

## Correlation between magnetic frustration and electrical conductivity in $R\text{InCu}_4$ compounds ( $R=\text{Gd-Tm}$ )

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$R\text{InCu}_4$ -compounds ( $R=\text{Gd-Tm}$ ) are geometrically frustrated antiferromagnets due to the  $R$ -ions forming tetrahedra on a  $fcc$ -lattice [V. Fritsch *et al.*, Phys. Rev. B **71**, 132401 (2005)]. Replacing In with Cd yields a strongly increased Néel temperature, while the Weiss temperature retains its original order of magnitude. Thus the frustration vanishes, though the original tetrahedral configuration of the rare-earth spins persists. While the  $R\text{InCu}_4$  compounds exhibit a very low electrical conductivity and the relevant magnetic interactions in those systems are short-range interactions, in  $R\text{CdCu}_4$  an enhanced conductivity is observed. Here, conduction electron mediated long-range interactions are introduced into the system, which relieve the frustration.

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### I. INTRODUCTION

Geometrical frustration is the result of the symmetry of a system precluding every pairwise interaction from being satisfied at the same time. A simple three-dimensional example for such a system is antiferromagnetic couplings between spins on a lattice of tetrahedra, as is realized on a  $fcc$ -lattice (face-centered cubic lattice). Most  $fcc$ -crystals, however, exhibit a defined magnetic order, since not only the short-range nearest-neighbor interactions are relevant for the system but also more long-range interactions, e.g., next-nearest neighbor interactions, Ruderman-Kittel-Kasuya-Yosida (RKKY) and others.<sup>1</sup>

Strong geometrical frustration was found in  $R\text{InCu}_4$  compounds with  $R=\text{Gd, Dy, Ho, and Er}$ ,<sup>2</sup> and can be found as well for  $R=\text{Tb and Tm}$ .<sup>3</sup> Here the rare-earth ions form a  $fcc$ -lattice yielding a network of edge-sharing tetrahedra. These tetrahedra are alternatingly filled with an In-ion or a tetrahedron of Cu-ions. The frustration parameter  $f := -\Theta_{CW}/T_N$ , the ratio of the Weiss and the Néel temperature, is an empirical measure of frustration. After this definition materials with  $f \approx 3$  can be called moderately frustrated, while materials with  $f \geq 10$  are considered to be strongly frustrated.<sup>4</sup> Measurements of susceptibility and heat capacity revealed high frustration parameters between 8 and 15 and a deficit of magnetic entropy at the respective Néel temperatures, indicating the presence of geometrical frustration.<sup>2,3</sup> In this case we proposed that a short-range interaction between the total magnetic moments of the rare-earth ions is the dominant interaction in  $R\text{InCu}_4$ , due to the moments being located on networks of tetrahedra facilitating geometrical frustration.<sup>2</sup>

In this paper we investigate the consequences of replacing In with Cd in  $R\text{InCu}_4$ . Though this replacement does not change the geometrical properties of the system and, therefore, maintains the symmetry, we will show via an enhanced conductivity long-range RKKY-type interactions are introduced reducing geometrical frustration.

### II. EXPERIMENTAL DETAILS

Single crystals of  $R\text{InCu}_4$  and their Cd-doped relatives were grown in InCu/CdCu-flux, respectively.<sup>5</sup> Conventional powder x-ray diffraction patterns were collected to check sample quality and determine lattice parameters. The dc magnetic susceptibility  $\chi(T)=M/H$  measurements were performed by means of a SQUID (superconducting quantum interference device) magnetometer (Quantum Design MPMS-5) in fields of 1 kOe in the temperature range 1.8–350 K. The specific heat data were obtained in a PPMS (Physical Properties Measurement System, Quantum Design) in the temperature range between 0.4 and 100 K as well as in a home-built setup between 1.3 and 20 K. Electrical resistivity was measured with a conventional four-probe method in a home-built setup between 1.3 and 300 K. In addition paramagnetic resonance (EPR) measurements were carried out at X-band frequencies (9.4 GHz) with a Bruker ELEXSYS E500-CW spectrometer using a continuous Helium gas-flow cryostat (Oxford Instruments) for temperatures  $4.2 \leq T \leq 300$  K.

### III. RESULTS

#### A. $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$

Figure 1 shows in the main frame the resistivity of  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$  normalized to its room temperature value. The resistivity of  $\text{GdInCu}_4$  is characterized by a broad maximum around 100 K, which was explained by a magnetic scattering mechanism.<sup>2</sup> With increasing Cd-concentration this maximum vanishes and is replaced by a typical metallic-like linear temperature dependence. Only when approaching the Néel temperatures, which were determined by measurements of susceptibility and specific heat (see Table I), do anomalies appear. The inset of Fig. 1 displays the resistivity at room temperature of  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$  versus Cd-concentration  $x$ . Between  $x=0$  and  $x=0.25$  it drops to a

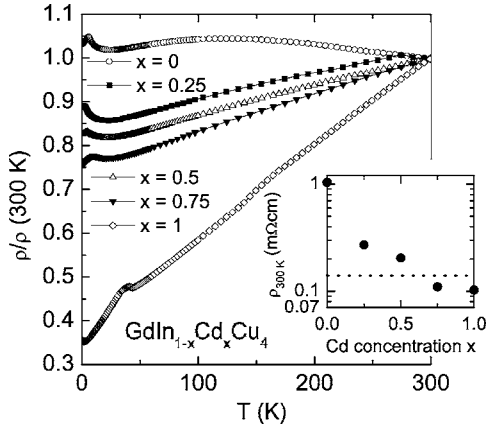


FIG. 1. Main frame: Resistivity of  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$  normalized to its room temperature value vs temperature. Inset: Resistivity at room temperature of  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$  vs Cd-concentration  $x$ . The dotted line corresponds to the vertical line in Fig. 9.

fourth of its value and continues sinking with increasing Cd-concentration. The reason for the conductivity improvement due to Cd-substitution is twofold: First, the sign of the Hall coefficient of  $\text{GdInCu}_4$  and  $\text{GdCdCu}_4$ : It is positive for both, indicating the charge carriers are holes rather than electrons and in a (maybe overly) simple picture Cd provides one electron less, i.e., one hole more, than In.<sup>3</sup> Second, we know from band structure calculations for  $\text{LuInCu}_4$  and  $\text{LuCdCu}_4$  that the Fermi edge is located in a minimum of the electronic density of states for the In-compound.<sup>6</sup>

In Fig. 2 the magnetic dc-susceptibility of  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$  is presented. The left axis marks the magnetic susceptibility, while the right axis denotes the inverse susceptibility. All samples show the onset of antiferromagnetic order. At high temperatures all curves follow a Curie-Weiss law, resulting in effective paramagnetic moments close to the expected value of  $7.94 \mu_B$  for  $\text{Gd}^{3+}$ . The exact values are summarized in Table I. The slight enhancement of the measured effective paramagnetic moment, especially for higher Cd-concentrations, may be ascribed to an additional contribution from on-site  $5d$ -moments parallel to the  $4f$ -moments, which is an already known phenomenon in Gd-intermetallics.<sup>7,8</sup> As can be seen from Table I the Weiss temperatures, obtained by fitting the high-temperature regions of the magnetic susceptibility with a Curie-Weiss law, remain of the same order of magnitude over the whole concentration range with an overall change less than a factor 2. On the other hand the Néel temperature increases from  $T_N=5.5$  K at  $x=0$  to a value nearly seven times higher at  $x=1$ . As a consequence the ratio between the Weiss temperature and the Néel temperature, i.e. the frustration parameter, decreases dramatically, indicating the complete relief of the frustration. The inset displays a magnification of the low temperature regime of the susceptibility of  $\text{GdCdCu}_4$ . A first peak at 38 K marks the onset of antiferromagnetic order. The second peak can be explained with a reordering of the spins, as observed in many Gd-compounds and in analogy to the situation in  $\text{GdInCu}_4$ .<sup>2</sup>

In its upper panel Fig. 3 displays the specific heat of  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$ . Peaks at the Néel temperatures indicate the onset of antiferromagnetic order in all samples as already

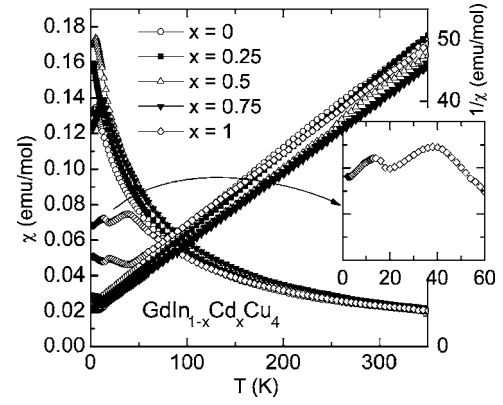


FIG. 2. Left axis: Magnetic susceptibility of  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$  vs temperature. Right axis: Inverse magnetic susceptibility of  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$  versus temperature. Inset: Magnification of the low temperature region of the susceptibility of  $\text{GdCdCu}_4$ .

concluded from the susceptibility measurements. At high temperatures all curves meet the nonmagnetic Lu-analog, suggesting that the specific heat is only due to phononic contributions in this temperature regime. An extrapolation to temperatures far above 100 K would probably result in a specific heat according to the Dulong-Petit law [as it does for  $\text{YbInCu}_4$  and  $\text{YbCdCu}_4$  (Ref. 3)]. In order to obtain the magnetic contribution to the specific heat, we subtracted the appropriate nonmagnetic analog from the data ( $\text{LuInCu}_4$ ,  $\text{LuCdCu}_4$  or an average of both). By integration over the magnetic part of the specific heat we calculated the magnetic entropies for  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$ , which are presented in the lower panel of Fig. 3. At high temperatures, well above the absolute value of the Weiss temperature, all entropies reach the  $R \ln 8$  value expected for Gd. The amount of entropy recovered at  $T_N$  is 67% for  $\text{GdInCu}_4$  and 86% for  $\text{GdCdCu}_4$ , which is a further indication of the frustration subsiding from  $\text{GdInCu}_4$  to  $\text{GdCdCu}_4$ .

The Gd-EPR spectra of all compounds consist of a single exchange-narrowed resonance line of Dysonian shape, i.e., an asymmetric Lorentz line due to admixture of dispersion to the absorption signal, which is typical for metals, because the skin effect drives electric and magnetic components of the microwave field out of phase.<sup>9,10</sup> The resonance field corresponds to a  $g$  value of  $g \approx 2$ , as one expects for the S-state ion  $\text{Gd}^{3+}$ . Figure 4 shows the temperature dependence of the linewidth  $\Delta H$  (HWHM=half width at half maximum). For all Cd-concentrations  $x$  one observes an approximately linear increase to high temperatures and a critical divergence to low temperatures on approaching magnetic order. This behavior

TABLE I. Magnetic data for  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$ .

$x$	$T_N$ (K)	$\Theta_{CW}$ (K)	$f := -\Theta_{CW}/T_N$	$\mu_{eff}$ ( $\mu_B/RE$ )
0	5.5	-52.0	9.45	7.88
0.25	3.4	-46.8	13.8	7.92
0.5	6.0	-42.0	7.45	8.14
0.75	12	-45.1	3.75	8.35
1	38.0	-72.0	1.89	8.28

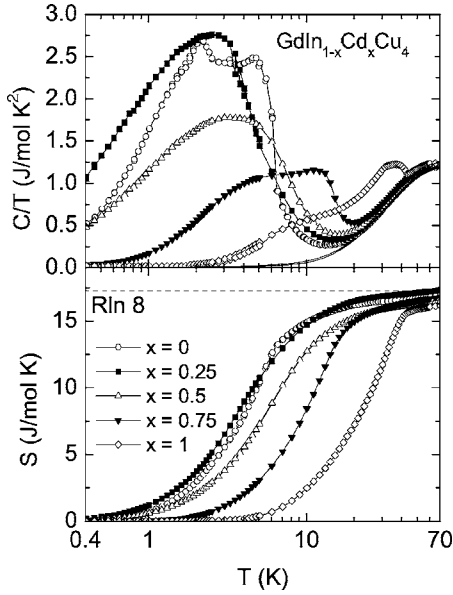


FIG. 3. Upper panel: Specific heat of  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$  for various Cd-concentrations  $x$  in the representation  $C/T$  vs  $T$ . The two solid lines are the heat capacities of the nonmagnetic analogs  $\text{LuInCu}_4$  and  $\text{LuCdCu}_4$ . Lower panel: Magnetic entropy of  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$ .

is well described by the expression (see Table II)

$$\Delta H = b \cdot T + \frac{C}{(T - T_{\text{crit}})^\alpha} + \Delta H_0. \quad (1)$$

The first term denotes the Korringa relaxation of the localized Gd spins to the conduction electrons, where the prefactor  $b \propto N^2(E_F)$  is proportional to the squared electronic density of states at the Fermi energy  $E_F$ . The second term describes the critical divergence at a temperature  $T_{\text{crit}}$  near  $T_N$ . Finally, a residual linewidth  $\Delta H_0$  accounts for temperature independent relaxation contributions.

The Korringa contribution increases from  $b=0.4$  Oe/K for  $x=0$  up to  $b=3.35$  Oe/K for  $x=1$ . Note that the values are comparable to the Korringa rate  $b=0.9$  Oe/K observed in the Gd doped reference compounds  $\text{LuInCu}_4$  (Ref. 11) and  $\text{YInCu}_4$  (Ref. 12). This indicates an increase of the electronic density of states by a factor of three, when replacing In by Cd. Indeed, this is in agreement with results from specific heat measurements (see below).

The inset illustrates the critical contribution of the linewidth  $\Delta H_{\text{crit}}$  after subtraction of Korringa relaxation and residual linewidth in logarithmic representation versus  $T - T_{\text{crit}}$ . One can clearly see that the temperature regime of

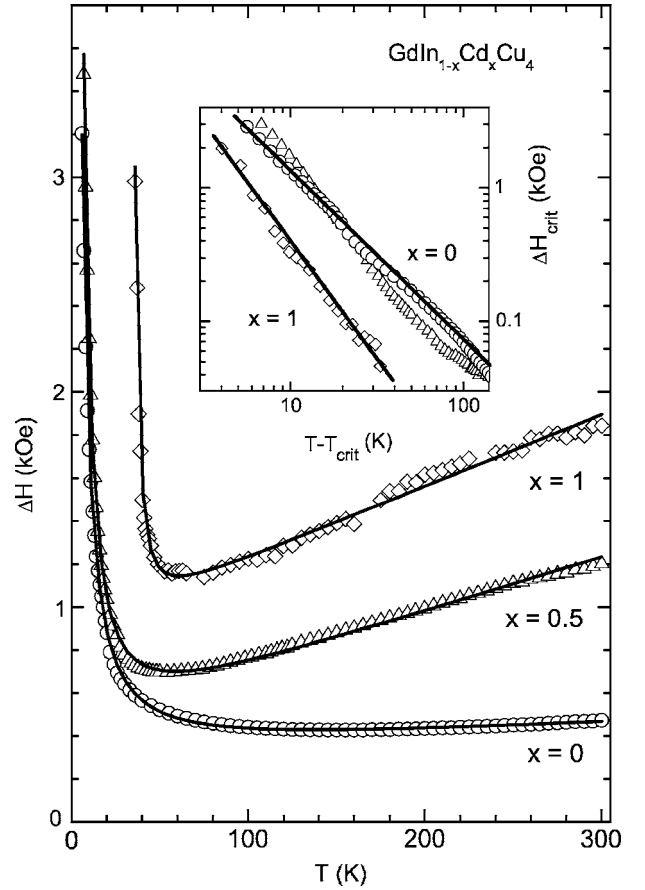


FIG. 4. Temperature dependence of the EPR linewidth for  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$ . The solid lines indicate the fit curves as described in the text. Inset: Critical contribution to the linewidth on approaching  $T_N$  in logarithmic representation. The solid lines illustrate the critical behavior with critical exponents 1.32 and 1.88, respectively.

the critical spin fluctuations is far broader (about  $20T_N$ ) for the In compound with the larger frustration parameter than for the Cd compound (about  $2T_N$ ). This is expressed by the critical exponent  $\alpha$  of the divergence on approaching magnetic order, which increases from  $\alpha=1.32$  for  $x=0$  to  $\alpha=1.88$  for  $x=1$ , i.e., frustration leads to a less abrupt divergence but extended to higher temperatures. The critical temperatures obtained from the fit are about 5 K below  $T_N$  for all samples under consideration.

## B. $\text{RCdCu}_4$

As reported previously, the lattice parameter of the series  $\text{RInCu}_4$  decreases from Gd to Lu due to

TABLE II. Fit parameters for the temperature dependent linewidth of  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$  following Eq. (1).

$x$	$b$ (Oe/K)	$T_{\text{crit}}$ (K)	$\alpha$	$C$ ( $10^4$ Oe K $^\alpha$ )	$\Delta H_0$ (Oe)
0.0	0.40	0.28	1.32	2.78	331
0.5	2.56	0.00	1.63	7.02	458
1.0	3.35	32.0	1.88	2.79	891

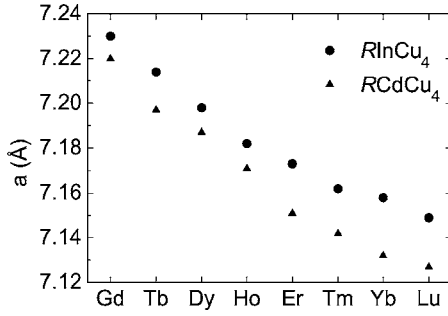


FIG. 5. Lattice parameters of  $R\text{InCu}_4$  (circles) and  $RCdCu_4$  (triangles).

lanthanoid-contraction.<sup>2</sup> As illustrated in Fig. 5 the lattice parameters of the series  $RCdCu_4$  are slightly smaller than the lattice parameters of the corresponding  $R\text{InCu}_4$  compounds. This effect was already known for the Yb-compound: The lattice parameter of  $\text{YbInCu}_4$  was reported as  $a=7.158 \text{ \AA}$  and for  $\text{YbCdCu}_4$   $a=7.135 \text{ \AA}$ .<sup>13</sup> Given the large difference between the lattice parameters of different rare-earth ions compared to the small difference between an In- and Cd-compound we can conclude that size effects due to In/Cd-substitution are negligible in  $R\text{In}_{1-x}\text{Cd}_x\text{Cu}_4$  compounds.

The replacement of In with Cd in  $R\text{InCu}_4$  is the replacement of one nonmagnetic ion with another. As we have seen in Cd-doped  $\text{GdInCu}_4$  the conductivity increases significantly with increasing Cd-concentration. Figure 6 compares the resistivities of  $R\text{InCu}_4$  with the resistivities of  $RCdCu_4$ . The main frame shows the temperature dependence. The resistivities of  $R\text{InCu}_4$  are not linear in temperature, as it was discussed in a previous paper.<sup>2</sup> The curves of the resistivities of  $RCdCu_4$ , on the contrary, show at high temperatures a linear temperature dependence, which is typical for metals. At low temperatures small anomalies occur, which will be shown to coincide with the onset of antiferromagnetic order

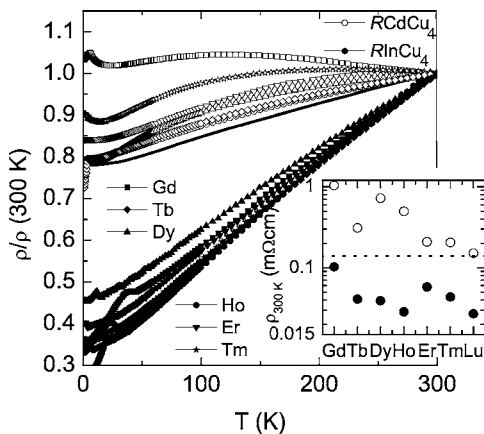


FIG. 6. Main panel: Resistivity of  $R\text{InCu}_4$  (open symbols) and  $RCdCu_4$  (closed symbols) normalized to their value at room temperature vs temperature. The solid lines represent the resistivities of the nonmagnetic  $\text{Lu}(\text{In}/\text{Cd})\text{Cu}_4$ -compounds. Inset: Values of the resistivity of  $R\text{InCu}_4$  (open symbols) and  $RCdCu_4$  (closed symbols) vs the various rare-earth ions  $R$ . The dotted line corresponds to the vertical line in Fig. 9.

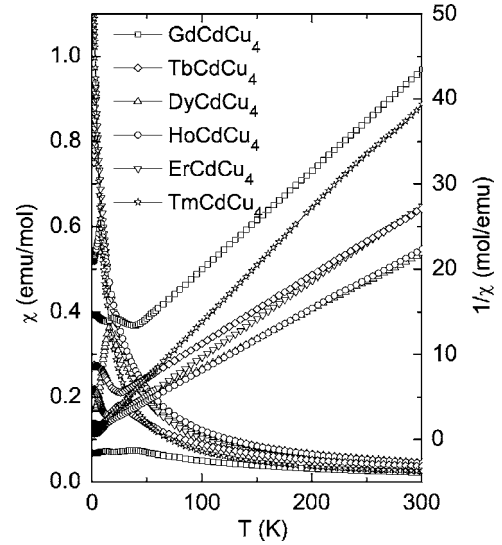


FIG. 7. Left axis: Magnetic susceptibility of  $RCdCu_4$  vs temperature. Right axis: Inverse magnetic susceptibility of  $RCdCu_4$  vs temperature.

in the corresponding samples (see below). The inset of Fig. 6 presents the values of the resistivity at room temperature of  $R\text{InCu}_4$  and  $RCdCu_4$  for  $R=\text{Gd}, \text{Dy}, \text{Ho}, \text{Er},$  and  $\text{Lu}$ . As reported previously the resistivity of  $R\text{InCu}_4$  decreases linearly from Gd to Lu.<sup>2</sup> The values of the resistivities of  $RCdCu_4$  are nearly an order of magnitude lower than in  $R\text{InCu}_4$ .

Figure 7 shows the magnetic susceptibility (left axis) and the inverse magnetic susceptibility (right axis) of  $RCdCu_4$  for  $R=\text{Gd} - \text{Tm}$ . All samples show the onset of antiferromagnetic order and follow a Curie-Weiss law above their respective Néel temperatures. The magnetic data are summarized in Table III. The effective paramagnetic moments found from fitting the susceptibilities with a Curie-Weiss law coincide nicely with the expected free-ion values of the corresponding rare-earths. As already stated for the Gd-case, the Weiss temperature remains of the same order of magnitude, while the Néel temperature increases significantly in comparison to the respective  $R\text{InCu}_4$  analog. As a consequence the frustration parameter  $f$  is strongly reduced in all  $RCdCu_4$  compounds. The Weiss and Néel temperatures of  $RCdCu_4$  follow the de Gennes expectation, as do the Weiss and Néel temperatures of  $R\text{InCu}_4$ .<sup>2</sup>

The specific heat data of our samples  $RCdCu_4$  are shown in the upper panel of Fig. 8. Maxima in the specific heat

TABLE III. Magnetic data for  $RCdCu_4$ .

$R$	$T_N$ (K)	$\Theta_{CW}$ (K)	$f := -\Theta_{CW}/T_N$	$\mu_{eff}$ ( $\mu_B/RE$ )
Gd	38	-72	1.89	8.26
Tb	26	-49	1.88	10.1
Dy	14	-21	1.50	10.8
Ho	7.0	-13	1.86	10.5
Er	2.8	-7.8	2.79	9.45
Tm	1.1	-4.6	4.18	7.89

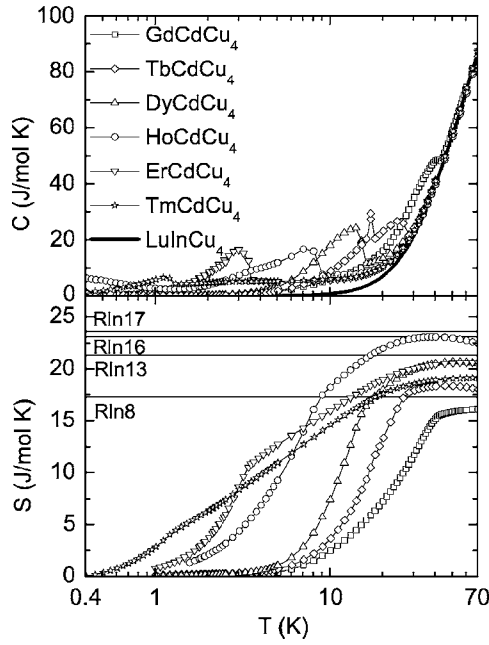


FIG. 8. Upper panel: Specific heat of  $RCdCu_4$  for various Cd-concentrations  $x$  in the representation  $C$  vs  $T$ . The solid line is the heat capacities of the nonmagnetic analog on  $LuCdCu_4$ . Lower panel: Magnetic entropy of  $RCdCu_4$ .

mark the Néel temperatures in the corresponding samples. At high temperatures all curves coincide with the specific heat of the nonmagnetic  $LuCdCu_4$ , indicating that at high temperatures the phonons provide the main contributions to the specific heat. In order to obtain the magnetic contribution to the specific heat we subtracted the specific heat of the nonmagnetic analog  $LuCdCu_4$ , which is displayed as a solid line in the upper panel of Fig. 8. By integration over the magnetic contribution of the specific heat we obtained the magnetic entropy, which is presented in the lower panel of Fig. 8. For all compounds the entropies released at high temperatures are close to the expected values for the corresponding rare-earths:  $R \ln 8$  for  $GdCdCu_4$ ,  $R \ln 13$  for  $Tb$  and  $Tm$ ,  $R \ln 16$  for  $DyCdCu_4$  and  $ErCdCu_4$ , and  $R \ln 17$  for  $HoCdCu_4$  with  $R$  being the gas constant. The amounts of entropy released at the Néel temperature are significantly higher for  $RCdCu_4$  than for  $RInCu_4$ : 67% for  $GdInCu_4$  and 86% for  $GdCdCu_4$ , 17% for  $DyInCu_4$  and 70% for  $DyCdCu_4$ , 18% for  $HoInCu_4$  and 68% for  $HoCdCu_4$ ,  $\approx 10\%$  for  $ErInCu_4$  and 49% for  $ErCdCu_4$  (values for the  $RInCu_4$  system are taken from Ref. 2). Replacing  $In$  with  $Cd$  replaces one nonmagnetic ion with a closed  $d$ -shell with another closed-shell nonmagnetic ion. Therefore we assume that there is no significant change in the crystal fields affecting the rare-earth ions associated with this change, an assumption corroborated by the fact that the Cd-substitution does not have a large effect on the Weiss temperature and the fact that the Néel temperatures and the Weiss temperatures follow the de Gennes expectation. Furthermore inelastic neutron scattering experiments were performed at  $YbInCu_4$  and  $YbCdCu_4$ , which did not show any evidence for sharp crystal field levels. Additionally, in  $YbInNi_4$  and  $YbAuCu_4$  the crystal fields are observed at 2–4 meV.<sup>14</sup> Anyway, the very nice linear temperature de-

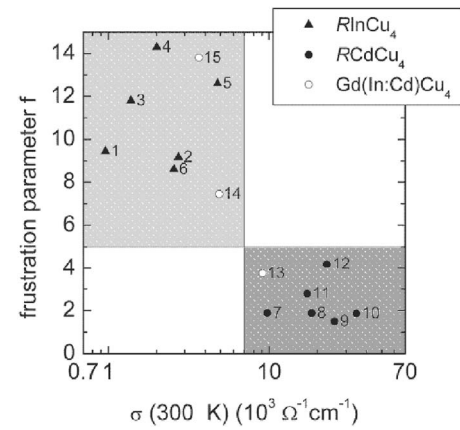


FIG. 9. Frustration parameter  $f$  vs electrical conductivity  $\sigma$ . Samples with a high frustration parameter exhibit a low conductivity (light gray area), while samples with a high conductivity are not frustrated (dark gray area). There are no samples with a high frustration parameter and a high conductivity, nor samples with low conductivity and low frustration parameter. 1:  $GdInCu_4$ , 2:  $TbInCu_4$ , 3:  $DyInCu_4$ , 4:  $HoInCu_4$ , 5:  $ErInCu_4$ , 6:  $TmInCu_4$ , 7:  $GdCdCu_4$ , 8:  $TbCdCu_4$ , 9:  $DyCdCu_4$ , 10:  $HoCdCu_4$ , 11:  $ErCdCu_4$ , 12:  $TmCdCu_4$ , 13:  $GdIn_{0.25}Cd_{0.75}Cu_4$ , 14:  $GdIn_{0.5}Cd_{0.5}Cu_4$ , 15:  $GdIn_{0.75}Cd_{0.25}Cu_4$ .

pendence of the inverse susceptibility shows no evidence for significant crystal fields. Therefore, at least the differences in the amount of entropy released at the Néel temperatures between  $RInCu_4$  and  $RCdCu_4$  can be assigned to the geometrical frustration present in  $RInCu_4$ .

#### IV. DISCUSSION

From Figs. 1 and 6 the empirical observation could be made that samples with a high frustration parameter have a low electrical conductivity, while samples with a low frustration parameter have a higher conductivity. This observation is more clearly depicted in Fig. 9, where the frustration parameter  $f$  is plotted against the electrical conductivity at room temperature  $\sigma$  for a series of compounds. Although one could argue that the room temperature resistivity is mostly determined by phonons, while the frustration parameter is dependent on the electronic structure, and therefore a low-temperature resistivity value would be more appropriate, we decided that the room temperature value is more reliable for our purposes. Since the samples with high conductivity also exhibit a high residual resistivity ratio, a resistivity at low temperatures at the  $x$ -axis of Fig. 9 would not qualitatively change the picture. However, the data points in that case are partially in the paramagnetic and partially in the antiferromagnetically ordered regime. Furthermore, if this plot is expanded to  $YbTCu_4$  ( $T$ : transition metal), where at intermediate temperatures a valence transition, accompanied by a significant drop of resistivity occurs,<sup>15,16</sup> or Kondo coherence develops, the resistivity at room temperature is the most consistent quantity to plot reflective of the background conduction electron density of states.

How can the correlation between the magnetic frustration and the electric conductivity be explained, at least qualita-

tively? As mentioned above, magnetic geometrical frustration on a fcc-lattice requires the relevant interactions between the magnetic moments to be short-range interactions, e.g., indirect exchange interactions. In this context it is noteworthy that in the series  $R\text{InCu}_4$  the compound with the highest effective paramagnetic moment,  $\text{HoInCu}_4$ , is also the compound with the highest frustration parameter.<sup>2</sup> For rare-earth compounds, where conduction electrons do not play a significant role, the most probable mechanism responsible for antiferromagnetic order is superexchange.<sup>17</sup>

Overall the Néel temperatures follow the de Gennes expectation, i.e., they are proportional to  $N(E_F)\Gamma^2(g_J-1)^2J(J+1)$  (Ref. 18). Here  $N(E_F)$  is the density of states at the Fermi level and  $\Gamma$  the exchange interaction constant between the magnetic ion and the conduction electrons. From specific heat measurements the Sommerfeld coefficients for these compounds were found to be  $\gamma=2.91$  mJ/mol K<sup>2</sup> for  $\text{LuInCu}_4$  and  $\gamma=9.94$  mJ/mol K<sup>2</sup> for  $\text{LuCdCu}_4$ , suggesting the density of states at the Fermi level is more than a factor of 3 higher in the Cd-compounds than in the In-compounds. The same holds for the Korringa relaxation detected by Gd ESR. This is consistent with band structure calculations showing the Fermi level for  $\text{LuInCu}_4$  lies in a quasi-gap, which separates the Cu- $p$ ,  $d$  and (In,Cd)- $p$ ,  $d$  states from the Cu- $p$  and  $R-d$  states.<sup>6</sup> This would account only for a small part of the increase of the Néel temperatures by replacing In with Cd in  $R\text{InCu}_4$ . The remainder of the increase has to be a result of a change in the exchange constant  $\Gamma$ . This exchange constant presumably describes three things: The sign of the exchange (ferromagnetic or antiferromagnetic), its strength and how its strength changes with distance. For the here investigated compounds the exchange is always antiferromagnetic. Given the fact that Cd provides one conduction electron less to the conduction band than In, it would be hard to believe that the strength of coupling between the rare-earth and the conduction electrons is weaker, when there are more conduction electrons. This leaves the distance-dependency. Exchanging In with Cd results in a higher conductivity, suggesting that there are more conduction electrons available to mediate long-range interactions. This changes the up to now short-range interactions, i.e., superexchange, in  $R\text{InCu}_4$  into more long-range interactions, i.e., RKKY-interactions, in  $R\text{CdCu}_4$ . Therefore, the geometrical frustration is relieved and the Néel temperatures increased.

The dipole interaction between the rare-earth spins depends solely on the strength of the magnetic moments and the distance between them. In a rough estimation these interactions are between 500 and 800 mK.<sup>19</sup> Since these values in most cases are about two orders of magnitude below the ordering or Néel temperatures in  $R\text{InCu}_4$  and  $R\text{CdCu}_4$ , the dipole interaction is certainly not responsible for the existence or nonexistence of frustration, but it might account for small deviations from the de Gennes expectation, which we observe for the Néel and Weiss temperatures of  $\text{ErInCu}_4$  and  $\text{TmInCu}_4$ . Additionally it should be noted that the dependency of the dipole interaction on the rare-earth ion is the same as the dependency of the frustration parameter of  $R\text{InCu}_4$  (Ref. 2) from the rare-earth ion. Though the dipole interaction decreases with  $1/r^3$  and is, therefore, more a long-range than a short-range interaction, there are heavy

debates, whether it lifts frustration or not. A very recent theoretical investigation even states that the dipolar interactions will not destroy frustration, due to its very peculiar properties.<sup>20</sup>

The situation is somewhat more complicated for the mixed compounds  $\text{GdIn}_{1-x}\text{Cd}_x\text{Cu}_4$ . The compound with  $x=0.25$  has a higher frustration parameter than the compound with  $x=0$ , although the electrical conductivity of the compound with  $x=0$  is smaller than the conductivity of the compound with  $x=0.25$ . The increase of the frustration parameter is due to the decrease of the Néel temperature (nearly 40%) rather than due to a change in the Weiss temperature (which decreases only about 10%). By replacing a quarter of the In in  $\text{GdInCu}_4$  with Cd we bring disorder into the system. Generally disorder is not helpful for magnetic order and therefore might very well suppress the Néel temperature further in addition to the already present frustration. For  $x=0.5$  the Néel temperature increases, while the Weiss temperature is still decreasing. The conductivity of the compound with  $x=0.5$  is not yet high enough to relieve the frustration completely: It is still in the upper portion of the inset of Fig. 1 and the frustration parameter is larger than five. Nevertheless, the enhanced conductivity already could relieve the frustration partially, yielding an increasing Néel temperature despite the disorder present. For the compound with  $x=0.75$  the conductivity is high enough to relieve the frustration, indicated by an increased Néel temperature and a frustration parameter below five. For  $\text{GdCdCu}_4$  the disorder is not an issue anymore, resulting in the increased Néel temperature  $T_N=38$  K and the equally increased Weiss temperature  $\Theta_{CW}=72$  K.

We argue that replacing In with Cd shifts the Fermi edge away from the minimum in the density of states,<sup>6</sup> and the resulting enhancement in conductivity relieves the frustration. The question arises, can greater frustration result in higher spin scattering and, therefore, reduced conductivity. Because the conductivity is mainly dependent on the position of the Fermi edge, the effect of enhanced spin scattering seems to be negligible in comparison. This assumption is corroborated by the fact that the dependence of the frustration parameter on the conductivity is rather scattered and that nonmagnetic analogs of the compounds in question have comparably high resistivities. From the data we can only see that there is a correlation between conductivity and frustration: If one is high the other is low and vice versa. Making a distinction between cause and effect is not possible from the data, it can only be concluded from the interpretation.

## V. CONCLUSION

We investigated the consequences of replacing In with Cd in the cubic compounds  $R\text{InCu}_4$ . These compounds crystallize in the cubic  $\text{AuBe}_5$ -structure, where the rare-earth ions form a fcc-lattice and, therefore, build a network of tetrahedra. Though all  $R\text{InCu}_4$  compounds order antiferromagnetically, they exhibit strong features of geometrical frustration. Replacing In with Cd enhances the electrical conductivity, as

was shown by measurements of the electrical resistivity. Measurements of magnetic susceptibility and specific heat revealed that simultaneously the frustration is relieved. The reason is that a higher conductivity results in more long-range interactions, which are usually not beneficial for geometrical frustration.

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- <sup>1</sup>H. Nakamura, N. Kim, M. Shiga, R. Kmiec, K. Tomala, E. Ressouche, J. P. Sanchez, and B. Malaman, *J. Phys.: Condens. Matter* **11**, 1095 (1999).
- <sup>2</sup>V. Fritsch, J. D. Thompson, and J. L. Sarrao, *Phys. Rev. B* **71**, 132401 (2005).
- <sup>3</sup>V. Fritsch, J. D. Thompson, and J. L. Sarrao (unpublished).
- <sup>4</sup>A. P. Ramirez, *Annu. Rev. Mater. Sci.* **24**, 453 (1994).
- <sup>5</sup>J. L. Sarrao, C. D. Immer, C. L. Benton, Z. Fisk, J. M. Lawrence, D. Mandrus, and J. D. Thompson, *Phys. Rev. B* **54**, 12207 (1996).
- <sup>6</sup>E. Figueroa, J. M. Lawrence, J. L. Sarrao, Z. Fisk, M. F. Hundley, and J. D. Thompson, *Solid State Commun.* **106**, 347 (1998).
- <sup>7</sup>L. D. Tung, K. H. J. Buschow, J. J. M. Franse, P. E. Brommer, H. G. M. Duijijn, E. Brück, and N. P. Thuy, *J. Alloys Compd.* **269**, 17 (1998).
- <sup>8</sup>S. Bobev, V. Fritsch, J. D. Thompson, and J. L. Sarrao, *J. Solid State Chem.* **179**, 1061 (2006).
- <sup>9</sup>R. H. Taylor, *Adv. Phys.* **24**, 681 (1975).
- <sup>10</sup>S. E. Barnes, *Adv. Phys.* **30**, 801 (1981).
- <sup>11</sup>P. G. Pagliuso, C. Rettori, S. B. Oseroff, J. Sarrao, Z. Fisk, A. Cornelius, and M. F. Hundley, *Solid State Commun.* **104**, 223 (1997).
- <sup>12</sup>C. Rettori, S. B. Oseroff, D. Rao, P. G. Pagliuso, G. E. Barberis, J. Sarrao, Z. Fisk, and M. Hundley, *Phys. Rev. B* **55**, 1016 (1997).
- <sup>13</sup>J. L. Sarrao, C. D. Immer, Z. Fisk, C. H. Booth, E. Figueroa, J. M. Lawrence, R. Modler, A. L. Cornelius, M. F. Hundley, G. H. Kwei *et al.*, *Phys. Rev. B* **59**, 6855 (1999).
- <sup>14</sup>J. M. Lawrence, P. S. Riseborough, C. H. Booth, J. L. Sarrao, J. D. Thompson, and R. Osborn, *Phys. Rev. B* **63**, 054427 (2001).
- <sup>15</sup>I. Felner and I. Nowik, *Phys. Rev. B* **33**, 617 (1986).
- <sup>16</sup>I. Felner, I. Nowik, D. Vaknin, U. Potzel, J. Moser, G. M. Kalvius, G. Wortmann, G. Schmiester, G. Hilscher, E. Gratz *et al.*, *Phys. Rev. B* **35**, 6956 (1987).
- <sup>17</sup>A. A. Sidorov and L. D. Falkovkaya, *Int. J. Magn.* **4**, 125 (1973).
- <sup>18</sup>J. Kitagawa, N. Takeda, and M. Ishikawa, *J. Alloys Compd.* **256**, 48 (1997).
- <sup>19</sup>S. T. Bramwell and M. P. Gingras, *Science* **294**, 1495 (2001).
- <sup>20</sup>S. V. Isakov, R. Moessner, and S. L. Sondhi, *Phys. Rev. Lett.* **95**, 217201 (2005).