Magnetic transitions in $CeCu_{0.86}Ge_2$ and $PrCu_{0.76}Ge_2$ as studied by magnetocaloric effect

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The results of heat capacity in the presence of an external magnetic field and resistivity measurements on the compounds $CeCu_xGe_2$ and $PrCu_yGe_2$ with the starting $x=0.86$ and $y=0.76$ are reported. The magnetocaloric effect in the compounds was calculated from in-field heat-capacity data. The results clearly indicate the nature of magnetic transitions in both compounds and the metamagnetic transition with field in the cerium compounds. The observed magnetocaloric effect is modest in spite of much smaller magnetic moment of Ce and Pr compared to heavy rare earths.

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During the last two decades there has been considerable interest in understanding the magnetic behavior of rare-earth intermetallic compounds. Compounds containing cerium and in some cases praseodymium are particularly interesting because of their anomalous magnetic behavior and the breakdown of de Gennes scaling[1] of magnetic ordering temperature. The breakdown of de Gennes scaling in lighter rare earths is generally due to the relatively extended $4f$ orbital compared to heavy rare earths. Recently the observation of the giant magnetocaloric effect (ΔT_{ad}) in $Gd_5(Si_2Ge_2)$ by Pecharsky and Gschneidner[2] has created much interest in studying the magnetocaloric effect particularly to find out suitable materials for magnetic cooling. We have used the magnetocaloric effect as a tool to understanding the magnetic transitions in rare-earth intermetallic compounds and made various interesting observations.

The intermetallic compounds chosen for our investigation are $CeCu_xGe_2$ and $PrCu_yGe_2$. The nonstoichiometric compounds crystallize in the $CeNiSi_2$-type structure in the narrow range of x and y values around 0.8 and 0.7, respectively.[3] The alloys are crystallographically interesting since they form with vacancies in the transition-metal sublattice. The $CeCu_xGe_2$ ($x\sim0.86$) compound is particularly interesting because of a reasonable high antiferromagnetic ordering temperature ($T_N\sim15$ K) in spite of the positive paramagnetic Curie temperature ($\theta_p\sim7$ K).[4] Since Pr is next to Ce in the Periodic Table it is also worthwhile to investigate the new nonstoichiometric compound $PrCu_yGe_2$ ($y\sim0.76$) in the series.

The polycrystalline samples were prepared by arc melting the constituent elements several times. The elements of purity better than "99.9 wt %" were purchased from Lico Industries, Inc., New York. The weight losses after arc melting were about 0.5%. The ingots, thus obtained, were wrapped in Mo foil, sealed in an evacuated ($\sim10^{-6}$ torr) quartz tube and homogenized at 1173 K for 5 days. To characterize the samples an x-ray diffraction pattern was taken on powdered sample using a rotating anode x-ray source working at 50 kV, 150 mA. The obtained data were analyzed using a full Rietveld profile fit of the line intensity. The lattice constants of the Ce and Pr compounds are in close agreement (within 0.3%) with the literature values[3] of $CeCu_{0.86}Ge_2$ and $PrCu_{0.76}Ge_2$. Our careful analysis indicates a small amount of (~1 wt %) $CeCu_2Ge_2$ present as an impurity phase in our Ce sample. In the case of the Pr compound no other phase was detectable.

The temperature dependence of resistivity (ρ) in the temperature interval 1.4–300 K were performed by the conventional four-probe method. The heat-capacity (C) measurements were performed by the semiadiabatic heat pulse method with absolute accuracy 0.5% in the presence of 0, 5, 8, 10, 20, 40, and 80 kOe fields. The magnetocaloric effect (ΔT_{ad}) was calculated from heat-capacity data in a similar way to that of Ref. 5.

The results of resistivity (ρ) measurements are plotted in Fig. 1. The temperature dependence of ρ of $CeCu_xGe_2$ is similar to that of an earlier report.[4] There is a noticeable

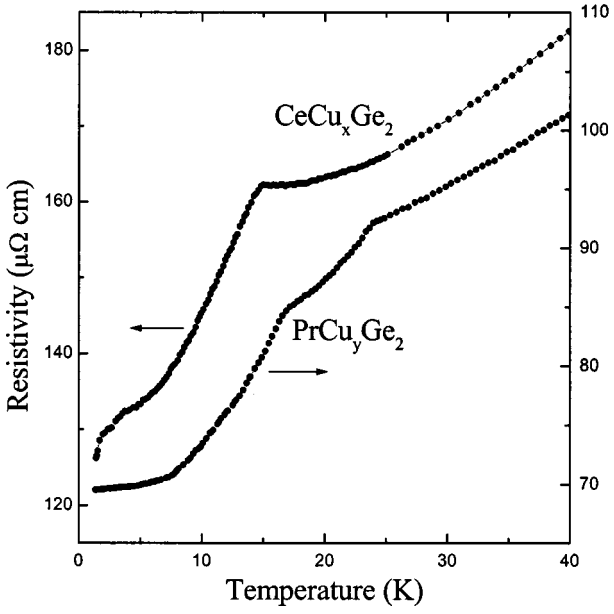

FIG. 1. Electrical resistivity in $\mu\Omega$ cm of the compounds $CeCu_xGe_2$ ($x\sim0.86$) and $PrCu_yGe_2$ ($y\sim0.76$) in the temperature interval 1.5–40 K.

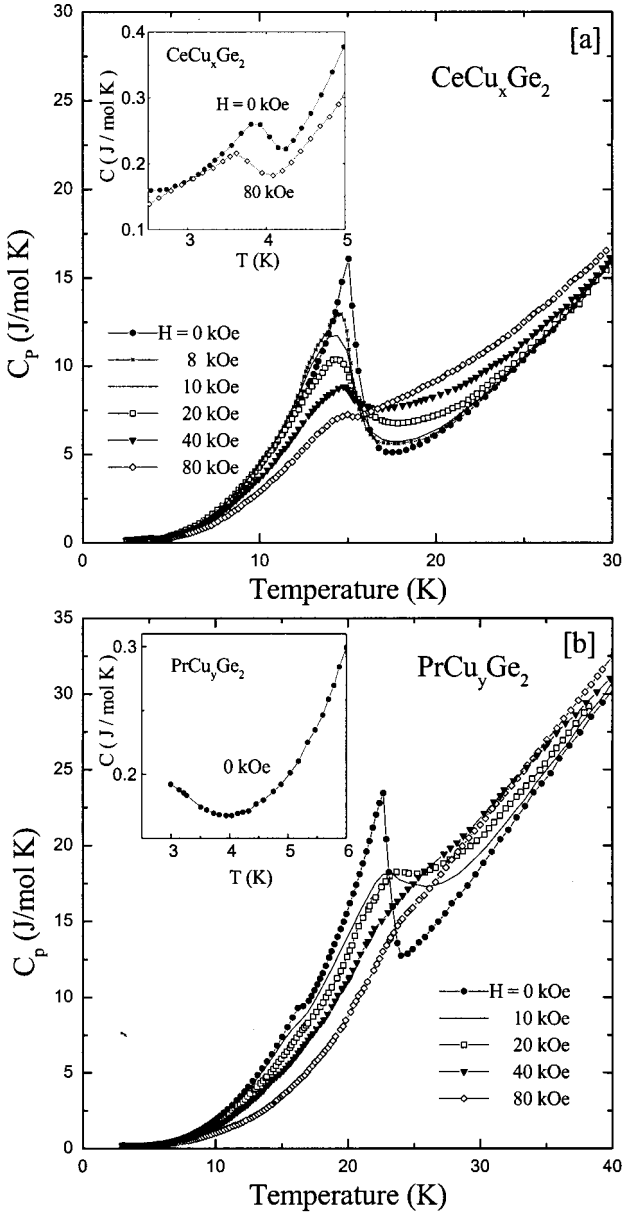

FIG. 2. Heat capacity as a function of temperature for the compounds $CeCu_xGe_2$ ($x \sim 0.86$) and $PrCu_yGe_2$ ($y \sim 0.76$) in the presence of zero and different constant magnetic field. The low-temperature features are highlighted in the insets.

decrease of ρ below 15 K due to the loss of a spin-disorder contribution. The ρ data of $PrCu_yGe_2$ indicates two transitions around 24 and 17 K.

The results of heat-capacity measurements C in the presence of external magnetic fields are plotted in Fig. 2. The data for the measurement in 5 kOe field is not shown in the figure for clarity. In the zero-field C data of $CeCu_xGe_2$ [Fig. 2(a)] there is a peak around 15 K due to magnetic ordering. In the presence of more than 10 kOe magnetic field the entropy of the system shifts to higher temperature, which is expected for a ferromagnetically ordered system. At fields less than 20 kOe there is a marginal increase of C compared to the zero-field C value below and above the heat-capacity peak around 15 K. There is a small but clear peak in C at 4 K; see the inset of Fig. 2(a), which shifts to lower temperature with increasing field. It indicates antiferromagnetic ordering at this temperature. Since $CeCu_2Ge_2$ orders antiferromagnetically at the same temperature (~4 K) possibly the heat-capacity peak at this temperature is due to a very small (~1 wt %) amount of the $CeCu_2Ge_2$ phase. The zero-field C data of $PrCu_xGe_2$ in Fig. 2(b) shows a peak at 23 K and a knee at 16 K. The 16 K heat-capacity anomaly in $PrCu_xGe_2$ cannot be attributed to the impurity phase. In the case of impurity at least 10 wt % of $PrCu_2Ge_2$ would be required for the observed C anomaly, which is ruled out from our x-ray diffraction (XRD) analysis. The observed C anomaly and the drop in ρ close to these temperatures can be attributed to magnetic ordering. With the application of magnetic field, entropy shifts to higher temperature for all the fields. There is a marginal increase of C with the lowering of temperature below 5 K, which is highlighted in the inset of Fig. 2(b).

The magnetocaloric effect is the change in temperature $\Delta T_{ad}\,[=T(H)-T(0)]$ of magnetic material in the adiabatic condition with the application of the external magnetic field. This effect originates due to the change of magnetic entropy of magnetic material in the presence of magnetic field. For ferromagnetic materials close to T_c magnetic entropy decreases with increasing magnetic field and in an adiabatic condition that gives rise to an increase in temperature, positive ΔT_{ad}. The temperature dependence of ΔT_{ad} is expected to be a caretlike shape with maxima at the ordering temperature (T_c). For antiferromagnetic material ΔT_{ad} is negative and the temperature dependence of that is a reverse caretlike shape with minima around T_N.[6] We have obtained ΔT_{ad} from total entropy (S_{total}) which was calculated from experimental specific-heat data at various constant magnetic fields. The ΔT_{ad} is the required difference in temperature to move isoentropically from the in-field to zero-field data points in the plot of S_{total} with respect to temperature. It was shown earlier by Dan'kov *et al.*[7] that the obtained ΔT_{ad} in this indirect method is essentially the same as that of the direct method.

The temperature dependence of ΔT_{ad} is plotted in Fig. 3. The ΔT_{ad} of the compound $CeCu_xGe_2$ for 80 kOe field is large and positive with a peak around 16 K. It indicates that at higher field the magnetic moments are ferromagnetically aligned and the magnetic transition temperature is 16 K. For a smaller (<20 kOe) field value ΔT_{ad} is positive in the paramagnetic region and its magnitude increases with decreasing temperature up to 16 K. Below 16 K ΔT_{ad} starts decreasing with lowering temperature and shows negative minima at 14 K. This observation indicates that the ferromagnetic interactions are dominant in the paramagnetic region resulting in positive ΔT_{ad} and around 16 K antiferromagnetic interactions starts dominating resulting in negative ΔT_{ad} at lower temperatures. The low-field features are highlighted in the inset of Fig. 3(a) for the compound $CeCu_xGe_2$. The ratio of positive peak value with negative minima is close to one for both 0–5 kOe and 0–8 kOe data; however, for 0–10 kOe data it suddenly increases. This indicates that if only for fields higher than 8 kOe, spins are flipping towards the field direction, giving rise to a larger increase of positive peaks compared to the negative minima in the plot of ΔT_{ad} as a

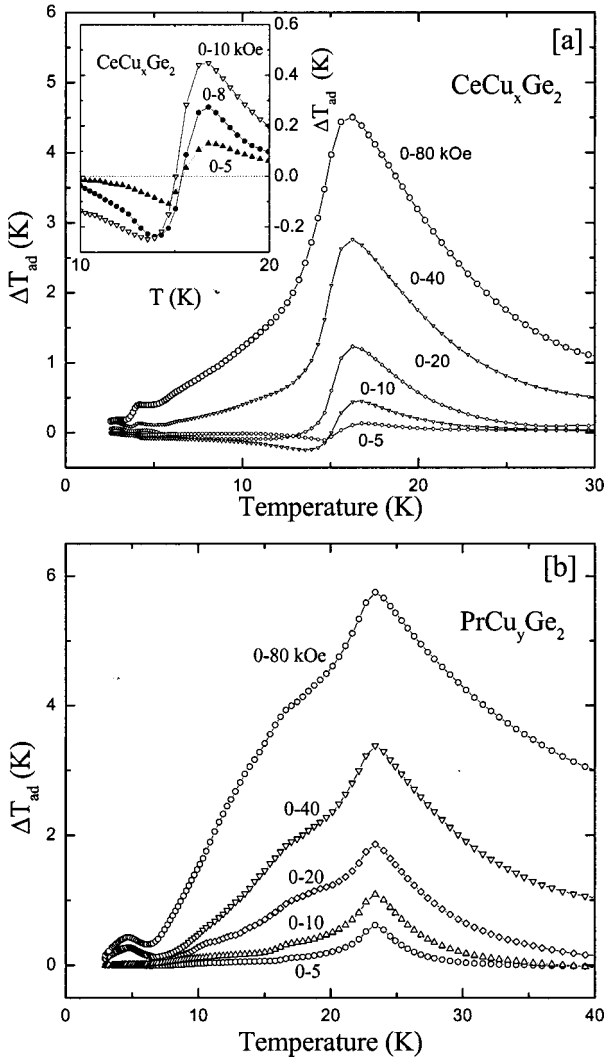

FIG. 3. Temperature dependence of the magnetocaloric effect (ΔT_{ad}) for the compounds $CeCu_xGe_2$ ($x \sim 0.86$) and $PrCu_yGe_2$ ($y \sim 0.76$). The inset in plot (a) highlights the low-field behavior of ΔT_{ad} near the 15 K transition for the compound $CeCu_xGe_2$.

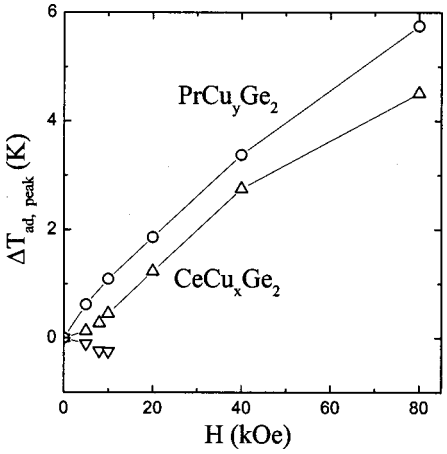

FIG. 4. Values of ΔT_{ad} at the peak position plotted as a function of field for the compounds $CeCu_xGe_2$ ($x \sim 0.86$) and $PrCu_yGe_2$ ($y \sim 0.76$).

function of temperature. This behavior indicates a metamagnetic transition for fields higher than 8 kOe. The metamagnetic behavior around the 10 kOe field was also observed earlier[4] in this compound in isothermal magnetization and magnetoresistance measurements.

Interestingly the temperature dependence of ΔT_{ad} shows a clear minima around 4 K even for the 40 kOe field, highlighting the antiferromagnetic nature of the ordering at this temperature. This also indicates that antiferromagnetic coupling at the 4 K transition is stronger than at the 16 K transition. Since the 4 K transition appears to be due to the very small amount ($\sim$1 wt%) of the $CeCu_2Ge_2$ phase, it may indicate the strength of the technique and sensitivity of our measurements.

The ΔT_{ad} of the Pr compound is shown in Fig. 3(b). It has a positive peak around 23 K indicating ferromagnetic ordering at that temperature. In contrast to the ΔT_{ad} data of the Ce compound the data for the Pr compound does not give negative minima even for 0–5 kOe. This shows the ferromagnetic nature of the magnetic ordering. Another peak in the ΔT_{ad} data is observed at 5 K, the origin of which is not clear at present. There is only a minor increase of C with the lowering temperature and the peak in ΔT_{ad} around 5 K is arising due to the crossing of the infield C curve with the zero-field curve. This rise in C with lowering temperature can be due to either nuclear Schottky effects or another magnetic transition at lower temperature. A similar increase in C at low temperature was observed earlier in Pr compounds and was attributed to nuclear Schottky effects. Our efforts to get a reasonable fit to low-temperature data considering the nuclear effect was not successful. However, to say something conclusively it is necessary to extend the measurements down to lower temperature. We have seen a small hump in ΔT_{ad} at 15 K [Fig. 3(b)]. Since it coincides with the temperature where a sharp anomaly was observed in resistivity and zero-field C data, this hump at 15 K is not due to the crystal-field effect but it is magnetic in origin.

The plot of the maximum value of ΔT_{ad} at different magnetic fields for the Ce and Pr compound is plotted in Fig. 4. It shows a modest magnetocaloric effect. The value for the Pr compound is about 1 K/tesla for fields up to 2 tesla. The rate of increase of ΔT_{ad} decreases at higher field. Since the effective magnetic moment of Ce and Pr is much smaller compared to the heavy rare earths the observed value of ΔT_{ad} is very interesting.

The magnetic transition temperature is the temperature where the change in magnetization as a function of temperature is maximum. It corresponds to the zero-field heat-capacity inflection point above the heat-capacity peak.[8,9] The magnitude of ΔT_{ad} is also maximum where the rate of change of magnetization (as a function of temperature) is maximum. The maximum value of ΔT_{ad} occurs at the temperature where the C as a function of temperature at two different magnetic fields ($H_{initial}$,H_{final}) crosses each other (T_{cross}). It implies that the T_{cross} can be considered as a magnetic ordering temperature for $H_{initial}=0$. Dan'kov *et al.*[7] has extended this idea to determine the magnetic ordering temperature even in the presence of a magnetic field considering the nonzero value of $H_{initial}$. They found a good agreement

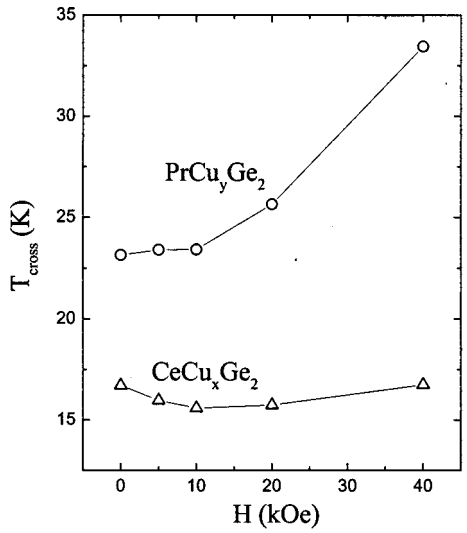

FIG. 5. The crossing point of C versus T data (T_{cross}) at two consecutive fields (H_{initial},H_{final}) in kOe (0,5), (5,10), (10,20), (20,40), and (40,80) plotted as a function of H_{initial}.

between the transition temperature obtained from the inflection point of C and the temperature corresponding to the maximum value of ΔT_{ad}. The T_{cross} for the Ce and Pr compounds for two consecutive fields (H_{initial},H_{final}) in kOe (0,5), (5,10), (10,20), (20,40), and (40,80) are plotted in Fig. 5 as a function of H_{initial}. In the case of the Ce compound the inflection point of C and the T_{cross} are almost the same and they remain nearly constant with increasing magnetic field. Whereas, in the case of the Pr compound the T_{cross} shows a rapid increase for field values higher than 20 kOe. For the 40 kOe initial field value T_{cross} is around 33 K. Our data highlight that one has to take this temperature as a transition temperature with caution. Since in this case there is no heat-capacity peak in the 40 kOe data, the determination of the transition temperature from the heat-capacity inflection point is not possible. Around 33 K, the heat capacity for the 40 kOe field is larger compared to the zero-field heat capacity. There is no other anomaly in the total heat capacity at 40 kOe magnetic field around this temperature. It indicates either the heat-capacity anomaly due to magnetic transition has been masked by the dominant lattice contribution (which is difficult to subtract in the absence of proper nonmagnetic reference) or the T_{cross} is not a true representative of the transition temperature. More studies by various other independent techniques and on different systems will justify the weakness and strength of this method.

To conclude, the results of the measurements on $CeCu_xGe_2$ and $PrCu_yGe_2$ compounds indicate the magnetocaloric effect is a useful and sensitive technique to understand the nature of the metamagnetic transition and modifications of transitions in the presence of the magnetic field. Both compounds show a modest magnetocaloric effect, which indicates the strong possibility of a much larger magnetocaloric effect for similar compounds with heavy rare earths.

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