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# Characteristic crossing point ( $T_* \approx 2.7$ K) in specific heat curves of samples $\text{RuSr}_2\text{Gd}_{1.5}\text{Ce}_{0.5}\text{Cu}_2\text{O}_{10-\delta}$ taken for different values of magnetic field

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## Abstract

Magnetic properties of polycrystalline samples of  $\text{RuSr}_2(\text{Gd}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$ , as-prepared (by solid-state reaction) and annealed (12 h at 845 °C) in pure oxygen at different pressure (30, 62 and 78 atm) are presented. The specific heat and magnetization were investigated in the temperature range 1.8–300 K with a magnetic field up to 8 T. The specific heat,  $C(T)$ , shows a jump at the superconducting transition (with an onset at  $T \approx 37.5$  K). Below 20 K, a Schottky-type anomaly becomes apparent in  $C(T)$ . This low-temperature anomaly can be attributed to splitting of the ground term  $^8S_{7/2}$  of paramagnetic  $\text{Gd}^{3+}$  ions by internal and external magnetic fields. It is found that curves  $C(T)$  taken for different values of magnetic field have the same crossing point (at  $T_* \approx 2.7$  K) for all the samples studied. At the same time,  $C(H)$  curves taken for different temperatures have a crossing point at a characteristic field  $H_* \approx 3.7$  T. These effects can be considered as a manifestation of the crossing point phenomenon which is supposed to be inherent for strongly correlated electron systems.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The, so called, crossing point phenomenon is one of the interesting and still puzzling effects in strongly correlated electron systems (see [1–4] and references therein). A typical example of this effect is the temperature behavior of specific heat curves  $C(T, X)$  taken at different values of a thermodynamic variable  $X$  (such as magnetic field  $H$  or pressure  $P$ ): the curves cross at one temperature  $T_*$ . This type of effect was found not only for thermodynamic but for dynamic quantities as well (for example, for frequency dependent optical conductivity). More generally this familiar effect is termed the *isosbestic point* [4].

Experiments have revealed *isosbestic points* in different systems of strongly correlated fermions such as liquid  $\text{He}^3$ , heavy-fermion compounds and others [1–4]. In particular, the crossing point in  $C(T, H)$  curves was found in the heavy-fermion compound  $\text{CeCu}_{5.5}\text{Au}_{0.5}$  [5], semimetallic  $\text{Eu}_{0.5}\text{Sr}_{0.5}\text{As}_3$  [6], superconducting cuprate  $\text{GdBa}_2\text{Cu}_4\text{O}_8$  [7] and manganite  $\text{NdMnO}_3$  [8]. Nevertheless, the general reasons and conditions for realization of *isosbestic points* are still not so clear. The known theoretical considerations [1–4] are based on rather different approaches. Available relevant experimental data can be considered as meager, therefore further experimental findings of this phenomenon in different systems should be helpful for an understanding of its nature.

In this study, the crossing point effect is revealed in  $C(T, H)$  curves of polycrystalline perovskite-like  $\text{RuSr}_2(\text{Gd}_{1.5}$

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$\text{Ce}_{0.5}\text{Cu}_2\text{O}_{10-\delta}$  (Ru1222–Gd). This compound is from the known family of ruthenocuprates  $\text{RuSr}_2\text{R}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10-\delta}$  (where  $\text{R} = \text{Gd}, \text{Eu}$ ) [9–12]. This family within the range  $0.4 \leq x \leq 0.8$  shows superconductivity with  $T_c$  up to  $\approx 50$  K for  $x = 0.5$ – $0.6$ . Below  $T_{\text{WF}} = 80$ – $100$  K, indications of a weak-ferromagnetic order are found. It is believed, on these grounds, that these compounds are magnetic superconductors. The superconductivity is associated with the  $\text{CuO}_2$  planes, while the magnetic order is thought to be connected with the  $\text{RuO}_2$  planes (see more in reviews [9–12]).

In the following we shall present and discuss the crossing point phenomenon in Ru1222–Gd found in this study together with an indispensable consideration of some specific features of the magnetic state of this compound. To reveal and compare paramagnetic effects of different rare-earth components, the properties of samples of  $\text{RuSr}_2(\text{Eu}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$  (Ru1222–Eu) are considered briefly as well.

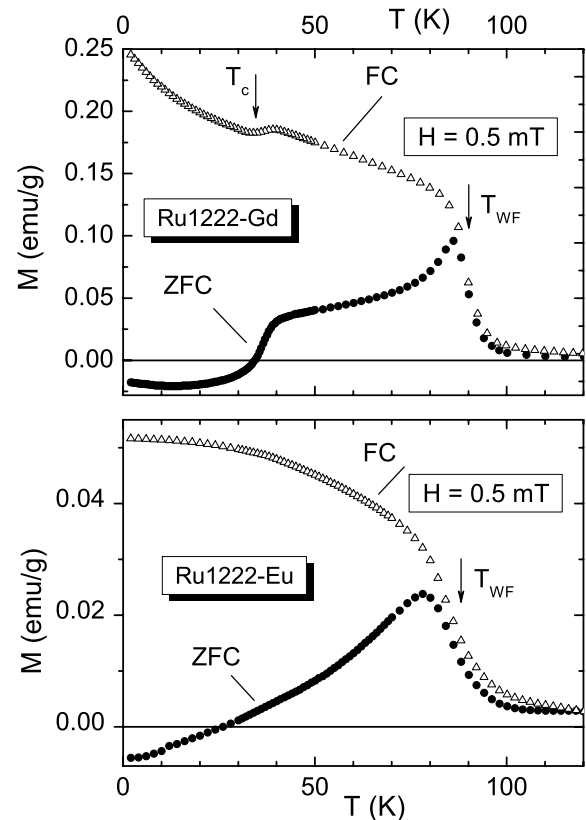
## 2. Results and discussion

### 2.1. Magnetic characterization of the samples

The samples of Ru1222–Gd and Ru1222–Eu were prepared by a solid-state reaction method [9]. Some of them were set aside (as-prepared samples), while others were annealed in pure oxygen at different pressures. The samples of Ru1222–Gd were annealed for 12 h in 30, 62, and 78 atm of pure oxygen at  $845^\circ\text{C}$ ; whereas, those of Ru1222–Eu were annealed for 24 h in 50 and 100 atm of pure oxygen at  $800^\circ\text{C}$ . The samples were polycrystalline with a grain size of a few micrometers. They were characterized by resistivity, thermoelectric power, magnetization and specific heat measurements, which were in part reported in [13, 14]. It was found there that superconductivity is affected by granularity and intergrain Josephson coupling.

In this section we present some general magnetic properties of the samples studied with an emphasis on paramagnetic effects of rare-earth ions. The measurements were made with Quantum Design devices (PPMS and SQUID magnetometer). The temperature behavior of magnetization,  $M(T)$ , for the cases of essentially low and appreciably high magnetic fields (figures 1 and 2) reveals important features of the complicated magnetic state of these compounds. It is clearly seen that for both Ru1222–Gd and Ru1222–Eu a magnetic transition takes place when the temperature is lowered below  $T_{\text{WF}} \approx 90$  K (figure 1). This is believed to be the transition to a weak-ferromagnetic state determined by Ru ions [9–11]. The large difference between the FC and ZFC curves is likely determined either by high magnetic anisotropy or spin-glass effects. The magnetic order induced in ruthenocuprates by  $\text{RuO}_2$  planes is, however, still unclear [9–12, 15–18] and will not be discussed in detail here. We shall only dwell briefly on the contribution of paramagnetic magnetic moments of rare-earth components to the magnetization of ruthenocuprates.

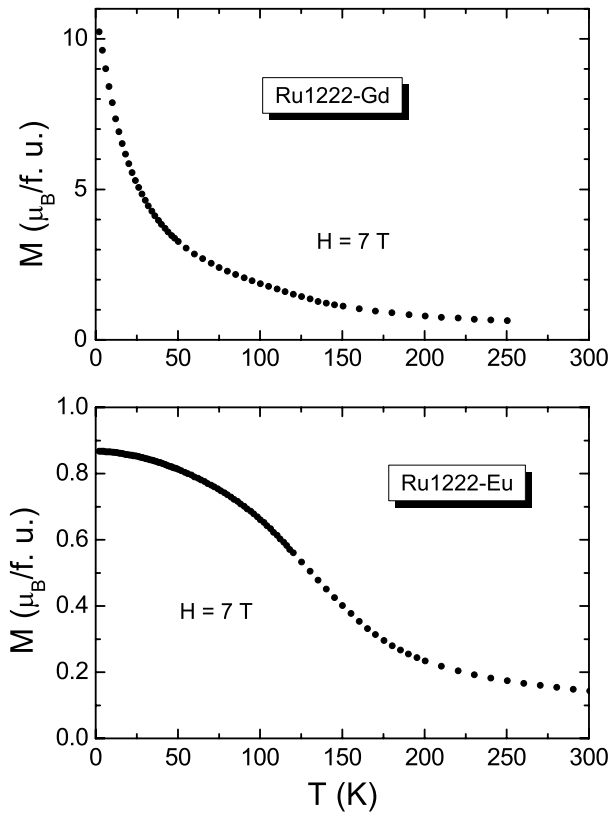
It was known long ago [19, 20] that the paramagnetic properties of trivalent rare-earth ions in chemical compounds are almost identical to those of quasi-free non-interacting ions.



**Figure 1.** Temperature behavior of specific magnetization (field-cooled (FC) and zero-field-cooled (ZFC) curves) at field  $H = 0.5$  mT for samples of Ru1222–Gd ( $\text{RuSr}_2(\text{Gd}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$ , annealed 12 h at  $845^\circ\text{C}$  in pure oxygen at a pressure of 78 atm) and Ru1222–Eu ( $\text{RuSr}_2(\text{Eu}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$ , as-prepared state). The temperature of the intragrain superconducting transition  $T_c \approx 34$  K is indicated by an arrow on  $M(T)$  curve for Ru1222–Gd. The temperature  $T_{\text{WF}}$ , for the presumed transition to a weak-ferromagnetic state in the Ru magnetic subsystem, is marked by arrows for both samples. Other features of the  $M(T)$  curves are discussed in the main text.

In both cases paramagnetism is determined by low-lying states of 4f electrons. The effective moment of a rare-earth ion is determined by the quantum numbers  $L, S, J$  and according to Hund's rule is  $\mu_{\text{eff}} = g[J(J+1)]^{1/2}$ , where  $g$  is the Landé factor. For the  $\text{Gd}^{3+}$  ion (ground state  $^8S_{7/2}$  with  $L = 0, S = J = 7/2$ )  $\mu_{\text{eff}}$  is therefore expected to be  $7.94 \mu_B$ , in agreement with experiment [19]. For the  $\text{Eu}^{3+}$  ion (ground state  $^7F_0$  with  $L = 3, S = 3, J = 0$ ) a significant deviation from Hund's rule (which predicts the effective moment to be zero) is found in experiment [19]. In particular at room temperature  $\mu_{\text{eff}} > 3 \mu_B$  is observed. The reason is that for  $\text{Eu}^{3+}$  ions at high enough temperature the separation of their ground 4f state (with  $J = 0$ ) from higher levels is comparable to  $kT$ , so that an additional contribution to susceptibility appears [19]. For fairly low temperatures, however, the effective paramagnetic moment for  $\text{Eu}^{3+}$  ions is expected to be zero [19].

It can be expected from the aforesaid that  $\text{Gd}^{3+}$  ions should give a considerable contribution to the total magnetization of ruthenocuprates, especially at low temperature; whereas, a significant contribution of paramagnetic moments

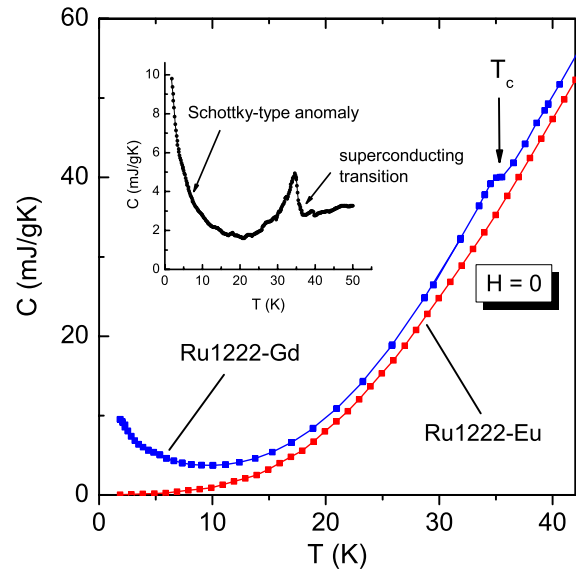


**Figure 2.** Temperature behavior of magnetization (in  $\mu_B/f.u.$ ) at field  $H = 7$  T for samples Ru1222–Gd ( $\text{RuSr}_2(\text{Gd}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$ , annealed 12 h at  $845^\circ\text{C}$  in pure oxygen at pressure 78 atm) and Ru1222–Eu ( $\text{RuSr}_2(\text{Eu}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$ , annealed 24 h at  $800^\circ\text{C}$  in pure oxygen at pressure 100 atm).

of  $\text{Eu}^{3+}$  is unlikely. Temperature dependences of magnetization (figures 1 and 2) correspond to the expected behavior. On the whole, the specific magnetization is much higher in the Gd sample as compared with that of the Eu sample. In particular,  $M \approx 10.5\mu_B/f.u.$  at  $T = 2$  K and  $H = 7$  T for Ru1222–Gd (figure 2). At the same time, the magnetization of the Ru1222–Eu sample is about  $0.9\mu_B/f.u.$  with the same conditions (figure 2).

For both low and high magnetic fields,  $M(T)$  increases as  $T \rightarrow 0$  for the Ru1222–Gd sample, displaying the paramagnetic behavior of Gd ions. In contrast to this,  $M(T)$  saturates at low temperature for the Ru1222–Eu sample. It is evident for the latter case that the contribution of Eu ions to the total magnetization is negligible in the low-temperature range where the magnitude of  $M$  is determined solely by the magnetic contribution of the Ru subsystem.

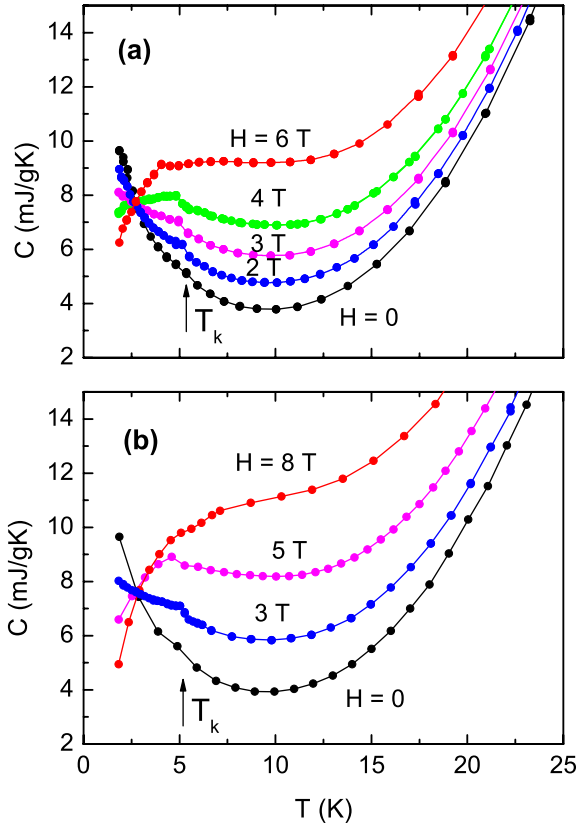
Superconductivity also shows itself to be somewhat different in the  $M(T)$  curves for the Gd and Eu samples. In both samples the diamagnetic response below the superconducting transition can be seen in the ZFC curves (figure 1), but an appropriate feature in the FC curve is evident only for Ru1222–Gd sample. With decreasing temperature when  $T$  approaches zero, the diamagnetic response of the Ru1222–Eu saturates; whereas, that of Ru1222–Gd decreases (figure 1).



**Figure 3.** Low-temperature behavior of total specific heat at zero magnetic field for samples Ru1222–Gd ( $\text{RuSr}_2(\text{Gd}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$ , annealed 12 h at  $845^\circ\text{C}$  in pure oxygen at pressure 78 atm) and Ru1222–Eu ( $\text{RuSr}_2(\text{Eu}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$ , annealed 24 h at  $800^\circ\text{C}$  in pure oxygen at pressure 100 atm). The difference between the  $C(T)$  curves of Ru1222–Gd and Ru1222–Eu (inset) shows more clearly the  $\lambda$ -like feature at the superconducting transition and a Schottky-type anomaly below 20 K.

Specific heat measurements have been performed for all of the Ru1222–Gd samples (as-prepared and annealed at different oxygen pressure). All of these samples have two pronounced features (figure 3) in the low-temperature part of  $C(T)$  curves: (1) the jump at the superconducting transition, and (2) the upturn below 20 K (Schottky-type anomaly). It was found [13, 14] that, although resistive superconducting transition depends strongly on the intergrain connection determined by oxygen annealing, the position of the jump in  $C(T)$  at the superconducting transition is the same for all samples studied and in this way reflects the bulk properties of the compound.

The Eu samples displayed smooth  $C(T)$  dependences, which were identical for all Eu samples studied. The curves were of the Debye type without any low-temperature magnetic anomaly or jump at the superconducting transition. The former is ascribed to the non-magnetic nature of Eu ions at low temperature; whereas, the latter is evidently determined by stronger intergrain disorder in the Eu samples as compared with the Gd samples [21]. The resistive superconducting transitions in the Eu samples are much broader and the normal-state resistivity is approximately ten times higher than those in the Gd samples [21]. It is known [22] that a sufficiently strong decoupling between grains causes smearing and disappearance of the superconducting feature (jump) in  $C(T)$  curves. It should be noted that no feature in the temperature dependence of the heat capacity,  $C(T)$ , associated with the magnetic transition at  $T \approx 90$  K in the Ru magnetic subsystem is found in this study. This can be attributed to the absence of long-range magnetic order in this subsystem at the transition point due to magnetic inhomogeneities. It is also possible that this



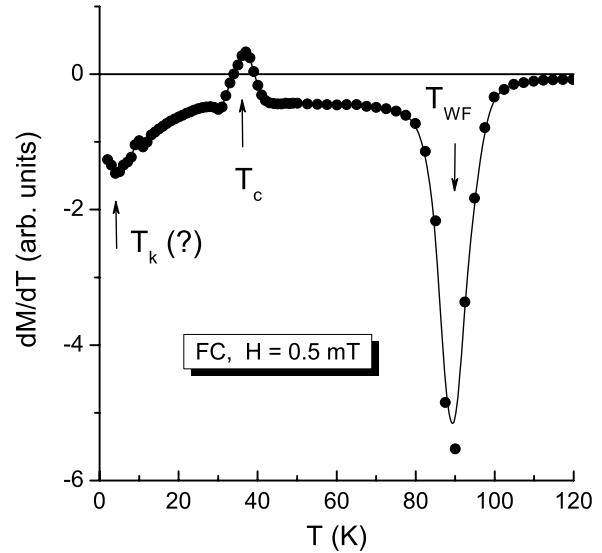
**Figure 4.** Low-temperature dependences of total specific heat,  $C$ , taken at different values of applied magnetic fields for two samples of  $\text{RuSr}_2(\text{Gd}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$ : (a) annealed 12 h at  $845^\circ\text{C}$  in pure oxygen at pressure 78 atm, and (b) as-prepared state. In both cases the  $C(T)$  curves cross at the same temperature  $T_* \approx 2.7\text{ K}$  (at the same specific heat value  $C_* = 7.7\text{ mJ g}^{-1}\text{ K}^{-1}$ ), revealing the crossing point phenomenon. Arrows indicate the temperature  $T_k$  of a kink in the  $C(T)$  curves, which is about 5.4 K for  $H = 0$  and moves to a lower temperature with increasing field.

feature is just too weak to be seen on the background lattice contribution to specific heat at this rather high temperature.

The absence of magnetic and superconducting anomalies in the  $C(T)$  curves for Ru1222–Eu makes it possible to obtain the part of  $C(T)$  without lattice contribution [13] by subtraction of the  $C(T)$  curves for Eu from that of the Gd samples, as shown in the inset of figure 3. This shows more clearly the  $\lambda$ -like feature at the superconducting transition and the Schottky-type anomaly below 20 K in the Gd sample. The low-temperature Schottky-type anomaly can be attributed to splitting of the ground term  $^8\text{S}_{7/2}$  of paramagnetic  $\text{Gd}^{3+}$  ions by internal and external magnetic fields, as discussed in more detail in [13].

### 2.2. Crossing point effect

It is found in this study that  $C(T)$  curves for Ru1222–Gd samples taken at different values of applied magnetic field cross at the same temperature (the crossing temperature)  $T_* \approx 2.7\text{ K}$  and specific heat value  $C_* = 7.7\text{ mJ g}^{-1}\text{ K}^{-1}$  (figure 4). This takes place for each of the Ru1222–Gd samples (as-prepared and annealed at different oxygen



**Figure 5.** Derivative  $dM/dT$  (of the FC  $M(T)$  curve at  $H = 0.5\text{ mT}$ , shown in figure 1) for the sample of  $\text{RuSr}_2(\text{Gd}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$ , annealed 12 h at  $845^\circ\text{C}$  in pure oxygen at pressure 78 atm. The arrows indicate temperatures  $T_{WF}$ ,  $T_c$  and  $T_k$  of the phase transitions discussed in the text.

pressure). Contrastingly, the  $C(T)$  curves of Ru1222–Eu with non-magnetic Eu ions were found to not depend on the magnetic field (up to 8 T), as can be expected from the discussion above.

Above the crossing point some clear kink in the  $C(T)$  curves occurs in the temperature range of the Schottky-type anomaly (figure 4). This kink is positioned at  $T_k \approx 5.4\text{ K}$  for  $H = 0$ , but with increasing field it shifts to lower temperature and seems to be smeared for a sufficiently large field (figure 4). In the low-field  $M(T)$  curves (upper panel of figure 1), nothing uncommon can be seen in this temperature range, but in the derivative  $dM/dT$  (figure 5), in addition to the very strong features at the superconducting and magnetic transitions at  $T_c$  and  $T_{WF}$ , a weak but quite clear peculiarity is seen at  $T \approx 5\text{ K}$ , that perhaps pertains to  $T_k$ .

The appearance and behavior of  $T_k$  with increasing field is suggestive of a transition to an antiferromagnetic state for the  $\text{Gd}^{3+}$  ion subsystem at low temperature. This type of transition is ubiquitous in high- $T_c$  cuprates with rare-earth components [23]. For example, it is found in Gd cuprates that antiferromagnetic ordering of  $\text{Gd}^{3+}$  ions takes place at a  $T_N$  of 2.3–2.4 K for double  $\text{CuO}_2$  layer compounds; whereas, for single-layer ones a higher  $T_N$  (up to 6.6 K) is revealed [7, 24]. In the related ruthenocuprate  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  (the Ru1212-type phase)  $T_N = 2.5\text{ K}$  is found [25].

Perhaps the decrease in the superconducting diamagnetic response with decreasing temperature in Ru1222–Gd (figure 1) might be connected with some kind of magnetic ordering in the  $\text{Gd}^{3+}$  magnetic subsystem. Unfortunately, the nature of magnetic order induced in the Ru1222 ruthenocuprates by  $\text{RuO}_2$  planes is still not clear [9–12, 15–18]. This also hampers the determination of the exact nature of the low-temperature magnetic ordering in the Gd ion subsystem. Another difficulty is that, to date, only samples of Ru1222 prepared by solid-state

reaction method have been studied. These samples usually contain different impurity phases [15–17, 26, 27]; thus it cannot be ruled out that the distinct but rather weak feature in  $C(T)$  at  $T = T_k$  may actually be associated with some magnetic impurity phase. For example, in the ruthenocuprate  $\text{RuSr}_2(\text{Gd}_{1.3}\text{Ce}_{0.7})\text{Cu}_2\text{O}_{10-\delta}$  (which is close in composition to that studied in this work) an impurity phase (5%) of  $\text{Sr}_2\text{GdRuO}_6$  was found [15] which showed antiferromagnetic ordering of  $\text{Gd}^{3+}$  ions near 3 K.

Now let us return again to the subject of the crossing point. We have found that in addition to the crossing point at  $T_* \approx 2.7$  K in the  $C(T)$  curves (taken at different  $H$ ) a crossing also takes place in the  $C(H)$  curves (taken at different temperatures). In this case the curves cross at  $H_* \approx 3.7$  T (figure 6). In both cases crossing takes place at the same value  $C_* = 7.7$  mJ g<sup>-1</sup> K<sup>-1</sup>. Figure 6(b) clearly suggests that  $C$  does not depend on  $H$  at  $T = T_* \approx 2.7$  K (dashed line). On the other hand it is temperature independent at  $H = H_* \approx 3.7$  T (dashed line in figure 6(a)). In either case a constant value of  $C$ ,  $C_* = 7.7$  mJ g<sup>-1</sup> K<sup>-1</sup> is observed.

The crossing point effect is considered [1–4] as some type of universality for strongly correlated electron systems, but no unified mechanism for this phenomenon is proposed. Only some general reasons and prerequisites for its occurrence have been formulated. It is believed, for example [1–4], that the crossing (*isobestic*) point occurs in systems which are close to some quantum or second-order phase transition, or in systems with some magnetic instability, so that the properties of such a system are rather sensitive to thermodynamic variables (such as temperature, pressure, magnetic field).

It is asserted [4], among other suggestions, that the crossing point should become apparent in a system which is a superposition of two (or more) components, like that in the known Gorter–Casimir two-fluid model of superconductivity. The total density of these components, depending, for example, on  $T$  and  $H$ , is constant,

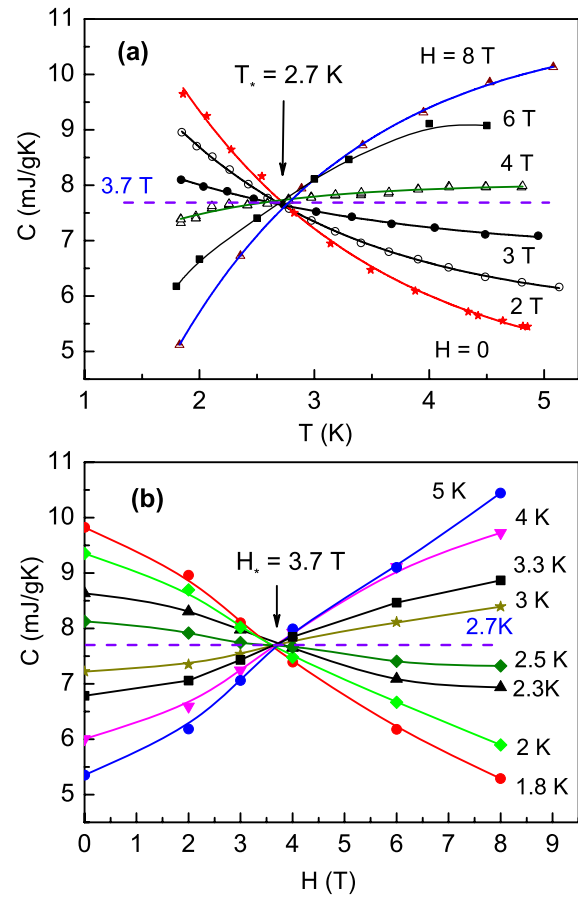
$$n = n_1(T, H) + n_2(T, H) = \text{const.} \quad (1)$$

Following the general concept of such a ‘two-fluid’ model [4], some function  $f(T, H)$ , describing the properties of this system, can be written as

$$f(T, H) = n_1(T, H)f_1(H) + n_2(T, H)f_2(H). \quad (2)$$

In this case the crossing point of curves for different temperatures  $T$  should occur at a single point  $H_*$  if  $f_1(H_*) = f_2(H_*)$ . This ‘two-fluid’ approach is perhaps relevant for the crossing point in  $C(T, H)$  curves below the superconducting transition temperature found in the cuprate  $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$  [28], where the crossing takes place at  $T \approx 0.5T_c$ .

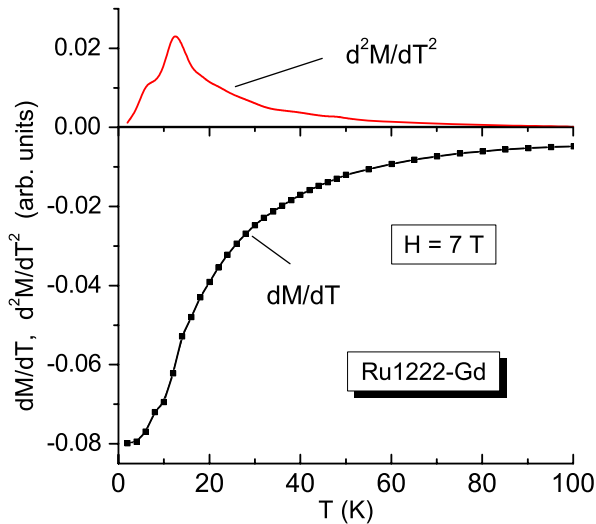
In considering the crossing effect in the  $C(T, H)$  curves what motive force for the strong magnetic field dependence of the specific heat should first be taken into account? In the case of the Gd ruthenocuprates considered in this study, the motive force is connected not with superconductivity, but with splitting of the ground term  $^8S_{7/2}$  of paramagnetic  $\text{Gd}^{3+}$  ions by internal and external magnetic fields [13]. According to



**Figure 6.** Temperature and magnetic field dependences of specific heat,  $C$ , taken, respectively, at different values of applied magnetic field (a) or temperature (b). All data shown are for the sample of  $\text{RuSr}_2(\text{Gd}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$ , annealed 12 h at 845 °C in pure oxygen at a pressure 78 atm, except the data for  $H = 8$  T, which is taken for the as-prepared sample. The  $C(T)$  or  $C(H)$  curves cross at the temperature  $T_* \approx 2.7$  K (a) or magnetic field  $H_* = 3.7$  T (b) for the same value  $C_* = 7.7$  mJ g<sup>-1</sup> K<sup>-1</sup>, demonstrating the crossing point phenomenon.

Kramers’ theorem [20], the degenerate ground term can be split into four doublets in tetragonal symmetry. In particular, internal molecular fields can arise in the ruthenocuprate from both the Gd and Ru sublattices and can coexist with superconductivity. Even though a direct Gd–Gd exchange interaction is unlikely, these ions can be magnetically polarized by the 4d–4f interaction. Generally, the Schottky term in the specific heat for compounds with  $\text{Gd}^{3+}$  ions should be attributed to splitting of all four doublets, although actually only some of them make the dominant contribution to the effect.

In the simplest case a Schottky term in the specific heat is determined by properties of a two-level system [29]. Paramagnetic ions in a solid have magnetic dipole moments ( $\mu$ ). To a first approximation, these do not interact with each other but can respond to an applied external magnetic field. In a magnetic field each dipole can exist in one of two states aligned with the field (spin up) or antialigned (spin down). Spin up ( $\uparrow$ ) and spin down ( $\downarrow$ ) dipoles have an energy  $-\mu H$  and  $+\mu H$ , respectively. The population of these discrete energy



**Figure 7.** Derivatives  $dM/dT$  and  $d^2M/dT^2$  of the  $M(T)$  curve at  $H = 7$  T (shown in figure 2) for the sample of  $\text{RuSr}_2(\text{Gd}_{1.5}\text{Ce}_{0.5})\text{Cu}_2\text{O}_{10-\delta}$ , annealed 12 h at  $845^\circ\text{C}$  in pure oxygen at pressure 78 atm.

levels depends on the temperature and applied field. This gives a contribution to the specific heat in a solid known as the Schottky anomaly [29], which is usually seen only at low temperature, where other contributions are sufficiently small.

It should be mentioned that the total number,  $N$ , of magnetic dipoles in the two-level system can be presented as the sum of two temperature and magnetic field dependent components  $N = n_\uparrow(T, H) + n_\downarrow(T, H) = \text{const}$ , where  $n_\uparrow(T, H)$  and  $n_\downarrow(T, H)$  are the numbers of the spin up and spin down dipoles. This relation is similar to equation (1), so that the ‘two-fluid’ approach [4] is apparently applicable to a degree in the two-level system as well.

The Schottky-type anomaly in the  $C(T, H)$  curves is by itself only a background for the crossing effect found in this study, like that previously seen in  $\text{NdMnO}_3$  [8]. For a deeper insight into this phenomenon the thermodynamic approach [1] can be helpful. It can be suggested, rather safely, that within the low-temperature range, where the crossing phenomenon takes place, the magnetic contribution to specific heat is dominant. The expression for the specific heat at constant  $H$  is [20]  $C_H = T(\partial S/\partial T)_H$ . Any crossing of specific heat curves  $C_H(T, H)$  means that [1]

$$\left. \frac{\partial C_H(T, H)}{\partial H} \right|_{T_*(H)} = T_*(H) \left. \frac{\partial^2 M(T, H)}{\partial T^2} \right|_{T_*(H)} = 0, \quad (3)$$

where the magnetization  $M$  is the conjugate thermodynamic variable for the field  $H$ . Only if  $T_*$  is independent of  $H$ , will all  $C_H(T, H)$  curves intersect in one point demonstrating a true crossing effect like that shown in figure 6.

It follows from equation (3) that the crossing occurs at the temperature  $T_*$  where  $\partial^2 M(T, H)/\partial T^2 = 0$ , that is  $M(T, H)$  must have some type of turning point. Figure 7 shows that  $dM/dT$  at  $H = 7$  T tends to some constant value with decreasing temperature, while  $d^2M/dT^2$  tends to zero in this temperature range. We have found that  $d^2M/dT^2$

becomes approximately zero for  $T$  below 3 K. More precise determination of the point where  $d^2M/dT^2 = 0$  is difficult due to the statistical uncertainty of the second derivative. In any case, however, results of this study substantially support the theoretical prediction of [1].

It is seen in figure 6 that at  $H = H_*$  the specific heat is temperature independent, that is equal to the constant value  $C_* = 7.7 \text{ mJ g}^{-1} \text{ K}^{-1}$ ,

$$C_{H_*}(T) = T(\partial S/\partial T)_{H_*} = C_*. \quad (4)$$

From this it follows that  $S_{H_*} = C_* \ln T + A$ , where  $A$  is a constant. It is also evident that at  $H \neq H_*$  except for the logarithmic term, some polynomial function of  $T$  should be added for the approximation of  $S_H(T)$ .

In summary, rather thorough models of *isosbestic points* have been developed for conjugate variables  $P$  and  $-V$ . Some models were developed for strongly correlated electrons in the frame of the Hubbard model [1–4]. We hope that results of this study will promote development of an adequate model for crossing points in  $C(T, H)$  curves for magnetic systems undergoing a transition from the classical to quantum behavior in  $C(T, H)$  with decreasing temperature.

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