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LETTER TO THE EDITOR

The similar dependence of the magnetocaloric effect and magnetoresistance in TmCu and TmAg compounds and its implications

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Abstract

We report the results of resistivity (ρ), magnetoresistance (MR) and in-field heat capacity (C) measurements on TmCu and TmAg compounds. Despite the different nature of magnetic transitions—first-order in TmCu and second-order in TmAg—the magnetocaloric effect (MCE) obtained from in-field heat capacity data is similar for higher fields. There are striking similarities between the MCE and MR as a function of temperature as well as magnetic field (H). We have shown that in the paramagnetic state, MCE has $-H^2$ dependence due to the suppression of spin fluctuation. Since the MCE and MR are related with thermodynamic and transport properties respectively, two different properties of a system and the similarities between the two indicate a deeper relation between the origin of MR and MCE.

1. Introduction

The magnetocaloric effect (MCE), which is well established [1], is the isothermal entropy change ($-\Delta S$) and the adiabatic temperature change (ΔT_{ad}) of magnetic materials with the application of a magnetic field. The study of MCE has recently acquired momentum [2,3,4] due to the discovery of giant MCE in Gd compounds [5] and the realization of its technological importance for magnetic cooling [6]. The giant MCE in $Gd_5Si_2Ge_2$ (2–5 times higher than that of pure Gd) [5], which was calculated indirectly from in-field heat capacity (C) data, was due to first-order transitions. The recent direct measurement of adiabatic temperature changes (ΔT_{ad}) in the compound results in much lower ΔT_{ad} (when compared to Gd) [7]. The MCE study of two similar compounds, one with first-order and the other with second-order transitions, may help to understand the relative importance of the various factors contributing to the MCE. With this motivation we have decided to study TmCu and TmAg compounds in detail.

TmCu and TmAg compunds form in a stable CsCl cubic structure [8] where Tm has a large magnetic and 4f-electric-quadrupole moment. The magnetic moments in TmCu

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order antiferromagnetically at 7.7 K in an incommensurate antiferromagnetic structure and it transforms to a commensurate structure below 6.7 K [9]. Due to the strong quadrupolar interactions the magnetic transitions in this compound are of first-order [10]. In TmAg the antiferromagnetic transition is at 9.5 K and the transition is second-order due to a weaker quadrupolar interaction compared to TmCu [10]. The isomorphous TmCu and TmAg compounds exhibit very similar crystalline electric field and bilinear interactions [10]. In contrast to the general belief that a compound with first-order transition will give much a larger magnetocaloric effect, our study indicates that MCE at higher fields is similar in both compounds. The MCE is strongly influenced by the metamagnetic transition, which is observed in both compounds. The most interesting finding is the similar dependence of $\Delta\rho(=\rho(H)-\rho(0))$ and ΔS both as a function of temperature as well as magnetic field. The comparison of $\Delta\rho$ and ΔS, which are two distinctly different quantities, one related with transport and the other related with thermodynamic properties, is shown to be helpful to gain a deeper understanding about the contributions of MR and MCE.

2. Experimental details

The polycrystalline samples were prepared by arc melting of constituent elements of purity better than 99.9% in Argon atmosphere. The samples were homogenized at 973 K in a vacuum for one week. X-ray diffraction pattern confirmed the single-phase CsCl-type structure for both compounds. The C measurements were performed using the semi-adiabatic heat-pulse method with absolute accuracy 0.5% in the presence of 0, 10, 20, 40, 60 and 80 kOe fields. The resistivity (ρ) measurements were performed using the conventional four-probe method in the presence of He exchange gas. The measurements for longitudinal magnetoresistance ($\Delta\rho/\rho=\{\rho(H)-\rho(0)\}/\rho(0)$) and the difference in resistivity ($\Delta\rho=\rho(H)-\rho(0)$) at 3, 5, 7, 10 and 15 K were carried out in magnetic field (H) up to 80 kOe. The ρ measurements in the presence of the 80 kOe magnetic field were carried out in the temperature interval 1.5 to 30 K with magnets in the persistent mode.

3. Results and discussion

The temperature dependence of C for TmCu and TmAg at various constant magnetic fields is plotted in figure 1. The inflection point of zero-field C data are considered as the magnetic ordering temperature. In agreement with [10], two first-order transitions at 6.7 K and 7.8 K in TmCu and a second-order transition at 9.2 K in TmAg was observed in zero-field C data. In the presence of small ($\sim$ 10 kOe) external magnetic field the peak of C in both the compounds shifts to lower temperatures, indicating the antiferromagnetic nature of the magnetic orderings. For higher magnetic fields, C of both the compounds is largely modified.

We have obtained isoentropic temperature change (ΔT_{ad}) and isothermal entropy change (-ΔS) from total entropy (S_{total}), which was calculated from experimental C data (2–30 K) at various constant magnetic fields. To calculate the entropy contribution from temperatures lower than 2 K, the linear variation of C data down to zero Kelvin was considered. The ΔT_{ad} is the required difference in temperature to move iso-entropically from zero-field to in-field data in the plot of S_{total} with respect to temperature [11]. It was shown earlier by Dan'kov *et al* [12] that the obtained ΔT_{ad} in this indirect method is essentially the same as that of the direct method. The $-\Delta S$ is obtained in a similar way to that of ΔT_{ad} from the same plot, the only difference being that one has to move isothermally. The plots of $-\Delta S$ and ΔT_{ad} as a function of temperature for 10, 20, 40, 60 and 80 kOe fields are shown in figures 2 and 3 respectively for

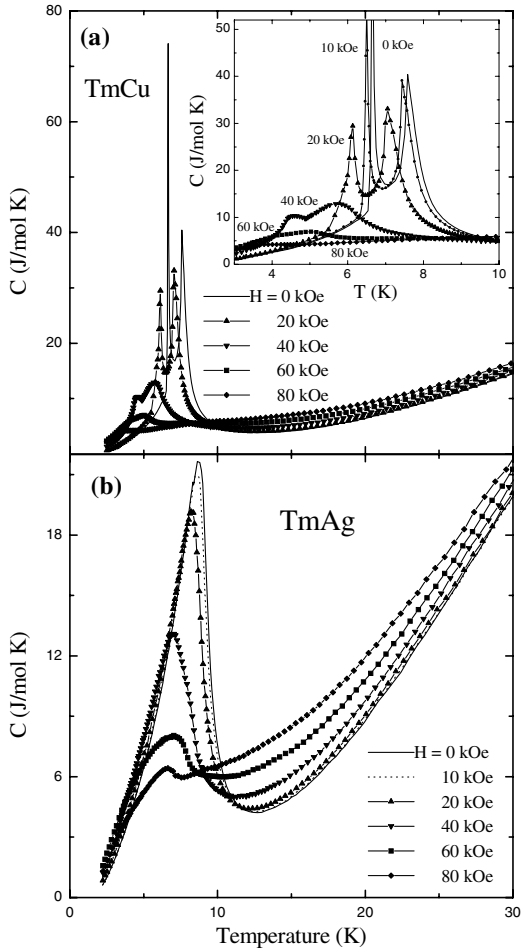

Figure 1. Heat capacity (C) as a function of temperature for (a) TmCu and (b) TmAg at constant magnetic fields. The inset in (a) shows the C behaviour for TmCu near magnetic transitions in expanded form. The line through the data points serve as a guide to the eye.

TmCu and TmAg compounds. For ferromagnetic ordering the plot of ΔT_{ad} as a function of temperature is expected to be a caret-like shape with maxima at the ordering temperature (T_c). For antiferromagnetic material ΔT_{ad} is negative and the temperature dependence is believed to be a reverse caret-like shape with minima around T_N [13]. At temperatures lower than 10 K, the ΔT_{ad} is negative for both the compounds. The minima closer to T_N is consistent with antiferromagnetic ordering. As expected, because of the first-order transition, the magnitude of negative ΔT_{ad} is much larger in TmCu than in TmAg. The ΔT_{ad} in the paramagnetic state is positive and increases with decreasing temperature, which is expected due to the partial alignment of the paramagnetic moments in the presence of external magnetic fields. MCE in the paramagnetic state is generally not large. The reasonably large and positive ΔT_{ad} in both of the compounds for 80 kOe field indicates that there may be a ferromagnetic orientation around 10 K. For field values higher than 40 kOe, the increase in the rate of change of ΔT_{ad} with field around 10 K and the decrease in the magnitude of negative minima at lower temperature, is an

indication of metamagnetic transition. The MCE below 8 K, especially for lower field values, are different in TmCu and in TmAg. However, the overall similar ΔT_{ad} in TmCu and TmAg for higher field values, indicates that the first-order transition in TmCu is not the dominating factor for magnetocaloric effect in this compound. The reasonably large positive ΔT_{ad} around 10 K in both the compounds arises due to the metamagnetic transition.

Magnetoresistance also gives a signature of metamagnetic transition. With the motivation to see metamagnetic transitions we performed MR measurements. Moreover, we had an interest in performing ρ measurements, both in the presence and in the absence of field. Recently, with the help of our study on $PrCo_2Si_2$, we have shown that the temperature dependence of ΔT_{ad} is similar to $-\Delta\rho[= \rho(0) - \rho(H)]$ in a region where the effect is negligible due to change in carrier concentration [14]. With the application of a magnetic field for ferromagnetic systems, the adiabatic temperature change (ΔT_{ad}) is positive due to the decrease in magnetic entropy because of the relatively more oriented magnetic moments in the presence of a field. For more oriented magnetic moments with increasing field the resistivity

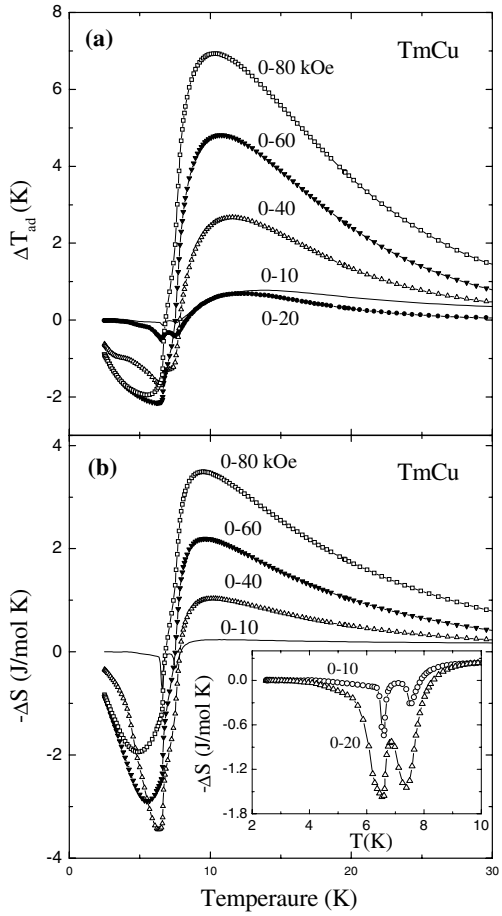

Figure 2. Magnetocaloric effect (a) ΔT_{ad} and (b) $-\Delta S$, for TmCu as a function of temperature calculated from heat capacity data at constant magnetic fields. The $-\Delta S$ for 10 and 20 kOe fields is shown as an inset in (b) for clarity. The line through the data points serve as a guide to the eye.

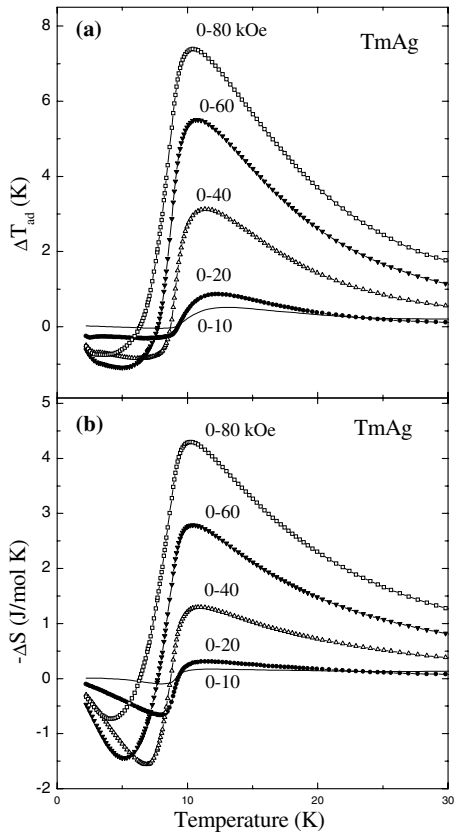

Figure 3. Magnetocaloric effect (a) ΔT_{ad} and (b) $-\Delta S$ for TmAg as a function of temperature calculated from heat capacity data at constant magnetic fields. The line through the data points serve as a guide to the eye.

decreases $[\rho(0) > \rho(H)]$ due to the reduced scattering of conduction electrons. So the change in orientation of magnetic moments by external magnetic fields can effect both ΔT_{ad} and $-\Delta\rho$; and the similar temperature dependence was observed [14]. Since ΔT_{ad} and $-\Delta S$ has similar dependence, the dependence of $-\Delta\rho$ can be compared with $-\Delta S$ as well. The temperature dependence of ρ in zero and 80 kOe field for TmCu and TmAg is shown in figures 4 and 5, respectively. The temperature dependence of $-\Delta S$ obtained from heat capacity data and $-\Delta\rho[= \rho(0\text{ kOe}) - \rho(80\text{ kOe})]$ is highlighted in the insets. For both TmCu and TmAg the temperature dependence of $-\Delta S$ and $-\Delta\rho$ is similar. Although the temperature dependence of ΔT_{ad} and $-\Delta\rho$ is also similar, the agreement between the temperature dependence of $-\Delta S$ and $-\Delta\rho$ is better. For TmCu below 7 K the magnitude of $-\Delta\rho$ is larger than expected. In the absence of a magnetic field the magnetic structure of TmCu changes from incommensurate to commensurate below 6.7 K. The incommensurate antiferromagnetic ordering can open up a super-zone energy gap at the Fermi level [15,16]. Possibly below 6.7 K, with the application of a magnetic field, the magnetic structure changes from commensurate to incommensurate, which results in larger positive MR due to the change in carrier concentration. As a result the MR of TmCu at 3 K is very large (∼55% for 40 kOe field). The modification of carrier concentration will have a larger influence on $\Delta\rho$ than on ΔS or ΔT_{ad}. A similar situation in the

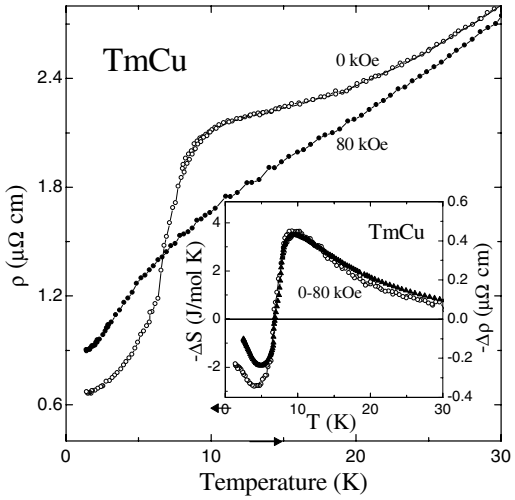

Figure 4. Resistivity (ρ) as a function of temperature for TmAg at 0 and 80 kOe magnetic fields. The inset shows the temperature dependence of $-\Delta$S (solid triangles) at 80 kOe on the left axis and $-\Delta\rho$ (open circles) calculated from ρ data at 0 and 80 kOe fields on the right axis. The lines through the data points serve as a guide to the eye.

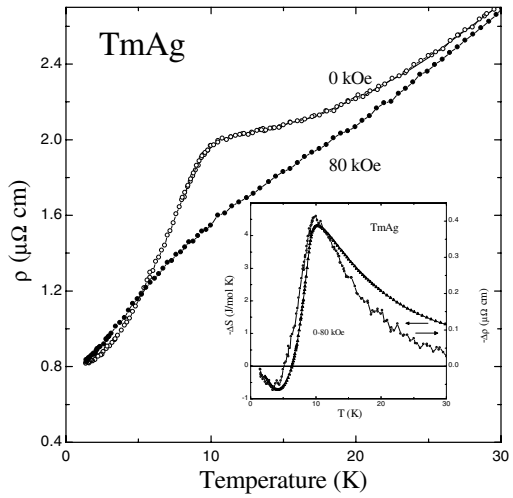

Figure 5. Resistivity (ρ) as a function of temperature for TmCu at 0 and 80 kOe magnetic fields. The inset shows the temperature dependence of $-\Delta S$ (solid triangles) at 80 kOe on the left axis and $-\Delta\rho$ (open circles) calculated from ρ data at 0 and 80 kOe fields on the right axis. The line through the data points serve as a guide to the eye.

case of $PrCo_2Si_2$ was discussed in our earlier report [14]. In the case of TmAg the agreement between the temperature dependence of $-\Delta S$ and $-\Delta\rho$ is not that good.

To show the similarities, the field dependence of $\Delta\rho$ is plotted with the dependence of ΔS in figures 6 and 7 for TmCu and TmAg, respectively. It should be mentioned that both compounds have large MR ($\Delta\rho/\rho$). For TmCu it is 55% (40 kOe) at 5 K and -20% (80 kOe)

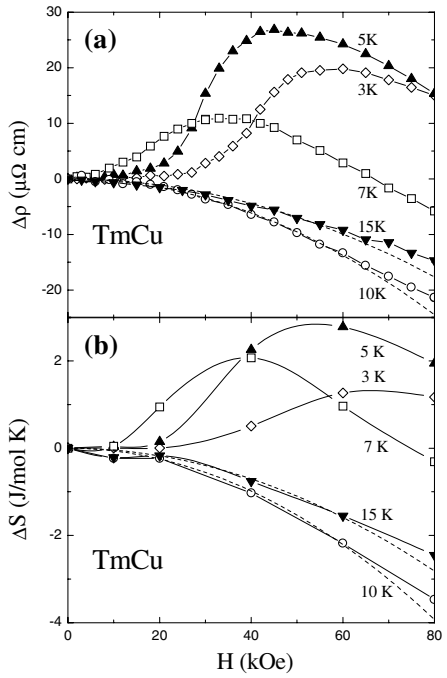

Figure 6. (a) shows the change in resistivity ($\Delta\rho = \rho(H) - \rho(0)$) and (b) shows the magnetocaloric effect ΔS, as a function of magnetic field (H) at constant temperatures for TmCu. Continuous lines through the data points serve as a guide to the eye. The dashed line shows the $-H^2$ fit 0–60 kOe for 10 and 15 K data.

at 10 K. For TmAg the MR is 20% (40 kOe) at 5 K and −20% (80 kOe) at 10 K. The field dependence of ΔS (shown in figures 6 and 7) was obtained from the temperature dependence of ΔS at various field values (figures 2(b) and 3(b)). As indicated in the figures, there are striking similarities between the field dependence of $\Delta\rho$ and ΔS of both compounds. In both compounds $\Delta\rho$ at 3, 5 and 7 K is positive and increases with increasing field up to 40 kOe. For the antiferromagnetic system $\Delta\rho$ is expected to be positive and increases with increasing field. After the initial increase in $\Delta\rho$ with increasing field, the decrease in $\Delta\rho$ is an indication of the metamagnetic transition. The maxima in 3, 5 and 7 K data of $\Delta\rho$ of the Tm compounds (figures 6 and 7) indicate the metamagnetic transition for field values higher than 40 kOe. A similar feature in the plot of ΔS versus H is an indication of the metamagnetic transition. The suppression of spin fluctuation in the presence of a magnetic field gives rise to negative $\Delta\rho$ with H^2 dependence. The dashed line associated with 10 and 15 K shows the H^2 variation of $\Delta\rho$ data in figures 6 and 7. This observation indicates that the suppression of spin fluctuation is the dominant contribution to $\Delta\rho$ at high field, for temperatures of 10 K and above. Because of the similar field dependence it may be expected that ΔS at 10 K and above is also dominated by the suppression of spin fluctuation.

4. Conclusions

There are striking similarities between $\Delta\rho$ and ΔS for TmCu and TmAg compounds, both as a function of field and temperature. The ΔS (and ΔT_{ad}) has $-H^2$ dependence in the

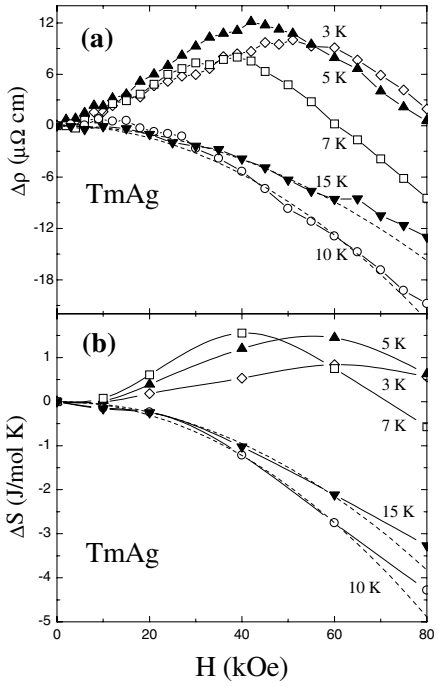

Figure 7. (a) shows the change in resistivity ($\Delta\rho = \rho(H) - \rho(0)$) and (b) shows the magnetocaloric effect ΔS, as a function of magnetic field (H) at constant temperatures for TmAg. Continuous lines through the data points serve as a guide to the eye. The dashed line shows the $-H^2$ fit 0–60 kOe for 10 and 15 K data.

paramagnetic state due to the suppression of spin fluctuations similar to that of $\Delta\rho$. The metamagnetic transition can also be observed in MCE data. The MCE at higher (80 kOe) fields of TmCu and TmAg is similar despite the different orders of transitions. The similar and large contribution from spin fluctuations and metamagnetic transitions of both compounds mask the minor difference created by the difference in the order of transition. The comparison of $\Delta\rho$ and ΔS is helpful to understand the various major contributions in MR and MCE.

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