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La-alloying study of $CeCoGe_2$: Magnetic susceptibility and specific heat measurements

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We report measurements of magnetic susceptibility and specific heat for polycrystalline $Ce_{1-x}La_xCoGe_2$ for $x=0$, 0.1, 0.2, 0.3, 0.5, and 1. $CeCoGe_2$ is considered as a concentrated $J=5/2$ Kondo system. We have found significant preferential orientation in the magnetic susceptibility implying magnetic anisotropy. Magnetic susceptibility and specific heat results do not corroborate the single impurity model and imply the importance of crystalline electric fields and magnetic correlations. Low-temperature specific heat and susceptibility data for $x=0.2$ suggest a possibility of a two-dimensional antiferromagnetic quantum critical point.

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I. INTRODUCTION

Lately, there have been reports of unusual heavy fermion behavior among Ce-based alloys, such as $CeNi_9Si_4$ (Ref. 1) and $CeCoGe_2$ (Ref. 2) described by the $J=5/2$ Kondo model.[3] This model seems to provide a good consistent description of the specific heat and magnetic susceptibility from room temperature down to the lowest temperatures of reported measurements, approximately 1 K. In general, low-temperature properties of Ce-based heavy fermions can be accounted for to some degree by either the $J=1/2$ or $3/2$ Kondo models. This is because the sixfold degeneracy of $4f^1$ moments is lifted by crystalline electric fields (CEF), resulting in a ground-state doublet or quartet. This latter possibility is rare and can occur for a cubic environment of Ce only. A lack of CEF effects in $CeNi_9Si_4$ and $CeCoGe_2$ has been explained by a somewhat unique hierarchy of relevant energy scales, $T_0 > \Delta_{CEF} \gg T_{RKKY}$, where T_0, Δ_{CEF}, and T_{RKKY} stand for the energy scales of Kondo interactions, CEF, and Ce-Ce intersite exchange coupling, respectively. Furthermore, all three energy scales have to be small ($T_0 \approx 100$ K) to result in enhanced values of the electronic specific heat coefficient γ.

We have further examined the applicability of the $J=5/2$ Kondo model to one of these exotic systems, $CeCoGe_2$.[2] Our choice was motivated by the fact that a related compound, $CeNiGe_2$, belonging to the same orthorhombic crystal structure, with almost identical lattice parameters, exhibits strong anisotropy in electrical resistivity and magnetic susceptibility implying the importance of CEF effects.[4–7] The importance of CEF's was also concluded from a previous investigation of Co-deficient material, $CeCo_{0.89}Ge_2$.[8]

Here we report on the alloying study of $CeCoGe_2$, in which La was partially substituted for Ce. Such an alloying study of $CePb_3$ proved the relevance of the $J=1/2$ Kondo model to Ce-based heavy fermions. In particular, bulk properties of $Ce_xLa_{1-x}Pb_3$, specific heat, and magnetic susceptibility showed almost perfect scaling[9] with the Ce concentration x. The search for a similar scaling of these properties in $Ce_xLa_{1-x}CoGe_2$ was among the objectives of the reported investigation.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of $Ce_{1-x}La_xCoGe_2$ with $x=0$, 0.1, 0.2, 0.5, and 1 were obtained in the same manner as $CeCoGe_2$ described in Ref. 2, by arc-melting elements under argon atmosphere, followed by vacuum annealing at 900 °C for three weeks. The starting constituents were Ce and La from Ames, Co and Ge from Alfa Aesar and Johnson-Matthey, 99.995% and 99.9999% purity, respectively. Mass losses during the arc-melting were less than 0.4% of the total mass of ~0.8 g each sample. At least two different samples were synthesized and characterized by x-ray powder diffraction and magnetic susceptibility, to minimize the effects of possible sample mishandling and verify the reproducibility of data. Magnetic susceptibility was measured using a Quantum Design SQUID magnetometer. Specific heat was measured by a standard relaxation method with a homemade ^{3}He calorimeter down to ~0.3 K.

III. EXPERIMENTAL RESULTS

A. X-ray diffraction

$CeCoGe_2$ and $CeCoGe_2$ belong to the orthorhombic $CeNiSi_2$-type[10] crystal structure, space group *Cmcm*. All x-ray diffraction lines for all samples were indexable to this crystal structure. However, we have observed some discrepancies between calculated and measured intensities. These discrepancies were not only for mixed alloys but also for the end compounds. This disagreement can be due to atomic disorder but also to preferential orientation reported in the x-ray powder diffraction for the isostructural polycrystalline $CeNiGe_2$.[11] The lattice constant b for $CeCoGe_2$ (and $CeNiGe_2$) is much larger than the lattice constants a and c. The corresponding values for the Co compound are 4.262, 16.781, and 4.215 Å for a, b, and c parameters, respectively. In $CeNiSi_2$, platelike grains with the (010) plains preferentially oriented parallel to the x-ray-diffraction slides were reported.[11] The discrepancy between the measured and calculated intensities for $CeCoGe_2$ is also consistent with (010) planes preferentially parallel to the x-ray slides.

The results of the lattice constant measurements for $Ce_{1-x}La_xCoGe_2$ are shown in Fig. 1. As expected, La being larger than Ce expands the lattice. However, this expansion is not isotropic. The lattice constants a and c are expanded more than b, such as the ratios b/a and b/c are reduced by La. Therefore, if there is some anisotropy in magnetic and transport properties, we would expect this anisotropy to be reduced by the La alloying.

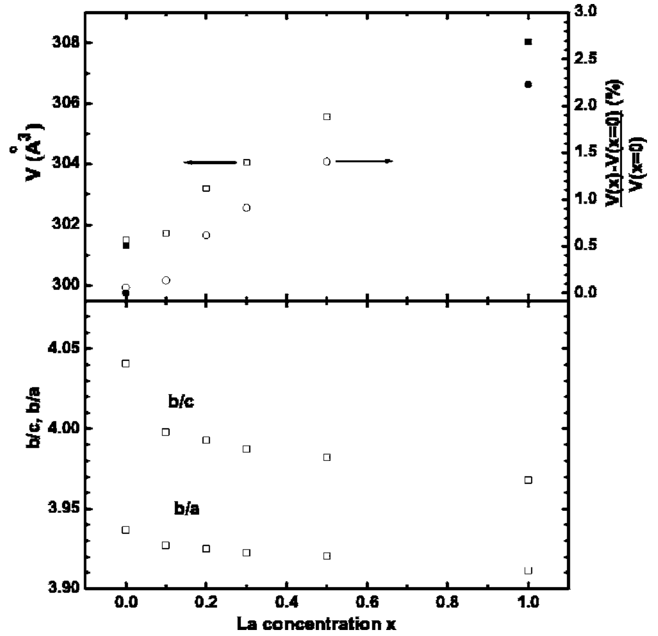

FIG. 1. Upper panel: Volume of the unit cell vs La concentration x. Full symbols are the data points from Ref. 1. Lower panel: Ratio of lattice constants b/c and b/a vs x of $Ce_{1-x}La_xCoGe_2$ for $x=0$, 0.1, 0.2, 0.3, 0.5, and 1.

B. Magnetic susceptibility

All samples used for magnetic susceptibility measurements were small buttons with similar dimensions in all three directions. These buttons were checked first for possible preferential orientation. A direction parallel to the axis of the arc-melter (perpendicular to the surface of the hearth of the arc-melter), which we denote a.m., was identified for all samples. Figure 2 shows the magnetic susceptibility for $CeCoGe_2$ and $LaCoGe_2$, upper and lower panels, respectively, for the two directions of the magnetic field: $H \parallel$a.m. and $H \perp$a.m. Before discussing the preferential orientation, we point to a rather good agreement between the susceptibility reported by Mun *et al.*[2] and our measurements for both compounds.

The magnetic susceptibility of $CeCoGe_2$ has larger values when magnetic field is parallel to the a.m. direction. This result, which cannot be explained by demagnetization effects (estimated to be less than 0.5%), was confirmed on all other $CeCoGe_2$ samples. Furthermore, all studied concentrations containing Ce showed systematically larger values in the magnetic susceptibility for the field direction parallel to a.m. This result suggests preferential orientation of arc-melted $Ce_{1-x}La_xCoGe_2$ samples and significant magnetic anisotropy. A similar preferential orientation in the magnetic susceptibility, i.e., larger susceptibility values for the field parallel to the a.m. axis, was previously reported for polycrystalline $CeNiGe_2$.[11] Subsequent susceptibility investigations on single crystals confirmed strong magnetic anisotropy.[4–7]

We have also observed preferential orientation in the susceptibility of $LaCoGe_2$. However, there is an important difference between the two compounds. All studied $LaCoGe_2$ samples had the susceptibility for $H \parallel$a.m. smaller than that for $H \perp$a.m. There is no reason to suspect different preferred grain orientation in arc-melted $CeCoGe_2$ and $LaCoGe_2$. Rather, these results imply that the magnetic anisotropy in $CeCoGe_2$ is different from that in $LaCoGe_2$. Thus, our magnetic susceptibility data suggest magnetic anisotropy in $CeCoGe_2$, similarly to the case of $CeNiGe_2$. Furthermore, there seem to be two magnetic subsystems, of Ce and Co, that show different magnetic anisotropy. This existence of magnetic anisotropy in $CeCoGe_2$ is obviously inconsistent with the single impurity $J=5/2$ Kondo interpretation. The Kondo model is a single-parameter model, thus isotropic. Therefore, the magnetic anisotropy in (Ce,La)$CoGe_2$ alloys implies the importance of crystalline electric-field effects.

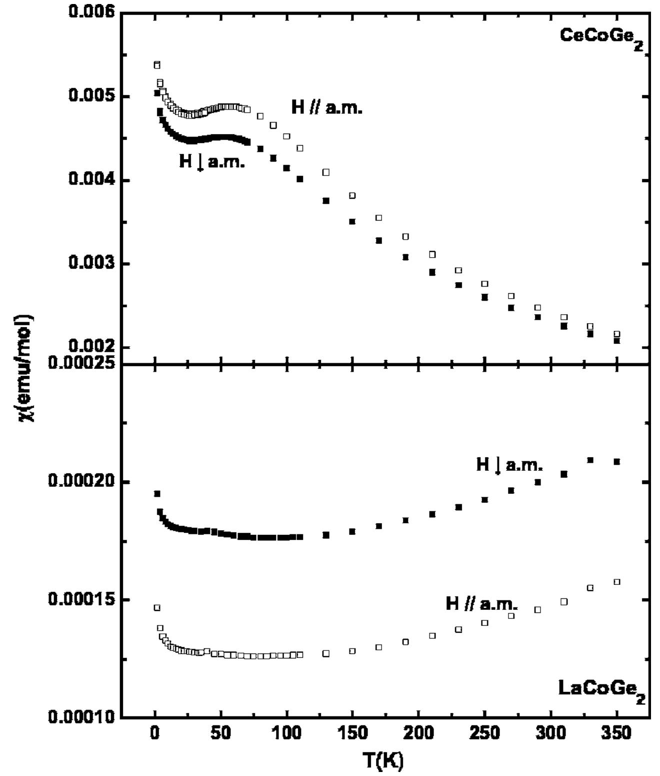

FIG. 2. Magnetic susceptibility of $CeCoGe_2$ and $LaCoGe_2$ for two directions of magnetic fields: $H \parallel$a.m. and $H \perp$a.m. $H = 1000$ Oe.

Figures 3–6 show the evolution of the magnetic susceptibility between $x=0$ and 0.5. The high-temperature susceptibility, when normalized to a mole of Ce, is similar for all alloys above 150 K. The effective moment obtained directly from the straight-line fits of the inverse of the high-temperature susceptibility to temperature is between 2.8 and $2.9\mu_B$. Subtracting $LaCoGe_2$ data results in a reasonable agreement with the expected moment for trivalent Ce, $2.54\mu_B$. The absolute value of the negative Curie-Weiss temperature Θ, implying predominance of antiferromagnetic-type interactions, decreases from 145 K for $x=0$ to 110 K for $x=0.5$ for H parallel to a.m. This Curie-Weiss temperature showed even smaller and less systematic variation for directions perpendicular to a.m. Thus, these high-temperature susceptibility results imply rather good scaling with the Ce concentration, suggesting that single-ion parameters are weakly affected by the La doping.

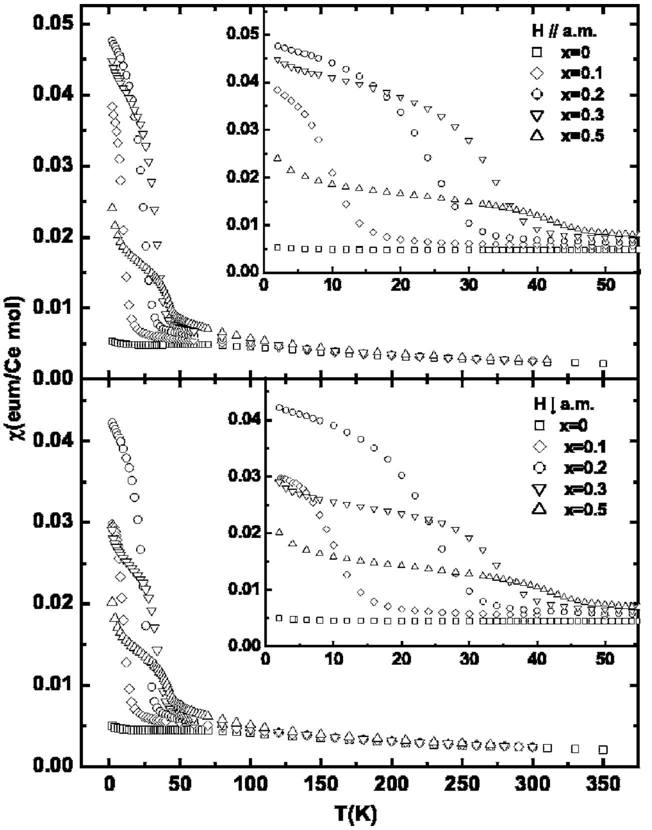

FIG. 3. Magnetic susceptibility of $Ce_{1-x}La_xCoGe_2$, for $x=0$, 0.1, 0.2, 0.3, 0.5, and 1; magnetic fields $H \perp$ a.m. and $H \parallel$ a.m., respectively. $H=1000$ Oe.

The low-temperature susceptibility, on the other hand, shows strong concentration dependence. La-containing alloys exhibit a rapid increase in χ at low temperatures. The temperature corresponding to the rapid rise in χ increases with x from about 20 K for $x=0.1$ to over 50 K for $x=0.5$. Quite possibly these low-temperature increases are related to a tail already observed in the pure compound below 10–15 K. This low-temperature upturn in $CeCoGe_2$ was argued to be due to a small fraction of Co atoms displaced from their correct crystallographic positions. However, we were not able to fit this upturn to the Curie expression. Furthermore, this upturn in several studied $LaCoGe_2$ samples was approximately 20 times smaller than in the Ce compound. The low-temperature increase in mixed alloys is clearly non-Curie-type. Susceptibility curves of mixed alloys have pronounced shoulders, whose temperature again increase with x. These shoulders do not seem to directly cor-

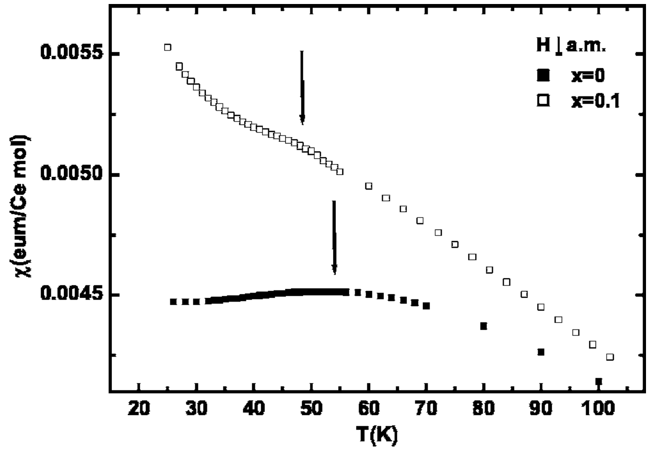

FIG. 4. Magnetic susceptibility of $Ce_{1-x}La_xCoGe_2$ divided by Ce mol, for $x=0$ and 0.1; magnetic field $H \perp$ a.m. The arrows indicate positions of broad maxima discussed in the text.

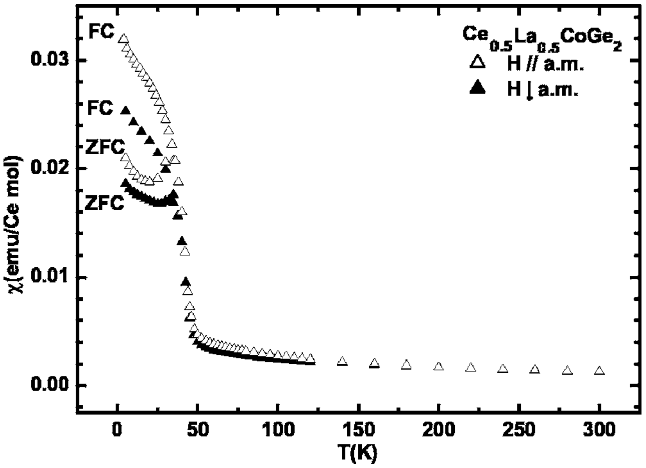

FIG. 5. Magnetic susceptibility of $Ce_{0.5}La_{0.5}CoGe_2$ cooled in zero field (zfc) and in 1000 Oe (fc) for two orientations of the field.

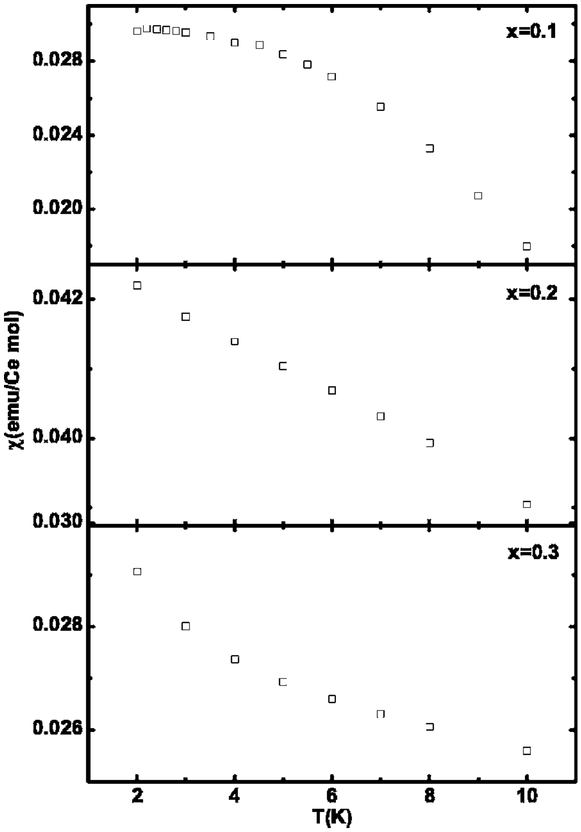

FIG. 6. Low-temperature magnetic susceptibility of $Ce_{1-x}La_xCoGe_2$ divided by Ce mol, for $x=0.1$, 0.2, and 0.3.

respond to a weak maximum in χ of the pure Ce compound between 50 and 60 K (Fig. 4). This weak maximum in $CeCoGe_2$, previously suggested to be due to a single-ion physics, seems to move to lower temperatures when 10% of Ce is replaced by La (Fig. 4). Also, all mixed $(Ce,La)CoGe_2$ alloys exhibit some discrepancies between field-cooled (fc) and zero-field-cooled (zfc) χ, which increase with x. The discrepancy is particularly strong for $x=0.5$, which also shows a sharp cusp in the zfc χ, typical of spin glasses (Fig. 5). Almost identical cusps were observed for two external fields applied at 100 and 1000 Oe.

These magnetic susceptibility data suggest a possible alternative explanation of the 50–60 K broad maximum in χ of $CeCoGe_2$ in terms of magnetic origin, probably due to a short-range magnetic order or two-dimensional magnetic correlations. Preferential orientation in magnetic susceptibility suggests strong magnetic anisotropy, similarly to the related $CeNiGe_2$. $CeNiGe_2$ is a layered material for which room-temperature electrical conductivity in *ac* planes is almost two orders of magnitude larger than along the *b* direction. Magnetic susceptibility of $CeNiGe_2$ is also anisotropic. However, there is a controversy whether the easy magnetization axis is along the *b* direction[4,6] or is in the *ac* plane.[5,7] Can similarly strong anisotropy in exchange interactions lead to a short-range order at 50–60 K in $CeCoGe_2$? An increase of the susceptibility below 10–15 K would be due to a precursor of a long-range magnetic order. Weakening of the anisotropy in La-doped alloys would result in three-dimensional ordering or spin-glass freezing. Finally, CEF excitations could also lead to a structure in the susceptibility similar to that observed in $CeCoGe_2$. For instance, the susceptibility of tetragonal $CeAuSb_2$, which shows strong two-dimensional character, is remarkably similar[12] to that for $CeCoGe_2$. The susceptibility of $CeAuSb_2$ has been accounted for by a CEF model. However, strong sensitivity of this structure in $CeCoGe_2$ to doping (Fig. 4) argues rather for its magnetic origin.

Very interesting is the evolution of the susceptibility below 10 K for nonmagnetic alloys. Figure 6 shows this susceptibility for $x=0.1$, 0.2, and 0.3. For $x=0.2$, the susceptibility has approximately a linear temperature dependence, $\chi=\chi_0-aT$. On the other hand, relatively strong curvatures are seen in $x=0.1$ and 0.3 with opposite signs. We will return to this observation while discussing the specific heat data.

C. Specific heat

Low-temperature specific heat was investigated between 0.3 and 10 K. The results for $x=0$, 0.3, and 0.5 in the form of $\Delta C/T$, where ΔC is a difference between the measured specific heat and the specific heat of $LaCoGe_2$ divided by Ce concentration, versus x are shown in Fig. 7. The values for $CeCoGe_2$ are in good agreement with the report of Mun *et al.*,[2] yielding an enhanced Sommerfeld coefficient $\gamma \approx 120$ mJ/K^2 mol. Our data suggest a possibility of a small increase of $\Delta C/T$ below 1.5 K, as reported previously for Co-deficient samples[8] and interpreted in terms of a precursor of a ferro-or ferrimagnetic transition. However, this upturn in our data is much weaker than that found in the Co-deficient material. $\Delta C/T$ increases with T above 2 K. Compositions $x=0.2$ (not shown), 0.3, and 0.5 exhibit a decrease of $\Delta C/T$ with T in the whole studied temperature range, from 0.3 to 10 K. Thus, this temperature variation seems to correlate with some aspects of the susceptibility. An increase of $\Delta C/T$ with T for the pure Ce compound reflects the existence of a weak maximum in the specific heat at much higher temperatures, 50–60 K.[2]

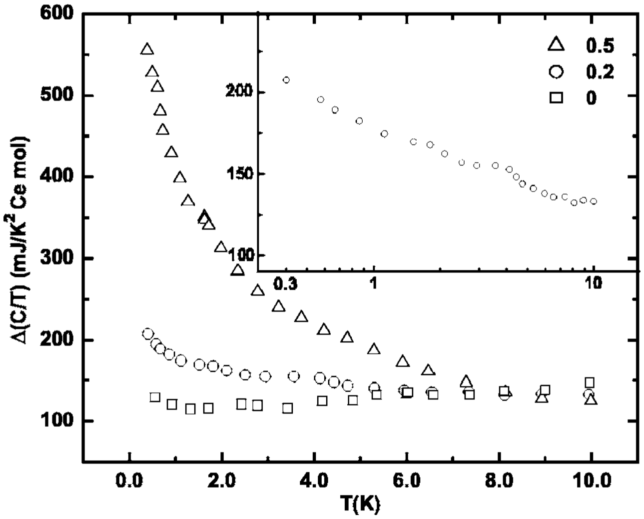

FIG. 7. Specific heat of $Ce_{1-x}La_xCoGe_2$ divided by Ce mol, for $x=0$, 0.2, and 0.5. The inset presents $\Delta C/T$ vs ln T for $x=0.2$.

There is a monotonic increase of the low-temperature $\Delta C/T$ values with x, such that $\Delta C/T$ for $x=0.5$ exceeds 550 mJ/K^{2}Ce mol at 0.3 K. Interestingly, two of the studied concentrations, $x=0.2$ (see inset to Fig. 7) and 0.5, have $\Delta C/T$ approximately proportional to ln T. This variation is a hallmark of non-Fermi liquids. The slopes of $\Delta C/T$ versus ln T are very different for the two compositions, suggesting a different origin of these behaviors. A logarithmic temperature variation and large values of $\Delta C/T$ for $x=0.5$ are surprising since some kind of magnetic ordering or spin-glass freezing takes place at 35 K. In this respect, $Ce_{0.5}La_{0.5}CoGe_2$ is similar to two other systems, UCu_5 (Ref. 13) and $U(Pt_{0.94}Pd_{0.06})_3$,[14] in which low-temperature heavy fermion states develop from high-temperature magnetic states. It is also interesting to note that logarithmic temperature variation of C/T has been observed over some temperature range for these two systems. There is no satisfactory explanation of these behaviors.

On the other hand, the nearly logarithmic variation of C/T with T for $x=0.2$, together with already discussed magnetic susceptibility linear in temperature, implies a possibility of a proximity to a two-dimensional AFM quantum critical point.[15] Obviously, these temperature variations of the specific heat and susceptibility could also be due to a large degree of disorder existing in mixed alloys. However, we would like to point out a somewhat similar evolution of magnetic properties in previously investigated $CeCo_{1-y}Ni_yGe_2$.[16] Alloys corresponding to $y>0.7$ show three-dimensional magnetic ordering. The $y=0.7$ composition has low-temperature magnetic susceptibility and specific heat consistent with two-dimensional quantum critical AFM behavior.

IV. CONCLUSIONS

The described alloying results present considerable challenge to the established $J=5/2$ single Kondo ion interpretation of $CeCoGe_2$. First of all, no single-impurity (even approximate) scaling is observed in the magnetic susceptibility and specific heat data for $Ce_{1-x}La_xCoGe_2$. Obviously, deviations from the single-impurity scaling are expected if the relevant single-impurity parameters are altered by the La alloying. This might be particularly relevant for Ce compounds involving $3d$ transition metals as ligands, since $3d$ orbitals are believed to be very sensitive to changes in local environment. On the other hand, a good concentration scaling has been recently reported in a noncubic system involving a transition metal, $Ce_{1-x}La_xNi_9Ge_4$.[17] High-temperature susceptibility of $Ce_{1-x}La_xCoGe_2$ scales well with Ce, suggesting that relevant single-ion parameters are not altered in any drastic manner across this pseudoternary system. Preferential orientation in magnetic susceptibility for all studied alloys implies the susceptibility to be anisotropic, similarly to $CeNiGe_2$.[11] The preferential orientation of crystallites is supported by direct x-ray-diffraction measurements. This magnetic anisotropy implies the importance of crystalline electric fields and, therefore, is clearly inconsistent with the $J=5/2$ Kondo model, which is istropic. A possibility of a two-dimensional antiferromagnetic critical point should be furthe explored on single crystals of $Ce_{1-x}La_xCoGe_2$, when they become available.

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