Magnetic transition and large reversible magnetocaloric effect in $EuCu_{1.75}P_2$ compound*

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The magnetocaloric effect (MCE) in $EuCu_{1.75}P_2$ compound is studied by the magnetization and heat capacity measurements. Magnetization and modified Arrott plots indicate that the compound undergoes a second-order phase transition at $T_C \sim 51$ K. A large reversible MCE is observed around T_C. The values of maximum magnetic entropy change $(-\Delta S_M^{max})$ reach 5.6 J·kg^{-1}·K^{-1} and 13.3 J·kg^{-1}·K^{-1} for the field change of 2 T and 7 T, respectively, with no obvious hysteresis loss in the vicinity of Curie temperature. The corresponding maximum adiabatic temperature changes (ΔT_{ad}^{max}) are evaluated to be 2.1 K and 5.0 K. The magnetic transition and the origin of large MCE in $EuCu_{1.75}P_2$ are also discussed.

Keywords: $EuCu_{1.75}P_2$ compound, magnetocaloric effect, magnetic transition, critical behavior

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1. Introduction

In recent years, the magnetocaloric effects (MCEs) in various magnetic materials have been extensively studied experimentally and theoretically, because of their great potential not only for magnetic refrigeration applications but also for further understanding the fundamental physical properties of the materials.[1–3] The MCE manifests an isothermal magnetic entropy change (ΔS_M) or an adiabatic temperature change (ΔT_{ad}) when the magnetic material is exposed to a varying magnetic field. Magnetic refrigeration based on the MCE is advantageous in that it is environmentally friendly and has an energy efficient refrigeration mechanism, which is expected to be an important future cooling technology.[1–3] A large value of MCE is considered to be the most important requirement of the application, and therefore it is desirable to find new materials with large MCE especially at low magnetic fields and with a wide temperature range. Recently, some rare-earth-based compounds each with an antiferromagnetic (AFM) or a ferromagnetic (FM) structure have been found to possess not only large magnetic entropy change but also a small hysteresis loss, which is crucially important for practical applications. [4–14]

The intermetallic compounds of the EuT_2X_2 (T = Fe, Co, Cu, etc.; X = Si, P, B, etc.) each with a $ThCr_2Si_2$-type crystal structure are extensively studied due to their interesting physical properties. Depending on the constituent element or composition, various properties like superconductivity, magnetic ordering, the Kondo effect, heavy-fermion properties, valence fluctuation, large MCE, etc. are observed.[15–17] $EuFe_2As_2$ is attracting much attention due to the discovery of Fe-based superconductivity.[18,19] $EuFe_2P_2$ is a rare Eu-containing dense Kondo lattice compound.[20] Recently, a ferromagnetic transition around 51 K for $EuCu_{1.75}P_2$ was confirmed by examining the temperature dependences of magnetization and electrical resistivity.[21] Very recently, Kim *et al*.[22] reported on a giant reversible anisotropic MCE in antiferromagnetic $EuFe_2As_2$ single crystal. To search new materials displaying large MCE and further understand the physical properties of EuT_2P_2 system, the critical behavior and MCE in $EuCu_{1.75}P_2$ are systematically studied in this paper.

2. Experiment

The samples of $EuCu_{1.75}P_2$ were synthesized by heating a reactant of high purity Eu, Cu, and P in an evacuated fused silica tube very slowly. Detailed descriptions of sample preparation and phase analysis are given in Ref. [21]. The magnetic measurement was performed on a vibrating sample magnetometer (VSM) which is an option of physical property measurement system (PPMS-9, Quantum Design). The specific heat measurements were carried out by the adiabatic heat relaxation method by using PPMS.

3. Results and discussion

Figure 1 shows the temperature dependence of magnetization (M, $H = 0.1$ T) for $EuCu_{1.75}P_2$. A sharp paramagnetic-to-ferromagnetic (PM–FM) transition can be observed around 50 K. The temperature dependence of zero field specific heat (C/T) for $EuCu_{1.75}P_2$ is also shown in Fig. 1. A clear λ-

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shaped peak in specific heat corresponds to the magnetic transition. These data provide a determination for $T_C = 51$ K which is consistent with that deduced from $M(T)$ curve and previous reported results.[21] A set of magnetic isothermals on increasing and decreasing field for $EuCu_{1.75}P_2$ is measured in a temperature range from 4 K to 90 K and in a magnetic field range from 0 T to 7 T. No obvious hysteresis can be observed in the whole temperature range. To make the figure readable, only several isotherms in an increasing field are presented in Fig. 2. At low temperatures, the values of magnetization M tend to be saturated at low fields. A large reversible MCE is expected to appear around the transition temperature where the magnetization rapidly changes with temperature varying. Since the MCE has a strong correlation with the order of the corresponding magnetic phase transition, it is important to understand the nature of magnetic transition in $EuCu_{1.75}P_2$ compound. According to Banerjee criterion,[23] the magnetic transition is of a second order if each of the curves of H/M versus M^2 (also named Arrott plots) has a positive slope. On the other hand, if some of the curves of H/M versus M^2 show a negative slope at some point, the magnetic transition is of the first order. To understand the order of the magnetic transition in $EuCu_{1.75}P_2$, some Arrott-plots, i.e., the curve of H/M versus M^2 for $EuCu_{1.75}P_2$ at some selected temperatures are shown in Fig. 3. Neither the inflection point nor negative slope can be observed, providing the occurrence of a second order magnetic transition for $EuCu_{1.75}P_2$ from paramagnetic to ferromagnetic.

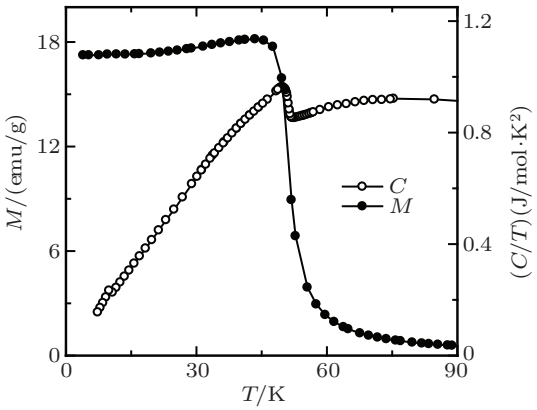


Fig. 1. Temperature dependences of magnetization (M) at $H = 0.1$ T and specific heat (C/T) at $H = 0$ for $EuCu_{1.75}P_2$.

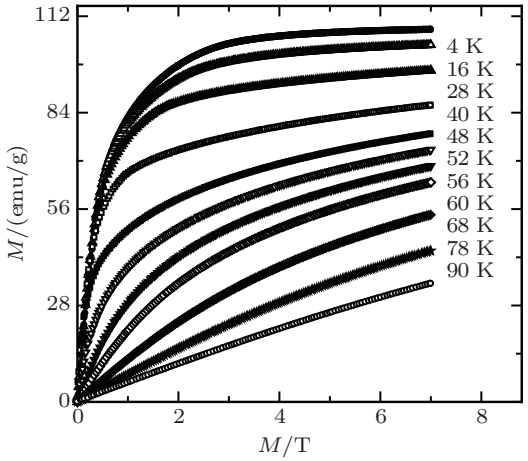


Fig. 2. Magnetic field dependences of the magnetization for $EuCu_{1.75}P_2$ at some selected temperatures in a magnetic field range from 0 T up to 7 T.

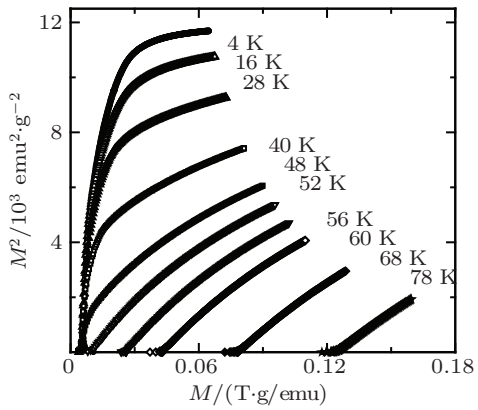


Fig. 3. Arrot-plots of $EuCu_{1.75}P_2$ at some selected temperatures.

The second-order magnetic phase transition around the Curie point is characterized by a set of critical exponents, i.e., β (related to the spontaneous magnetization M_s), γ (related to the initial magnetic susceptibility χ_0^{-1}), and δ (related to the critical magnetization isotherm at T_C). The mathematical definitions of those exponents from magnetization measurements are given as follows: [24]

$$M_s(T) = \lim_{H\to 0}(M) = M_0(-\varepsilon)^{\beta}, \quad \varepsilon < 0,\ T < T_C, \tag{1}$$

$$\chi_0^{-1}(T) = \lim_{H\to 0}(H/M) = (h_0/M_0)\varepsilon^{\gamma}, \quad \varepsilon > 0,\ T > T_C, \tag{2}$$

$$M = X H^{1/\delta}, \quad \varepsilon = 0,\ T = T_C, \tag{3}$$

where M_0, h_0, and X are the critical amplitudes, and $\varepsilon = (T - T_C)/T_C$ is the reduced temperature. The fitting procedure is as follows. By selecting the initial values for β and γ, we first plot $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$. Then we determine M_s from the intersection of the linearly extrapolated curve with the $M^{1/\beta}$ axis and plot M_s as a function of temperature, $M_s(T)$. A similar procedure is also used for $\chi_0^{-1}(T)$ with the $(H/M)^{1/\gamma}$ axis. The values for the critical exponents are obtained and are then reintroduced into the scaling of the modified Arrott plot. These procedures are repeated until the iterations converge and lead to the optimum fitting values. Figure 4 shows the modified Arrott plots of $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$ for $EuCu_{1.75}P_2$ with optimized $\beta = 0.45 \pm 0.03$ and $\gamma = 1.22 \pm 0.04$ values at various temperatures, deduced from fitting $M_s(T)$ and $\chi_0^{-1}(T)$ data using Eqs. (1) and (2) as shown in the inset of Fig. 4. The critical exponents from this static scaling analysis are related

to the Widom scaling relationship,[25]

$$\delta = 1 + \gamma/\beta. \tag{4}$$

Using the above scaling relation and estimated values of β and γ, the value of δ is determined to be 3.71 ± 0.07. The value of δ is also determined using Eq. (3) from two $M(H)$ curves (shown in Fig. 5) with the nearest temperatures (50 K and 52 K) around T_C. The value of δ is determined to be 3.93 and 3.58 for $T = 50$ K and 52 K, respectively. These values are in agreement with each other, indicating that the critical exponents obtained from the magnetization data are reliable. The critical values for $EuCu_{1.75}P_2$ deviate from those of the mean field theory,[26] which is probably due to the valence fluctuation of the Eu-containing compound and/or the magnetic inhomogeneity in the alloy.

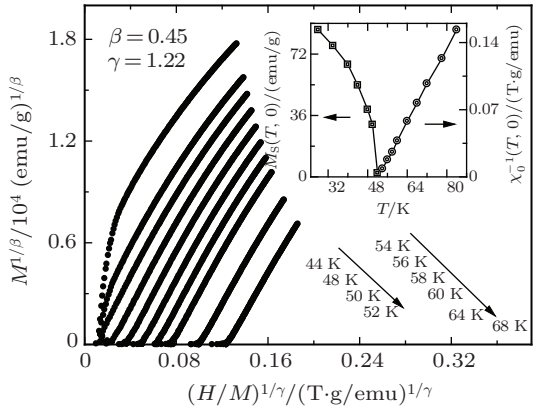


Fig. 4. The modified Arrott plot isotherms for $EuCu_{1.75}P_2$ in the vicinity of T_C. The inset shows the temperature dependences of spontaneous magnetization $M_s(T,0)$ and the inverse initial susceptibility $\chi_0^{-1}(T,0)$.

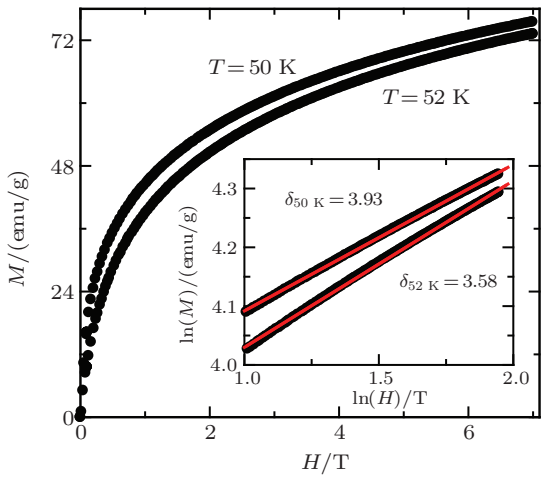


Fig. 5. (color online) Curves of isothermal M versus H at 50 K and 52 K, with the inset showing the same curves in ln–ln scale.

According to Maxwell's thermodynamic relation, the isothermal magnetic entropy changes associated with a magnetic field variation is given by

$$\Delta S_M(T, \Delta H) = \int_0^{H_{max}} \left(\frac{\partial M(H,T)}{\partial T}\right)_H \mathrm{d}H, \tag{5}$$

where S, M, H, and T are the magnetic entropy, magnetization of the material, applied magnetic field, and the temperature of the system, respectively. From the magnetization measurements made in discrete field and temperature intervals, ΔS_M can be approximately calculated by the following expression

$$\Delta S_M(T, \Delta H) = \sum_i \frac{M_{i+1}(T_{i+1}, H) - M_i(T_i, H)}{T_{i+1} - T_i} \Delta H. \tag{6}$$

The temperature dependence of magnetic entropy change $-\Delta S_M$ for $EuCu_{1.75}P_2$ with magnetic field change of up to 7 T is calculated using Eq. (4) in the vicinity of its ordering temperature based on the results of magnetization isotherms, and the results are shown in Fig. 6. A large magnetocaloric effect can be observed around 50 K. The maximum values of magnetic entropy change ($-\Delta S_M^{max}$) reach 5.6, 10.7, and 13.3 J·kg^{-1}·K^{-1} for field changes of 2, 5, and 7 T, respectively. The observed large MCE in $EuCu_{1.75}P_2$ is believed to be related to the second order magnetic phase transition which was discussed above. The refrigerant capacity or relative cooling power (RCP) is a quality factor of a refrigerant material which is a measure of the amount of heat transfer between the cold and hot reservoirs in an ideal refrigeration cycle. The RCP is defined as the product of the maximum magnetic entropy change ΔS_M^{max} and full width at half maximum in $\Delta S_M(T)$ curve, δT_{FWHM}. The RCP values of $EuCu_{1.75}P_2$ are 101, 331, and 478 J/kg for field changes of 2, 5, and 7 T, respectively. Another important parameter for MCE material is the temperature dependence of adiabatic temperature change, ΔT_{ad}, which is also roughly evaluated using the $\Delta S_M(T)$ and zero-field specific heat results (Fig. 1). The temperature dependences of ΔT_{ad} for $EuCu_{1.75}P_2$ for various magnetic field changes of up to 7 T are shown in Fig. 7. The overall nature of ΔT_{ad} as a function of temperature is remarkably similar to that of $\Delta S_M(T)$. The maximum values of adiabatic temperature change (ΔT_{ad}^{max}) reach 2.1, 4.0, and 5.0 K for field changes of 2, 5, and 7 T, respectively. Despite the fact that the values of MCE parameters (ΔS_M^{max}, ΔT_{ad}^{max}, and RCP) for $EuCu_{1.75}P_2$ are smaller than those for the first order magnetic transitions, the present values are comparable to those for the second order magnetic transitions. The giant reversible anisotropic MCE in antiferromagnetic $EuFe_2As_2$ single crystal is attributed to the first order magnetic transition in *a*–*b* plane and the second order magnetic transition out of plane.[22] The maximum value of the out-of-plane magnetic entropy change for field change of 5 T is 10.3 J·kg^{-1}K^{-1}, which is comparable to the value of 10.7 J·kg^{-1}K^{-1} for our ferromagnetic $EuCu_{1.75}P_2$ polycrystalline sample. The present $EuCu_{1.75}P_2$ compound exhibits a high reversible MCE, which makes it a competitive material for active magnetic-refrigeration application.

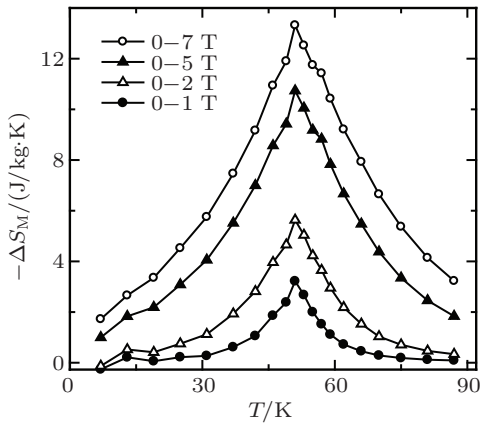


Fig. 6. Curves of magnetic entropy change $-\Delta S_M$ versus temperature for $EuCu_{1.75}P_2$ in the cases of different field changes.

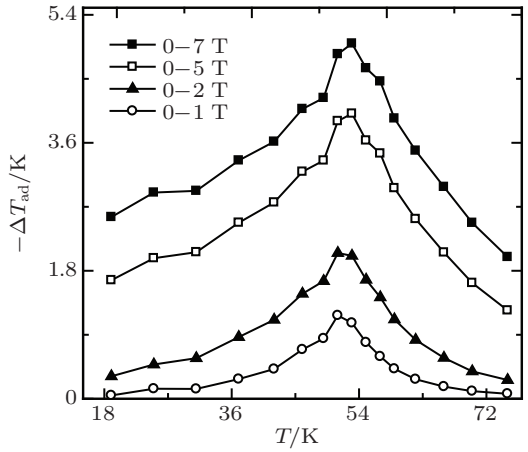


Fig. 7. Temperature dependences of adiabatic temperature change ΔT_{ad} for $EuCu_{1.75}P_2$ in the cases of different field changes.

4. Conclusions

In this paper, the critical behavior and magnetocaloric effect in $EuCu_{1.75}P_2$ are systematically investigated by determining the magnetization and heat capacity. The values of β, γ, and δ are estimated to be 0.45 ± 0.03, 1.22 ± 0.04, and 3.71 ± 0.07, respectively. The observed reversible MCE around 51 K is related to a second-order magnetic phase transition. The maximum values of magnetic entropy change $(-\Delta S_M^{max})$ reach 5.6 $J \cdot kg^{-1} \cdot K^{-1}$ and 10.7 $J \cdot kg^{-1} \cdot K^{-1}$ for the field changes of 2 T and 5 T, respectively. The corresponding values of relative cooling power are 101 J/kg and 331 J/kg. The present results may give some clues for searching for new materials with large MCE.

References

[1] Kitanovski A and Egolf P W 2010 *Int. J. Refrig.* **38** 449
[2] Gschneidner K A, Pecharsky V K Jr and Tsoko A O 2005 *Rep. Prog. Phys.* **68** 1479
[3] Oliveira N A and Ranke P J 2010 *Phys. Rep.* **489** 89
[4] Geng Y X, Tegus O and Bi L G 2012 *Chin. Phys.* B **21** 037504
[5] Zou J D 2012 *Chin. Phys.* B **21** 037503
[6] Wang F, Shen B G, Zhang J, Sun J R, Meng F B and Li Y X 2010 *Chin. Phys.* B **19** 067501
[7] Ma S C, Wang D H, Xuan H C, Shen L J, Cao Q Q and Du Y W 2011 *Chin. Phys.* B **20** 087502
[8] Li Z, Jing C, Zhang H L, Cao S X and Zhang J C 2011 *Chin. Phys.* B **20** 047502
[9] Li L, Nishimura K, Hutchison D W, Qian Z, Huo D and Namiki T 2012 *Appl. Phys. Lett.* **100** 152403
[10] Flores1 R C, Franco V, Conde A, Knipling K E and Willard M A 2011 *Appl. Phys. Lett.* **98** 102505
[11] Zhang Q, Cho J H, Li B, Hu W J and Zhang Z D 2010 *Appl. Phys. Lett.* **94** 182501
[12] Li L, Nishimura K, Usui G, Huo D and Qian Z 2012 *Intermetallics* **23** 101
[13] Shen J, Zhao J L, Hu F X, Wu J F, Sun J R and Shen B G 2010 *Chin. Phys.* B **19** 047502
[14] Hui X D, Xu Z Y, Wang E R, Chen G L and Lu Z P 2012 *Chin. Phys. Lett.* **27** 117502
[15] Steglich F, Aarts J, Bredl C D, Lieke W, Meschede D, Franz W and Sehafer H 1977 *Phys. Rev. Lett.* **43** 1892
[16] Yoshimura K, Nitta T, Mekata M, Shimizu T, Sakakibara T, Goto T and Kido G 1988 *Phys. Rev. Lett.* **60** 851
[17] Mathur N D, Grosche F M, Julian S R, Walker I R, Freye D M, Haselwimmer R K W and Lonzarich G G 1998 *Nature* **394** 39
[18] Ren Z, Zhu Z W, Jiang S, Xu X F, Tao Q, Wang C, Feng C M, Cao G H and Xu Z A 2008 *Phys. Rev.* B **78** 052501
[19] Ren Z, Tao Q, Shuai J, Feng C M, Wang C, Dai J H, Cao G H and Xu Z A, 2009 *Phys. Rev. Lett.* **102** 137002
[20] Ni B, Abd-Elmeguid M M, Micklitz H, Sanchez J P, Vulliet P and Johrendt D 2001 *Phys. Rev.* B **63** 100102
[21] Huo D, Lin J, Tang G, Li L, Qian Z and Takabatake T 2011 *J. Phys.: Conf. Ser.* **263** 012014
[22] Kim M S, Sung N H, Son Y, Ko M S and Cho B K 2011 *Appl. Phys. Lett.* **98** 172509
[23] Banerjee S K 1964 *Phys. Lett.* **12** 16
[24] Fisher M E 1967 *Rep. Prog. Phys.* **30** 615
[25] Widom B 1964 *J. Chem. Phys.* **41** 1633
[26] Kaul S N 1978 *J. Magn. Magn. Mater.* **7** 113