systems as well as Lave phases such as YCo_2 [25]. As this relation can be explained in terms of the spin fluctuation theory [26], the obtained value is another evidence of the possibility for Mo_3Sb_7 to be considered as a spin fluctuator.

On the basis of this assumption, it can be interesting to try to estimate the critical temperature of this compound using the modified McMillan expression which takes into account paramagnon effects [6,27–30]

$$T_C = \frac{\theta_D}{1.45} \exp\left(-\frac{1.04(1 + \lambda_{\mathrm{eff}})}{\lambda_{\mathrm{eff}} - \mu^*_{\mathrm{eff}}(1 + 0.62\lambda_{\mathrm{eff}})}\right), \quad (2)$$

where θ_D is the Debye temperature and λ_{eff} and μ^*_{eff} the renormalized parameters which can be expressed as [6,28,29]

$$\lambda_{\mathrm{eff}} = \lambda_{e\text{-ph}}(1 + \lambda_{\mathrm{sf}})^{-1}, \quad (3)$$

$$\mu^*_{\mathrm{eff}} = (\mu^* + \lambda_{\mathrm{sf}})(1 + \lambda_{\mathrm{sf}})^{-1}, \quad (4)$$

where λ_{sf} is a contribution arising from spin fluctuations, $\lambda_{e\text{-ph}}$ the electron-phonon coupling constant and μ^* the renormalized Coulomb parameter. This last parameter is assumed to be equal to 0.08 and does not significantly deviate from this value in various compounds [27,29].

A direct evaluation of λ_{sf} can be made using [31]

$$\lambda_{\mathrm{sf}} = 4.5\left(1 - \frac{1}{S}\right)\ln\left(1 + p_1^2 \frac{S-1}{12}\right), \quad (5)$$

where p_1 is an adjustable cutoff parameter and S is the Stoner factor defined as $S \equiv N^{\chi}(E_F)/N(E_F)$ with $N^{\chi}(E_F)$ the enhanced susceptibility density of states and $N(E_F)$ the bare density of states. $N(E_F)$ has been determined from band structure calculations which will be reported in details elsewhere [32]. Briefly, the density of states at the Fermi level is found to be high due to the contribution of the d-Mo states, leading this material on the border of magnetic ordering. Moreover, as the Fermi level lies on a strongly decreasing slope, an incertitude in the determination of this density of states has to be accounted for. An analysis based on different computational methods (KKR and KKR-CPA) brings us to assume that $N(E_F)$ should be included in the range 115–120 states/Ry/f.u., consistent with a previous result based on LMTO calculations reported by Dashjav, Szczepenowska, and Kleinke [33]. The experimental value of the Pauli susceptibility leading to $N^{\chi}(E_F)$ was estimated by subtracting the diamagnetic contribution of the Mo_3Sb_7 compound, evaluated as being 280×10^{-6} EMU · mol^{-1} using Pascal's constants [34,35] to the measured magnetic susceptibility at $T = 0$ K. Consequently, we obtain $N^{\chi}(E_F) = 265$ states/Ry/f.u. and the Stoner factor is within the range $2.2 \leq S \leq 2.3$.

Despite the estimation of p_1 is quite difficult, a reasonable assumption consists of taking the value $p_1 \approx 0.6$ experimentally derived for Pd and V_3Ga by NMR measurements [6,31,36]. It must be mentioned that taking another value does not change qualitatively the present discussion. As a result, from Eq. (5), an estimation of λ_{sf} gives $0.088 \leq \lambda_{\mathrm{sf}} \leq 0.097$.

Furthermore, the electron-phonon coupling constant, $\lambda_{e\text{-ph}}$, can be determined from the specific-heat data using

$$\gamma_n = \frac{\pi^2}{3} k_B^2 N(E_F)(1 + \lambda_{e\text{-ph}} + \lambda_{\mathrm{sf}}) \quad (6)$$

where k_B is the Boltzmann's constant. By applying Eq. (6), it results that the $\lambda_{e\text{-ph}}$ values span the range 0.56–0.62. These data suggest that, with respect to electron-phonon coupling, Mo_3Sb_7 can be seen as an intermediate coupled superconductor [37].

As a first approximation, the Debye temperature was extracted from the β_n value within the framework of the Debye model, leading to $\theta_D \sim 310$ K.

Finally, from the physical parameters obtained previously, the transition temperature T_c was estimated to lie within the range 1.4–2.0 K. It is worth noting that the transition temperature obtained by the McMillan relation without spin fluctuation rescaling is substantially higher, i.e., $T_c \sim 8.7$–11.0 K. Alternatively to this work, one might expect a reduction of T_c without allowing for paramagnons effects but only by increasing the Coulomb parameter μ^* in the classical McMillan's formula. This approach would require $0.2 \leq \mu^* \leq 0.23$. In our opinion, such values would be unusually large, and therefore underline the irrelevance of the simple formula in the present case. As a consequence, all these results strongly indicate that paramagnon effects markedly improve the correlation between theoretical background and experiment.

In summary, we have explored the electrical, magnetic, and thermal properties of a polycrystalline Mo_3Sb_7 sample. The characteristic specific-heat anomaly at T_c clearly confirms the bulk nature of the superconductivity which is well corroborated by electrical resistivity measurements. These results, combined with the magnetic susceptibility study, provide a unified picture of both transport and magnetic properties of Mo_3Sb_7 within the framework of spin fluctuation theory.

C. C. greatly thanks M. Amiet and P. Maigné, and financial support of the DGA (Déléguation Générale pour l'Armement, Ministry of Defence, France). J. T. thanks for the financial support of INPL and Polish Ministry of Science and Higher Education (Grant No. N202-2104-33).

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