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Low-temperature specific heat of Sr_2RuO_4

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Abstract. We report low-temperature measurements 0.07 K $\leq T \leq$ 2 K of the specific heat, C, of the perovskite superconductor Sr_2RuO_4. Based on a detailed analysis of our data with respect to both sample quality (as measured by T_c = 0.43 K – 1.17 K) and magnetic-field dependence, it is shown that the electronic contribution to the specific heat, which contains the desired information on the gap structure, is superimposed by at least two additional contributions: a Schottky-type hump at $T \approx 0.1 - 0.2$ K and a low-temperature upturn in C/T at $T < 0.1$ K. We discuss possible origins of these additional contributions and their implications for the interpretation of low-temperature $C(T)$ data.

PACS. 74.70.Pq Ruthenates – 74.25.Bt Thermodynamic properties

Besides the fact that Sr_2RuO_4 is the first copper-free layered perovskite superconductor [1], this compound gained strong interest due to its unusual superconducting properties. The bulk of experimental results indicate that Sr_2RuO_4 represents one of the exceptional cases where the Cooper pairs of the superconductor are formed by electrons with equal spin orientation [2–6]. However, the symmetry of the superconducting order parameter is still under intensive discussion [7–12].

Here we report measurements of the low-temperature heat capacity, a quantity that provides important information on the structure of the superconducting gap at the Fermi surface. In particular, it is a most sensitive probe to elucidate the question whether the gap remains finite all over the Fermi surface or vanishes at certain parts. An exponential temperature dependence of the electronic contribution to the specific heat, C_s, is characteristic for a fully-gapped superconducting state. On the other hand, power-law temperature dependencies indicate gap zeroes at the Fermi surface: while $C_s \propto T^2$ corresponds to zeroes along lines, $C_s \propto T^3$ is expected for point nodes [13]. It is important, however, to keep in mind that the above characteristic temperature dependencies of C_s, which allow for an identification of the gap structure, are strictly valid only at temperatures $T \ll T_c$. As will be shown in this paper, it is very difficult for the present material to discriminate between an exponential and a power-law temperature dependence of C_s, especially as additional, non-superconducting contributions are present at low temperatures even in crystals of considerably high quality.

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For the specific heat experiments, a thermal-relaxation technique [14] attached to a dilution refrigerator has been used so that measurements can be made in the temperature range 0.07 K $\leq T \leq$ 2 K. Single crystalline samples were prepared by the travelling solvent floating zone technique [15] and characterised *via* DC-and AC- susceptibility measurements.

Four different single crystals have been investigated #3, #4-2, #6-5 and #6-6. They differ by (i) the ratio of $SrCO_3$ (99.99% purity) and RuO_2 (99.9% purity) used to prepare the polycrystalline starting material and (ii) the speed of the crystal growth ranging from 10 mm/h (#3 and #4-2) to 40 mm/h (#6-5 and #6-6). All single crystals have been checked by powder X-ray diffraction and Laue photographs. Within the resolution of these experiments, all crystals are free of foreign phases. In addition, high-resolution DC-magnetisation measurements have been carried out on single crystal #6-5. No traces of magnetic impurities (especially ferromagnetic $SrRuO_3$) have been found within a resolution of 10^{-4} μ_B/f.u.. Further on, the crystals have been characterised by resistivity measurements yielding a residual resistivity ratio $RRR = \rho(300\text{ K})/\rho(1.5\text{ K})$ of 42 (#3) and 290 (#6-5 and #6-6).

Figure 1 shows the specific heat results of four different single-crystalline samples in a representation C/T *vs.* T. Differences in the sample quality manifest themselves in both variations of the superconducting transition temperature, T_c (determined by the usual entropy-conserving way), varying between 0.43 and 1.17 K as well as the size and width of the phase-transition anomaly in $C(T)$ at T_c. Surprisingly, for all crystals investigated, additional

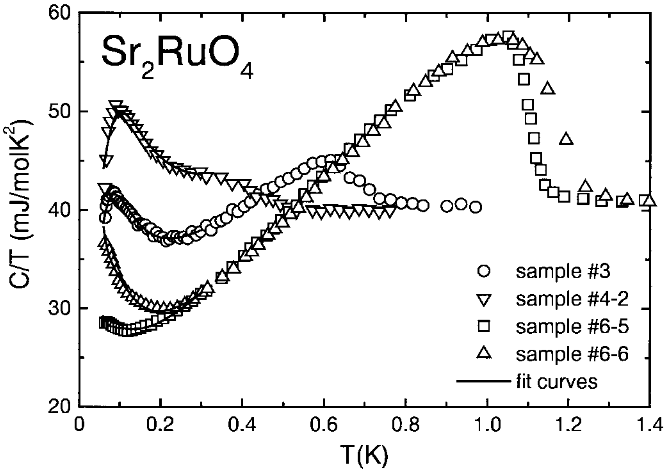

Fig. 1. Specific heat results of four different samples as C/T *vs.* T. The solid lines are fits to the data $T < 0.3$ K according to the fitting procedure described in detail in the text.

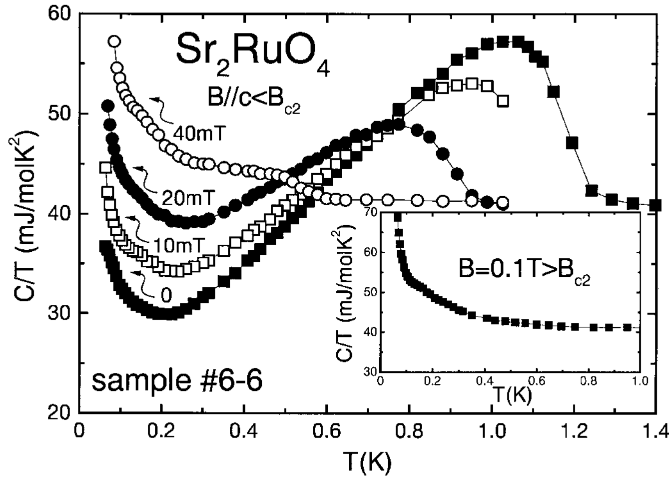

Fig. 2. Specific heat of sample #6-6 measured in varying magnetic fields along the c-axis as C/T *vs.* T. The inset shows the data taken in a magnetic field of $B = 0.1$ T which is well above the upper critical field for this field orientation. Thin solid lines are guides for the eye.

contributions to the specific heat show up at low temperatures $T < 0.3$ K. These are (i) a hump-like structure around $T = 0.1-0.2$ K which is most strongly pronounced in the samples #3 and #4-2 and (ii) a low-temperature upturn in C/T. The latter dominates the low-T data for the samples #6-5 and #6-6 but is also visible for the samples #3 and #4-2 when a magnetic field is applied (not shown here). In order to decide whether these anomalies are related to the superconducting state in Sr_2RuO_4, measurements have been performed in magnetic fields both below and above the upper critical field B_{c2}. For the field configuration used, $B \parallel c$, $B_{c2}(0)$ is about 0.06 T [16]. Figure 2 shows the specific heat results for sample #6-6 in a representation C/T *vs.* T for varying magnetic fields. As demonstrated in the inset of Figure 2, both additional contributions are present also in an overcritical field of $B = 0.1\ T > B_{c2}$, which rules out any direct interrelation to superconductivity.

As pointed out above, the information on the gap structure is contained in the temperature dependence of the quasiparticle contribution C_s in the superconducting state at temperatures far below T_c. Obviously, this contribution is covered by the additional features which, unfortunately, occur exactly in the most relevant temperature range $T \ll T_\mathrm{c}$. Therefore, the determination of $C_\mathrm{s}(T)$ from the measured $C(T)$ requires a careful analysis of the data. To this end, we model the hump-like structure by assuming a two-level Schottky anomaly C_Sch. This appears justified by both the shape of the anomaly and its distinct field dependence: with increasing fields the anomaly broadens and shifts to higher temperatures. For simplicity, we consider a two-level system only. For the low-temperature upturn we use a term $C_N \propto \alpha/T^2$ which represents the high-temperature tail of a nuclear Schottky contribution [17]. In addition, the extrapolation of the C/T data from about half of T_c down to the lowest temperatures suggests the presence of a residual normal-conducting contribution $C_n = \gamma_n T$. Such a term has been frequently observed in Sr_2RuO_4 [18]. Finally, for the quasiparticle contribution to the specific heat of the superconductor – the quantity of interest – we add a term $C_\mathrm{s} = \delta T^2$ that corresponds to a gap structure with line nodes. A T^2 temperature dependence has been suggested by Maeno *et al.* [19] based on their specific heat measurements on various samples including those with the highest $T_\mathrm{c} = 1.47$ K achieved so far. The resulting fit function is of the form:

$$C/T = \left(C_N + C_n + C_\mathrm{s} + C_\mathrm{Sch}\right)/T = \alpha/T^3 + \gamma_n + \delta T + \frac{A}{T}\left(\frac{\Delta}{T}\right)^2 \frac{\mathrm{e}^{\frac{\Delta}{T}}}{\left(1+\mathrm{e}^{\frac{\Delta}{T}}\right)^2}. \quad (1)$$

As demonstrated in Figure 1, this function provides an excellent fit to the $C(T)$ data for the various samples at low temperatures $T < 0.3$ K. It is clear, that due to the large number of free parameters (5) involved in the fitting procedure, the results have to be checked for consistency very carefully. We note, that an attempt to describe the quasiparticle contribution by an exponential term of the form $C_\mathrm{s} \propto a \exp(-b/T)$ results in a fit of almost identical quality. However, since this implies even one more free parameter, we refrain from a more detailed discussion. Figure 3 compiles the resulting fit parameters derived from a least-square fit of equation (1) to the data of Figure 1 as a function of T_c for the four samples investigated.

In the following, we discuss the various terms one by one starting with the Schottky contribution C_Sch. Figure 3a shows the prefactor A of the latter contribution in units of the molar gas constant R. The quantity A/R specifies the number of two-level systems per formula unit involved. We find A/R of the order 10^{-4} per formula unit. Provided that our assumption of a Schottky anomaly is correct, this number clearly indicates that we are dealing

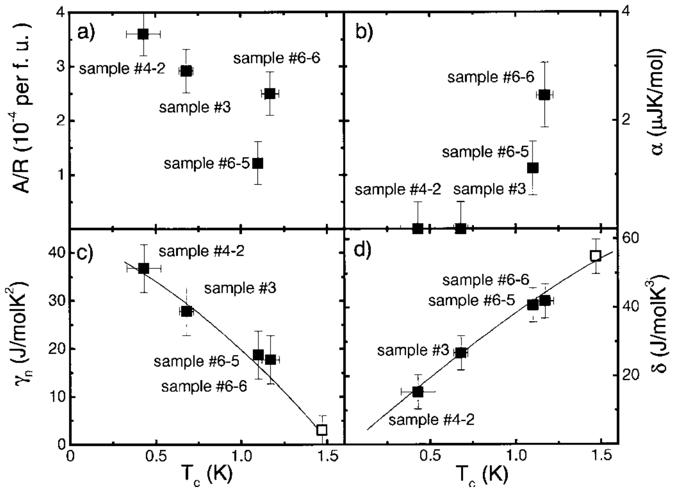

Fig. 3. Results for the fit parameters based on a least-square fit of equation (1) to the data shown in Figure 1 as a function of T_c. (a) the prefactor A of the Schottky-anomaly divided by the molar gas constant R; (b) the coefficient α of the term $C_N = \alpha/T^2$; (c) the coefficient γ_n of the residual normal-conducting contribution and (d) the coefficient δ of $C_s = \delta T^2$. Open symbols in (c) and (d) are read off the data of Maeno *et al.* [19]. Lines are guides for the eye.

with a small impurity contribution. Surprisingly enough, no obvious correlation is found between the concentration of impurities and T_c. In light of the well-known strong sensitivity of T_c of this material to non-magnetic impurities or defects [5], we conclude that the present two-level systems are of somewhat different nature with only little effect on T_c as opposed to the imperfections studied in reference [5]. The level splitting Δ extracted from the fits is in the range $0.25\ \mathrm{K} \leq \Delta \leq 0.35\ \mathrm{K}$ (not shown) which does not provide further insight into the nature of the physical subsystem involved. The observation of Schottky-like contributions to the specific heat of Sr_2RuO_4 is not surprising given the situation in the structurally related high-T_c cuprates. Especially in $YBa_2Cu_3O_{7-\delta}$, low-temperature Schottky contributions to $C(T)$ have been observed frequently. Despite extensive investigations including state-of-the-art material, the origin of C_{Sch} in the cuprates has not been fully understood yet [20].

Figure 3b shows the resulting coefficients α of the (nuclear hyperfine) contribution $C_N = \alpha/T^2$. The so-derived α values are of the order of 1 μJK/mol. To prove whether this contribution is actually of nuclear origin, these numbers have to be compared to those expected for the two possible hyperfine processes which are already present in zero external magnetic field. These are (i) a hyperfine quadrupolar contribution [17] or (ii), a contribution due to the presence of internal magnetic fields at the Ru nucleus.

In fact, NQR-measurements by Ishida *et al.* [2] reveal a splitting of the Ru-nuclear spin-levels due to quadrupolar interactions. Using the quadrupole frequency $\nu_Q \approx 3.3$ MHz observed in reference [2], the corresponding contribution to the specific heat $C_N^Q = \alpha_Q/T^2$ can be evaluated. We find $\alpha_Q = 0.06$ μJK/mol which is one to two orders of magnitude smaller than the values observed.

As for the second possibility, large internal fields of 6–7 T are required to account for the α value found for sample #6-6. The presence of internal magnetic fields of such a magnitude is very unlikely for the following reasons: first of all, they are not seen in NQR measurements [2]. In addition, such fields would require – as a source – an electronic moment at the Ru site of about 0.2 μ_B, assuming a hyperfine coupling constant for Ru of about $30\mathrm{T}/\mu_B$ [2]. This is not found in DC-magnetisation measurements performed on our crystals. Furthermore, the observed large sample-to-sample variations for α are not expected for hyperfine contributions. Therefore, an explanation of the observed low-temperature upturn in C/T in Sr_2RuO_4 in terms of the above hyperfine processes seems unlikely. This calls for an alternative explanation which may also include terms characterised by temperature dependencies slightly different from $1/T^2$.

Figure 3c shows the results for the Sommerfeld-coefficient γ_n, of the residual normal-conducting contribution C_n as a function of T_c for the four samples studied. Obviously, there is a clear correlation between the size of γ_n and T_c or, equivalently, the sample quality. An extrapolation of $\gamma_n(T_c)$ to higher T_c values suggests that $\gamma_n \to 0$ for T_c of about 1.5 K – in agreement with the results by Maeno *et al.* [19] ($\gamma_n = 3 \pm 3$ mJ/molK^2 for $T_c = 1.47$ K). Figure 3d demonstrates that in the same manner as γ_n decreases with increasing T_c, the prefactor δ of the quasiparticle contribution $C_s = \delta T^2$ increases. We find a smooth increase in δ with increasing T_c that extrapolates to the value $\delta_{\max} = 55 \pm 8$ mJ/molK^3 as read off the data of Maeno *et al.* [19] (open symbol in Fig. 3d) for a sample with a T_c of 1.47 K. For a two-dimensional superconductor with line nodes of the energy gap at the Fermi surface, Momono *et al.* [21] were able to connect the coefficient δ with the maximum extension of the gap $\Delta_{\max}$. Neglecting anisotropies of the quasiparticle dispersion within the plane, they found $\Delta_{\max}/k_B = 3.288\ (\gamma_N/\delta)$ with γ_N being the Sommerfeld-coefficient of the normal-state specific heat determined just above T_c (*c.f.* Fig. 1) and k_B the Boltzmann constant. Using $\gamma_N = 40$ mJ/molK^2, the experimentally derived $\delta_{\max}$ corresponds to a $\Delta_{\max}/k_B = 2.4 \pm 0.4$ K.

In conclusion, we have measured the low-temperature specific heat of Sr_2RuO_4 of four samples covering a wide range of T_c values. It is shown that at low temperatures two unexpected contributions add to the specific heat of the superconductor. The first is a low-temperature upturn in C/T which has been shown to be not of nuclear origin. A search for an alternative explanation is needed. A clue to this problem might be provided by studying the Ti-doped counterparts where an even enhanced low-T upturn has been observed in recent specific heat measurements [22]. The second additional contribution is a Schottky-type hump which is most likely due to impurities and has only little effect on T_c. The presence of this contribution is reminiscent to the situation in some high-T_c cuprates, notably $YBa_2Cu_3O_{7-\delta}$.

Owing to these extraneous contributions, a decisive statement on the temperature dependence of C_s is rather difficult. Our results are consistent with a $C_s \propto T^2$, *i.e.* line nodes of the energy gap. An important result of the present investigation is the observation of a low-temperature upturn in the specific heat which is not nuclear in origin. Accordingly, this contribution may have an actual temperature dependence different from a $1/T^2$. Since this contribution grows with decreasing temperatures, it may become considerably large at low temperatures. Therefore, an incorrect subtraction of it may have a strong impact for the temperature dependence extracted for C_s. Therefore, unless this contribution has been unequivocally identified, an exponential temperature dependence of C_s cannot be safely discarded.

Since both additional contributions are not related to the actual sample quality (estimated in an easy way from the size of T_c), it is recommended to check for these effects by performing measurements also in overcritical fields, even for samples of apparently high quality.

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