Spin-glass-like behaviour in IrSr$_2$RECu$_2$O$_8$ (RE = Sm and Eu)

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A R T I C L E   I N F O

A B S T R A C T

We report the results of magnetic and specific heat measurements on the 1212-type compounds IrSr$_2$RECu$_2$O$_8$ with RE = Sm and Eu, prepared by high-pressure and high-temperature synthesis. The magnetic susceptibility of these compounds shows a large difference in the temperature dependence of the magnetization measured under zero-field-cooled and field-cooled conditions below 87 and 71 K, respectively, and upon further cooling below ~10 K substantial maxima are observed too. Further AC susceptibility measurements support a glassy behaviour in lower magnetic transitions whereas the specific heat measurements do not show the typical long-range ordering commonly displayed in ferro, ferri or antiferromagnetic transitions. Hysteresis loops suggest the presence of magnetic clusters in the otherwise paramagnetic zone, indicating that these compounds probably display a reentrant spin-glass transition. Results are presented and discussed.

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1. Introduction

The discovery of coexistence of superconductivity and magnetism in the so-called ruthenates or ruthenocuprates [1], RuSr$_2$RE Cu$_2$O$_8$ (RE = rare-earth element and Y), has attracted the interest of the research community in the last 10 years [2–6]. At room pressure, Sm, Eu and Gd are the only RE elements that accept to enter into the 1212-type structure [1]. For the rest of the family member high-pressure and high-temperature techniques are needed [7]. Moreover, the pressure synthesis conditions of these 1212 compounds bear a novel and unexpected relation with the rare-earth size that appears to have a gaussian functionality [8,9]. While the yttrium compound shows the highest superconducting critical temperature in this family, $T_C = 51$ K [7], the gadolinium one has been the most studied material due to the fact that it can be prepared at room pressure.

An important number of *partial* substitutions on the different lattice sites have been performed in order to study its effect on the superconducting temperature or, in many cases, to improve the delicate balance between superconducting and magnetic properties [3–5,10–13]. It is worth noting that replacing Ru by either Sn [3] or Cu [4] seems to be the only effective substitution to increase T_C. The *complete* substitution of Ru by other transition metal has been tried less frequently since, in many cases, the 1212 system is unstable at room pressure conditions [14–16]. We have recently obtained a series of phases in which Ru has been completely replaced by iridium (IrSr$_2$RECu$_2$O$_8$) using high-pressure and high-temperature synthesis. This family shows a wide range of magnetic behaviour mainly attributed to the rare-earth ions anisotropy. For instance, the IrSr$_2$GdCu$_2$O$_8$ compound presents ferrimagnetism [15] and metamagnetic behaviour is observed in the IrSr$_2$TbCu$_2$O$_8$ compound [16]. This systematic change of the M-1212 properties with the lanthanide contraction has also been observed in the MoSr$_2$RECu$_2$O$_8$ system [17]. Felner and co-workers have found paramagnetism in the samples with light RE ions (La–Nd), antiferromagnetism (AFM) of the Mo sublattice in the intermediate range (Sm–Tb) and finally, coexistence of AFM and superconductivity for the heavy RE ions (Ho–Tm and Y).

In this paper we report the structural and microstructural characterization as well as the thermal and magnetic properties of the Sm and Eu Ir-1212 compounds. Two magnetic transitions were observed by DC susceptibility measurements for each compound. The specific heat signal does not show evidence typical of long-range magnetic ordering; however, AC susceptibility and the hysteresis loop in the paramagnetic range support the developing of magnetic clusters which seem to indicate that a reentrant spin-glass (RSG) behaviour is present, at low temperature, in both systems.

2. Experimental

The IrSr$_2$SmCu$_2$O$_8$ and IrSr$_2$EuCu$_2$O$_8$ compounds were prepared at pressure up to 6 and 3 GPa, and 1373 and 1173 K temperatures, respectively. Experimental synthesis details can be

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found in the previously reported ruthenates [9], chromates [14] and iridates [15,16].

Samples were characterized by X-ray powder diffraction (XRD) performed in a Philips X'Celerator diffractometer (Cu $K\alpha_1$-radiation, $\lambda = 1.54056$ Å). The XRD pattern was refined with the Rietveld procedure using the Fullprof_Suite program [18].

Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) were performed on a Jeol JEM 3000EX microscope. Sample compositions were checked by EDS (Link Pentafet 5947 Model, Oxford Microanalysis Group) by *in situ* observations.

DC magnetic susceptibility measurements were performed over the temperature range 1.9–300 K, using a Squid Quantum Design XL-MPMS magnetometer in zero-field-cooling (ZFC) and field-cooling (FC) conditions, while AC measurements were made in the same temperature range, at 1, 100 and 1000 Hz frequencies and 3.5 Oe amplitude. Specific heat measurements were performed using a Quantum Design PPMS.

3. Results and discussion

3.1. Structure and microstructural characterization

Though the samples are nearly single phases, a few weak extra reflections from $SrCO_3$ (13.6(4) wt%) and the disordered $(Sr_2Eu)(Cu_2Ir)O_{9-\delta}$ single perovskite (11.0(3) wt%) [19] are seen in the $IrSr_2EuCu_2O_8$ XRD pattern (Fig. 1a). The disordered $(Sr_2Sm)(Cu_2Ir)O_{9-\delta}$ single perovskite (12 wt%) is the only significant impurity apparent in the $IrSr_2SmCu_2O_8$ XRD pattern (data not shown).

The X-ray diffraction patterns confirm that both samples adopt an M-1212-type perovskite structure, unit cell $a_p \times a_p \times 3a_p$ (S.G. $P4/mmm$), where a_p is the basic perovskite unit cell parameter ($a_p \sim 3.8$ Å). The lattice parameters of $IrSr_2SmCu_2O_8$ and $IrSr_2EuCu_2O_8$ have been determined to be $a = 3.8686$, 3.8486 Å and $c = 11.4196$, 11.5472 Å, respectively, and are in line with those expected for these M-1212-type compounds [14,15,20].

On the other hand, there is clear experimental evidence, by means of SAED (inset of Fig. 1b), for superlattice spots defining a so-called diagonal cell, i.e. $\sqrt{2}a_p \times \sqrt{2}a_p \times 3a_p$ (S.G. $P4/mbm$) [15,16,21,22]. Therefore, a "simple" cell, $\sim a_p \times a_p \times 3a_p$, is supported by XRD [14,20] while a "diagonal" one, $\sim \sqrt{2}a_p \times \sqrt{2}a_p \times 3a_p$, by SAED [15,21,22]. This situation, which appears to be contradictory, is due to the longer coherence length required in X-ray diffraction as compared with electron diffraction [23].

The high-resolution transmission electron microscopy (HRTEM) observation of local ordering (Fig. 1b) is in agreement with HRTEM observations of multiple misoriented domains previously reported [15,21,22]. As a resume of these observations, one can conclude in the light of the microstructural study, that the vast majority of the crystals are formed by three subsets of microdomains in which the unit cell is $\sim a_p \sqrt{2} \times a_p \sqrt{2} \times 3a_p$ and the long $3a_p$ c-axis is oriented, in each set, along one of the three space directions.

3.2. Magnetic properties

3.2.1. Observations

Figs. 2 and 3 show the temperature dependence of the susceptibility from 300 down to 2 K measured at ZFC and FC mode at 10 Oe for $IrSr_2SmCu_2O_8$ and $IrSr_2EuCu_2O_8$ compounds, respectively. It is worth noting that the above mentioned impurities have no influence in the magnetic measurements of the 1212 compounds since, susceptibility measurements per-
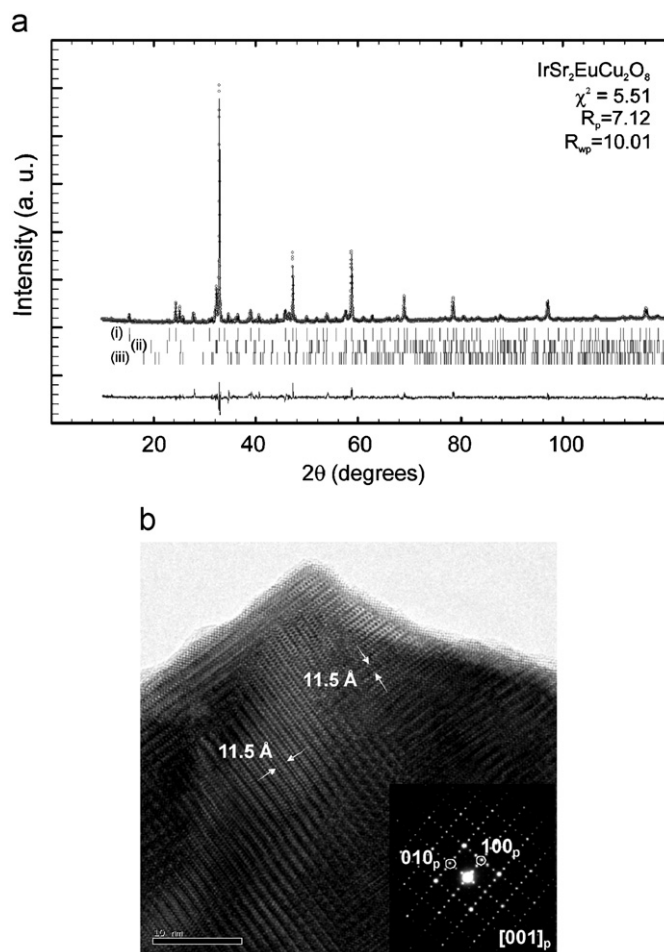

Fig. 1. (a) Rietveld refinement fit of the XRD pattern for (i) $IrSr_2EuCu_2O_8$. (ii) $(Sr_2Eu)(Cu_2Ir)O_{9-\delta}$ single perovskite and (iii) $SrCO_3$ are present as impurities. Inset shows the agreement factors of the refinement. (b) Electron micrograph of a crystal showing two subsets of domains (a and b-axes) of the $IrSr_2EuCu_2O_8$ sample. Inset shows the corresponding SAED along the $[001]_p$ zone axis.
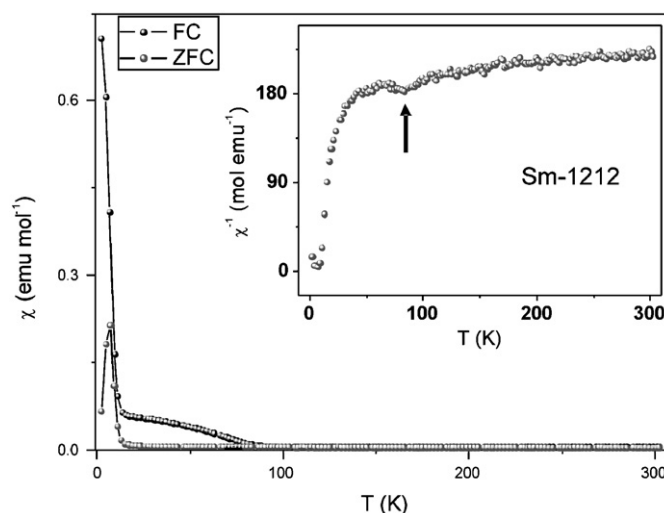

Fig. 2. Magnetic susceptibility (FC and ZFC plots) as a function of temperature of the Sm sample. In the inset, the reciprocal ZFC susceptibility plot allows one to detect the magnetic transition, marked with an arrow.
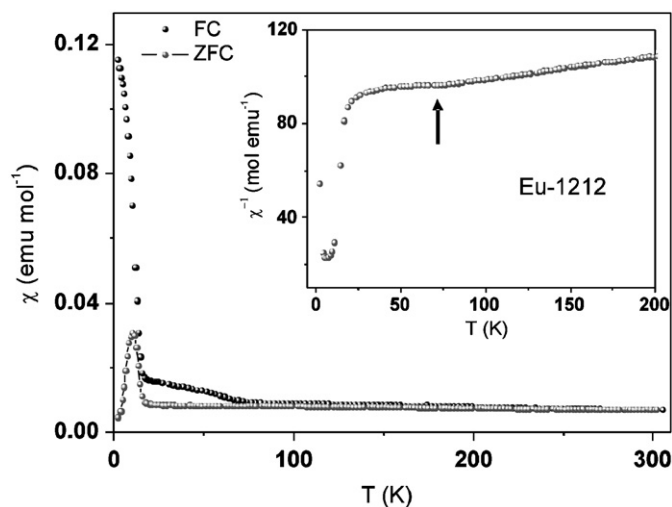
Fig. 3. Magnetic susceptibility (FC and ZFC plots) as a function of temperature of the Eu sample. In the inset, the reciprocal ZFC susceptibility plot allows one to detect the magnetic transition, also marked with an arrow.

Fig. 4. Hysteresis loops at different temperatures of the Sm sample. Hysteresis at 2 K and non-linearity at 150 K can be appreciated in the inset.

Fig. 5. Hysteresis loops at different temperatures of the Eu sample. Hysteresis at 2 K and non-linearity at 150 K can be appreciated in the inset.

formed in the $(Sr_2RE)(Cu_2Ir)O_{9-\delta}$ perovskites clearly suggest paramagnetic behaviour [19]. The divergence of the temperature dependence between the ZFC and FC magnetization seems to indicate a magnetic transition at 87 and 71 K temperatures, respectively. Although no maxima are observed in the corresponding ZFC plots at these temperatures, a careful observation of the corresponding inverse susceptibility ZFC plots (inset of Figs. 2 and 3) shows a rather broad minimum at the transition temperatures. In addition, when the temperature is decreased, further apparent maxima are observed at 7 and 10 K for the Sm and Eu samples, respectively.

Magnetic hysteresis measurements (Figs. 4 and 5) indicate a non-linear M–H variation even above the highest magnetic transitions, i.e. 87 and 71 K, where the system should be paramagnetic. Also, low-temperature measurements show a tiny hysteresis at intermediate temperatures (i.e. 50 K) and the possibility of a weak ferromagnetic (WFM) contribution at 2 K to the magnetic behaviour. However, our findings in specific heat measurements (see below, Figs. 8 and 9) for both the Sm and Eu Ir-1212 samples do not show the presence of long-range ordering and, therefore, a WFM transition should not occur in these Ir-1212 compounds.

In contrast to DC magnetization measurements, AC susceptibility ones, made at different frequencies, are direct probes of the spin relaxation time. In this context, Figs. 6 and 7 show the characteristic cusps as commonly observed in canonical spin-glasses [24].

3.2.2. Discussion

In light of these observations it appears that these materials have three magnetic transitions, one at high temperatures $T > 150$ K (deduced from the observation of non-linearity in M vs. H) followed by one at $T = 87$ and 71 K for the Sm and Eu compounds, respectively and, finally one at $T \sim 10$ K in both of them. While an initial interpretation could be given that these transitions correspond to the system going from a paramagnetic to a cooperative/spin liquid to a spin-glass to, finally, a long-range ordered state, this does not allow us to explain all of our experimental finding. Instead we suggest that this materials show RSG (i.e. coexistence of ferromagnetism and spin-glass order) behaviour.
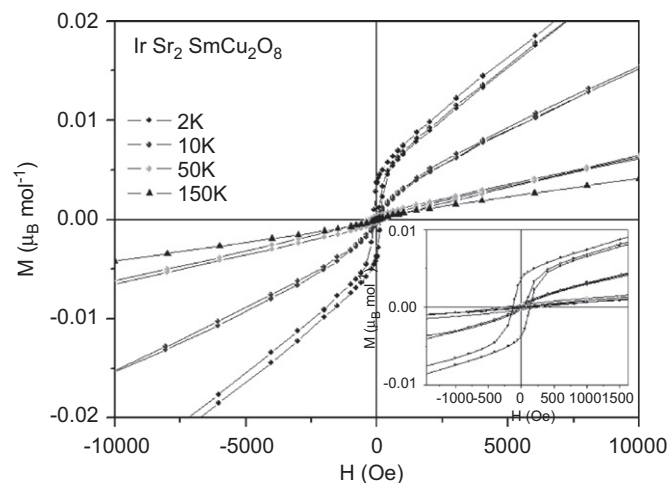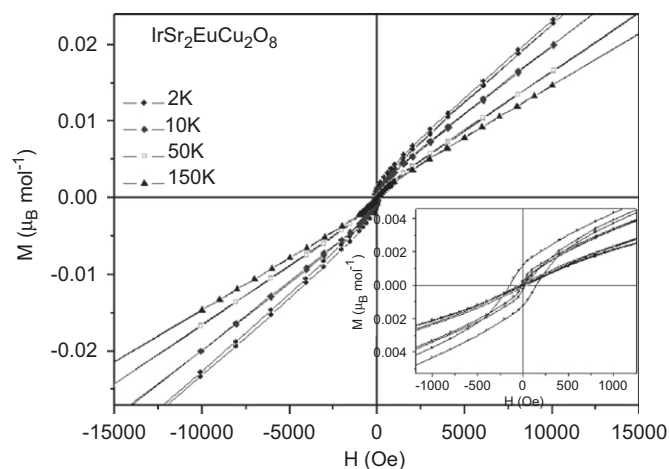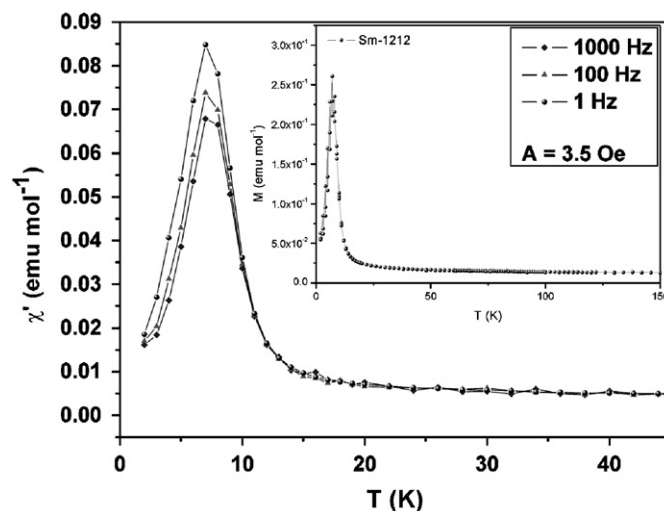

Fig. 6. In the inset, magnetic susceptibility (AC mode) at different frequencies from 2 to 300 K of the Sm sample. The main plot shows in detail the frequency variation of the low-temperature transition peak.
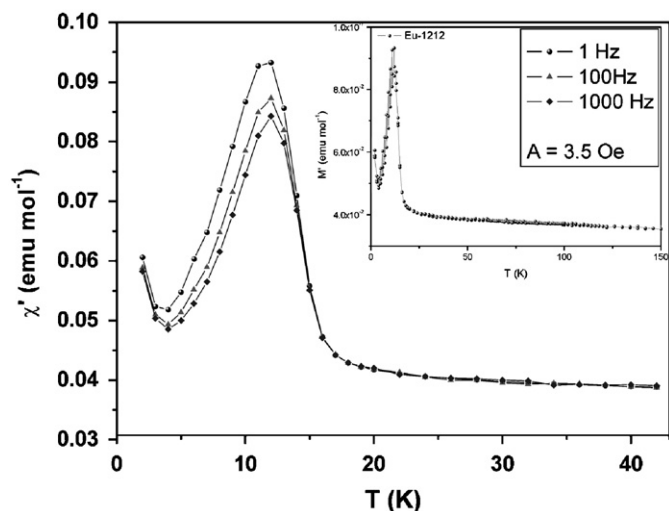
Fig. 7. In the inset, magnetic susceptibility (AC mode) at different frequencies from 2 to 300 K of the Eu sample. The main plot shows in detail the frequency variation of the low-temperature transition peak.

Fig. 8. C/T vs. T^2 representation for the $IrSr_2EuCu_2O_8$ sample. Linear fit at low temperatures and, parameters obtained from this fit, is shown in the inset.

Gabay and Toulouse [25] have extended the mean-field theory of Ising SG systems proposing a well-known phase diagram where SG and ferromagnetism coexist. Recently, several groups have proposed a complementary model, in which a "cluster by cluster freezing" occurs instead of an individual spin (or their components) freezing in random directions [26,27]. In fact, the non-linearity that we observe in the M–H plots at temperatures over 150 K (Figs. 4 and 5) indicates the presence of magnetic clusters in the otherwise paramagnetic system. Such a behaviour has been seen in other SG systems, for instance in the doped and undoped Ba_2PrRuO_6 double perovskite [28], and in the related M-1222 compound $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ [29]; also a close examination of the 1212 $RuSr_2GdCu_2O_8$ compound, suggests the possibility of it being superconducting and a spin-glass [30,31].

Theoretically, in an RSG system there are three transition temperatures, namely T_C or T_N, T_{M1} and T_{M2} according to the Gabay and Toulouse [25] notation. T_N and T_C, are Neel and Curie temperatures, respectively; T_{M1} and T_{M2} represent the first and second transition temperatures to the mixed states, respectively. Furthermore, in the complementary cluster model, clusters are formed at a certain temperature, T_{CF}, in the paramagnetic state itself and normally $T_{CF} > T_C$, $T_N > T_{M1} > T_{M2}$. From Figs. 4 and 5 we can conclude that $T_{CF} > 150$ K for both compounds since M vs. H plots show a non-linear variation at this temperature. At the temperatures T_C or T_N, assigning a spin S_{cl} to a cluster (and not to an individual spin), all these z-components $(S_{cl})_z$ get magnetically ordered and the transverse x $(S_{cl})_x$ and y $(S_{cl})_y$ components average out to zero. T_{M1} is the temperature below which M_{irr} appears and, at this temperature, $(S_{cl})_z$ remains magnetically ordered but $(S_{cl})_x$, $(S_{cl})_y$ freeze to an SG configuration: One can see (in Figs. 2 and 3) that T_C or T_{WFM} (and no T_N because there is a tiny hysteresis below the transition temperature) and T_{M1} are so close that one can consider them as equal, therefore $T_C/T_{WFM} \approx T_{M1} = 87$ and 71 K for the Sm and Eu compounds, respectively. Finally, at temperatures below T_{M2} the irreversibility becomes strong, the ZFC curve has a peak and all the three components $(S_{cl})_x$, $(S_{cl})_y$ and $(S_{cl})_z$ get randomly frozen isotropically as a consequence of the spontaneous breaking of replica symmetry [25]. The maxima in ZFC plots indicate that $T_{M2} = 7$ and 10 K for the Sm and Eu compounds, respectively.

The T_{M2} temperatures were also confirmed by AC susceptibility measurements since the universal signature of systems exhibiting spin-g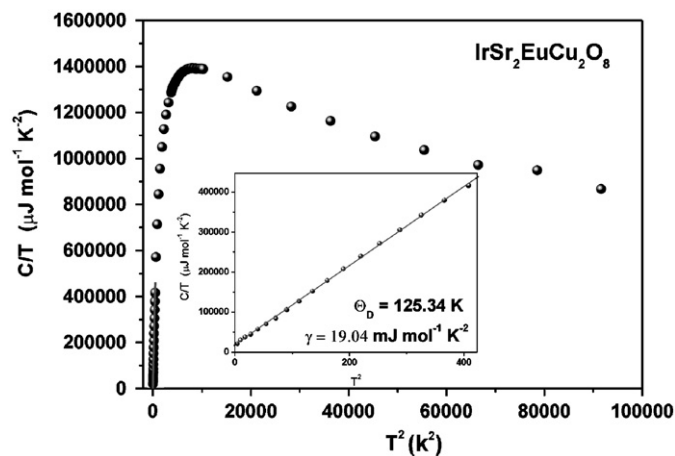lass behaviour is the presence of sharp cups at the freezing temperature in the frequency-dependent susceptibility at low fields [24]. Furthermore, the location of the cusp is dependent on the frequency of the AC susceptibility measurement, a feature that is not present in other magnetic systems and therefore confirms the spin-glass phase. In this context we show the AC susceptibility as a function of temperature at different frequencies in Figs. 6 and 7 for both samples. As expected, the maxima present at T_{M2}, from which all the three components $(S_{cl})_x$, $(S_{cl})_y$ and $(S_{cl})_z$ are randomly frozen in SG configuration, display the classical frequency dependence that confirms the SG phases.

In general, the freezing process of spin-glasses is still not fully understood but it appears to be a cooperative phase transition. However, there is not a phase transition to a magnetically ordered state; there are no magnetic Bragg peaks found in scattering experiments as would be the case if the system showed long-range magnetic order. Furthermore, the presence of the quite absorbent Sm, Eu and Ir cations in the 1212 compounds, adding to the small quantity obtained from a high-pressure synthesis, makes for no viable neutron diffraction experiment. In light of this, we have also performed further specific heat measurements at zero magnetic fields. Although the mean-field theory predicts a cusp in specific heat at the freezing temperature, no maxima are apparent in the C vs. T measurement (data not shown) confirming that there is no long-range magnetic ordering or a massive magnetic transition at any temperature. Of course, the absence of a visible singularity at any temperature does not probe the non-existence of a phase transition either [32]. In fact, the experimental value of the Sommerfeld coefficient, $\gamma = 19.04$ mJ mol^{-1} K^{-2}, extracted from the linear fit at low temperatures in the C/T vs. T^2 representation, as shown in Fig. 8, strongly suggests the presence of magnetic correlations. This value is in line with other previously reported iridium compounds showing electron–electron interactions or magnetic correlations [33]. Moreover, a characteristic bump in the C/T^3 vs. T plot (Fig. 9) appears at T_{M1} and a sharp increase of the specific heat is observed at T_{M2} for the Eu sample.

Taking into account these results, the origin of this SG behaviour can be understood from the presence of several ions with different magnetic moments (Ir^{+4}, Ir^{+5}, Cu^{+2}, Cu^{+3}, Sm^{+3} or even, although less probable, Eu^{+2} and Sm^{+2}), whether in high- or low-spin configuration, giving rise to frustration in the lattice. More explicitly, if the charge reservoir layer [Ir–O$_6$] contains a mixture of magnetic Ir^{+4} ions embedded in a non-magnetic matrix of Ir^{+5} ions, the Ir^{+4}–O–Ir^{+5} layer gets divided into several short-range ordered parts due to the presence of randomly magnetic

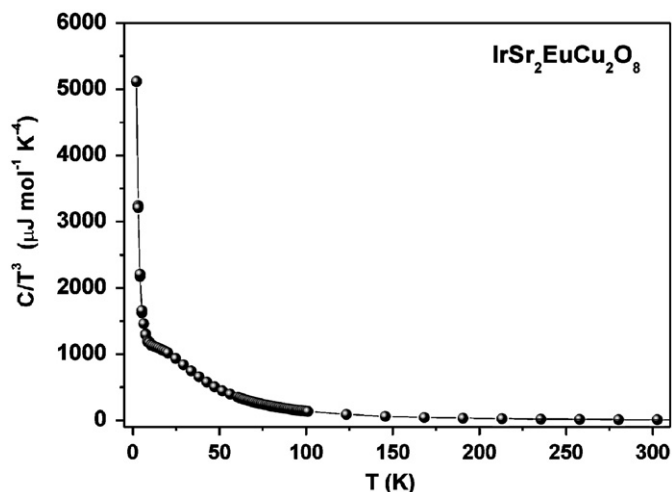**Fig. 9.** C/T^3 vs. T plot for the $IrSr_2EuCu_2O_8$ sample.

Ir^{+4}/non-magnetic Ir^{+5} ions which break the long-range and uniform magnetic ordering. It should also be emphasized that frustration in the 1212 lattice can also arise from the Cu pyramids [26]; In fact, the random distribution of diamagnetic Cu^{+3} in the O–Cu–O bonds is the main cause of frustration of Cu^{+2} moments in the high T_C superconductors [34,35].

4. Conclusions

We have been able to prepare two new members of the iridocuprate family of oxides at high-pressure and high-temperature conditions. They show the so-called M-1212-type structure and a microdomain texturing of the long c-axis is observed by TEM. DC and AC susceptibility experiments along with hysteresis curves and heat capacity measurements in these 1212 Sm and Eu, indicate a very interesting an uncommon magnetic behaviour observed in these materials. A "cluster by cluster freezing" model is proposed, instead of the classical individual spin freezing one to explain the spin-glass-like behaviour that seems to coexist with weak ferromagnetism in both compounds.

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