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Linear magnetoresistance and structural distortion in layered $SrCu_{4-x}P_2$ single crystals

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We report a systematic study on layered metal $SrCu_{4-x}P_2$ single crystals via transport, magnetization, thermodynamic measurements and structural characterization. We find that the crystals show large linear magnetoresistance without any sign of saturation with a magnetic field up to 30 T. We also observe a phase transition with significant anomalies in resistivity and heat capacity at $T_p \sim 140$ K. Thermal expansion measurement reveals a subtle lattice parameter variation near T_p, i.e., $\Delta L_c/L_c \sim 0.062\%$. The structural characterization confines that there is no structure transition below and above T_p. All these results suggest that the nonmagnetic transition of $SrCu_{4-x}P_2$ could be associated with structural distortion.

Keywords: linear magnetoresistance, thermal expansion, specific heat, structural distortion

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In the past, a number of materials with rhombohedral $CaCu_4P_2$-type structures[1] have been synthesized, including the arsenides ACu_4As_2 (A = Na, K, Ca, Sr, Ba, Eu)[2–5] and AAg_4As_2 (A = Sr, Eu),[6–9] the antimonides ACu_4Sb_2 (A = Na, K),[10] and the phosphides $ACu_{4-x}P_2$ (A = Ca, Sr, Ba, Y, La–Nd, Eu–Yb).[11–13] These compounds exhibit complex interplay between different orders, such as the coexistence, competition, and/or correlation of magnetism,[6,7,14] charge density waves,[15] and structural phase transitions.[16] For example, in the layered magnetic compound $EuAg_4As_2$, a phase transition was observed at 120 K, and incommensurate noncollinear long-range antiferromagnetism developed below 9 K.[6] In $CaCu_4As_2$, multilayer quantum Hall effects and phase transition below 51 K were observed.[15] Meanwhile, in recently reported $EuCu_4As_2$, both a large negative magnetoresistance (−55%, at 35 K, 9 T) near the magnetic transition temperature and a large positive magnetoresistance (60% at 2 K, 9 T) at lower temperatures were observed.[4] As a result of these observations, the investigation of other members of the $CaCu_4P_2$ family may help to explore more exotic phenomena that contribute to this area.

In this work, we focus on the phosphides $SrCu_{4-x}P_2$, which adopt the space group of $R\bar{3}m$ in the rhombohedral $CaCu_4P_2$ structure.[13] We synthesized high-quality $SrCu_{4-x}P_2$ single crystals and performed detailed physical property measurements and structural characterization, together with electrical transport, magnetization, specific heat, thermal expansion and transmission electron microscope (TEM) analysis. Linear magnetoresistance (LMR) was observed, with no signature of saturation up to 12 T. As a result of detailed data analysis, we consider that this LMR originates from mobility fluctuation, and the PL model can be applicable here. Meanwhile, we observed a phase transition at 140 K, where both the resistivity and heat capacity showed significant anomalies. Thermal expansion revealed a subtle lattice parameter variation near T_p, while the structural characterization showed that there is no structure transition below and above T_p. Our experimental data suggested that this transition is a nonmagnetic transition and likely in relation to the structural distortion.

Single crystals $SrCu_{4-x}P_2$ were grown via the Bi–Cu flux method. The stoichiometry of the starting raw materials of Sr shots (3N purity), Cu plates (4N purity), red phosphorus pieces (3N purity) and Bi shots (5N purity) was 1:8:2:35 in molar ratio. The oxide layers of the Sr shots were scraped off from the surface. The mixture was placed inside an alumina crucible and sealed in a quartz tube, slowly heated to 1050 °C, then kept at this temperature for 20 h, and finally cooled to 850 °C at a cooling rate of 3 °C/h before separating the flux in a centrifuge. Phase purity was checked via x-ray

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diffraction using a Rigaku-TTR3 with Cu-K_α radiation. The chemical stoichiometry of both samples was determined from an energy dispersive spectrum (EDS) equipped upon a Helios nanolab600i. Resistivity and specific heat measurements were performed using a physical properties measurement system (PPMS-14T, QD Inc.). Magnetization measurement was performed using a magnetic properties measurement system (MPMS3-7T, QD Inc.). TEM analysis and selected area electron diffraction (SAED) were performed using a Talos F200X equipped with a liquid-nitrogen-cooled holder. Thermal expansions were measured using a homemade strain gauge[17] and capacitance dilatometer,[18] respectively.

The layered compound $SrCu_{4-x}P_2$ crystallizes in the rhombohedral $CaCu_4P_2$ structure. The structure can be regarded as the insertion of an additional itinerant Cu_2 layer within the Cu_2P_2 layer of the trigonal $CaAl_2Si_2$-type stacking of $–A–Cu_2P_2–A–$, as illustrated in Fig. 1(a).[13] Sr ions are located between the Cu_2P layers. The single-crystal chemical composition in this work, obtained by EDS, is Sr:Cu:P = 15.17:55.61:29.21, i.e., $SrCu_{3.67}P_{1.93}$. Figure 1(b) shows the XRD patterns of the single crystals of $SrCu_{4-x}P_2$. The diffraction peaks of the crystal face are well indexed with the (00l) plane, which is the same as those reported in $EuAg_4As_2$.[6,7] As shown in the inset of Fig. 1(b), the full width at half maximum (FWHM) of the rocking curve of the (003) peak reaches as low as 0.24°, indicating the high quality of the as-grown single crystals.

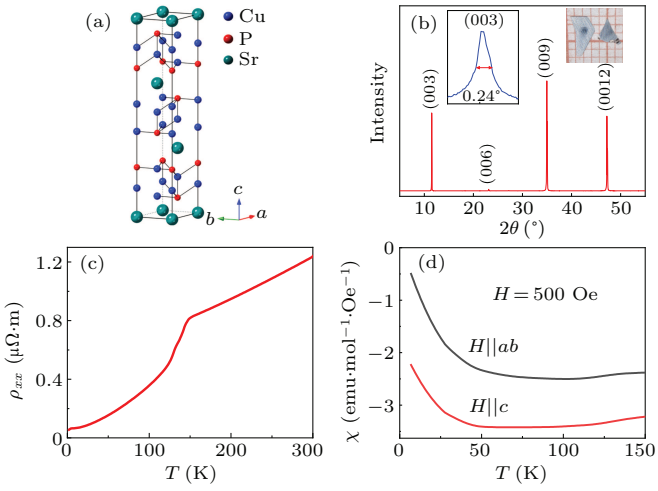


Fig. 1. (a) An illustration of the crystal structure of $SrCu_{4-x}P_2$ in one unit cell. (b) The XRD patterns of the as-grown single crystals of $SrCu_{4-x}P_2$. The inset is the rocking curve at the (003) peak. (c) The temperature dependence of resistivity at zero field. (d) The temperature-dependent magnetization of $SrCu_{4-x}P_2$ in the low-temperature region.

We firstly measured the temperature-dependent resistivity (ρ–T) of $SrCu_{4-x}P_2$ at zero magnetic field, as shown in Fig. 1(c), which exhibits metallic behavior with a kink at 140 K; the possible origin of this kink could be related to structure distortion and will be discussed briefly later. The magnetization curve suggests a paramagnetic background in $SrCu_{4-x}P_2$ at low temperatures, as shown in Fig. 1(d). The observed negative susceptibility could be due to the diamagnetic background of the sample holder during the measurement.

Figure 2(a) shows the field-dependent magnetoresistance (*MR*), defined as $[\rho(B)-\rho(0)]/\rho(0)\times 100\%$, with the $H||c$-axis. The *MR* reaches 130% up to 12 T at 2 K with no sign of saturation. It exhibits semiclassical quadratic dependence in the low field.[19] and linear behavior in the high field. As the temperature increases, the *MR* gradually decreases to 13% at 120 K. We also carried out *MR* measurement with a magnetic field up to 30 T, as shown in Fig. 2(c). The *MR* reaches 370% at 32 T at 1.6 K and continues to increase with the magnetic field. Similar linear *MR* has been observed in many materials, such as Cd_3As_2, TlBiSSe, and $BaMnBi_2$.[20–22]

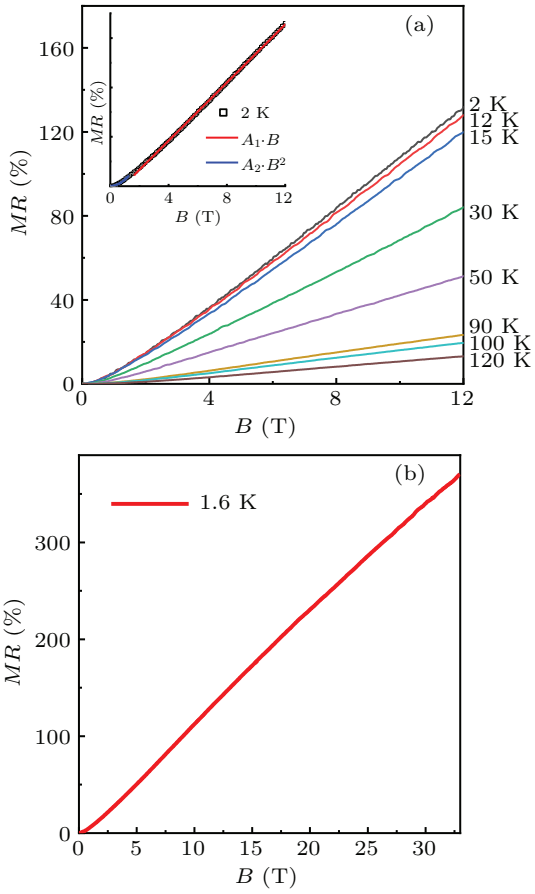


Fig. 2. (a) The *MR* as function of the magnetic field at various temperatures with $H||c$. Inset: quadratic fitting using the relationship $MR = A_2 \cdot B^2$ in the low-field region, and linear fitting using $MR = A_1 \cdot B$ at $T = 2$ K. (b) The *MR* curve at 1.6 K with a magnetic field up to 32 T.

The origin of linear *MR* can arise from distinct mechanisms, including Abriskosov's theory for materials with gapless linear energy–momentum dispersions for electrons and the classical Parish–Littlewood model (PL model) for strongly inhomogeneous systems. According to Abriskosov's theory,[23,24] in the quantum limit, linear *MR* arises when all the electrons fill the lowest Landau level. However, linear *MR* could be observed in a low magnetic-field range, which is not the case in our $SrCu_{4-x}P_2$; thus, Abriskosov's theory should not be applicable here.

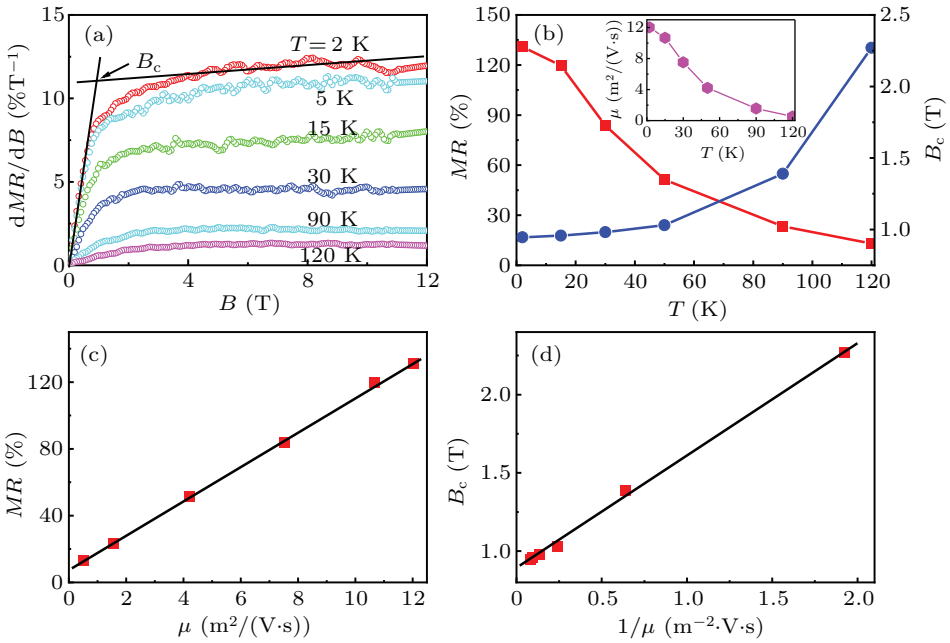


Fig. 3. (a) The magnetic-field-dependent dMR/dB at various temperatures. A crossover field B_c is defined as the intersection between the two fitting lines. (b) The temperature dependence of MR at $H = 12$ T and the crossover field B_c. The inset is the temperature dependence of the mobility μ. (c) Linear behavior of MR at $H = 12$ T and mobility μ. (d) Linear behavior of the crossover field with inverse mobility $1/\mu$.

We now turn to the classic PL model,[25] which has been used widely to understand the linear MR behavior in disordered $Ag_{2\pm\delta}Se/Ag_{2\pm\delta}$ Te, n-doped Cd_3As_2,[20,26–28] and narrow-band semiconductors.[29] In these materials, linear MR could be observed due to the existence of large mobility fluctuation. Based on this model, the MR should be proportional to the mobility ($MR \propto \mu$) and the crossover field B_c, and the mobility obeys the relation with $B_c \propto 1/\mu$. Figure 3(a) presents the field derivative of the MR, dMR/dB, at various temperatures. The crossover field B_c can be determined from the intersection of the quadratic and linear regimes. According to Kohler's rule, $R(B)/R(0) \approx 1 + (\mu B)^2$, the mobility can be estimated from the low-field slope of dMR/dB curves. As the temperature increases, the MR and mobility monotonically decrease, while the crossover field B_c increases, as shown in Fig. 3(b). The MR vs. μ and B_c vs. $1/\mu$ relations are demonstrated in Figs. 3(c) and 3(d); both display linear relations, in good agreement with the PL model. We noticed that the linear MR of n-Cd_3As_2.[20]and $Ag_{2-\delta}Se$[30] originated from the disorder caused by Cd-rich and Ag defects, respectively. Therefore, we propose that the LMR of $SrCu_{4-x}P_2$ originates from disorder caused by a Cu deficiency.

We now return to the kink of the $SrCu_{4-x}P_2$ on the ρ–T curve. As shown in Fig. 4(a), the temperature-dependent resistivity ρ_{xx} presents a small hysteresis between the cooling and heating cycles. Such a kink on ρ_{xx}–T curves has been observed in $EuAg_4As_2$[6] and $CaCu_4As_2$,[15] which has been attributed to the structural distortion or charge density wave (CDW). In the following, we will focus on this transition, together with specific heat, thermal expansion and TEM analysis.

We firstly compare the temperature-dependent resistivity ρ_{xx} with the heat capacity. Figure 4(b) shows the temperature-dependent heat capacity (C_p) measurements. It is found that the heat capacity C_p shows a remarkable hump anomaly around T_p, with independence from the applied magnetic fields. These results demonstrate that the anomaly near T_p originates from a thermodynamic phase transition with a non-magnetic nature. By subtracting the background from the data and integrating $(C_p - C_{fit})/T$, we obtain ΔS to be 0.72 J/mol·K. Temperature dependences of thermal expansion ($\Delta L/L$) in the ab plane and along the c-axis. As shown in Fig. 4(c), a slight drop of the c-axis about $\Delta L_c/L_c \sim 0.062\%$ and ab plane about $\Delta L_{ab}/L_{ab} \sim 0.075\%$ were probed when the temperature decreased from 145 K to 130 K. We note that this lattice distortion is significantly smaller than a typical crystal structural transition with a lattice change of the order of $\sim 0.5\%$–1%.[31,32]

To check whether the anomaly near T_p is related to the structure transition, we carried out structural characterization via SAED studies using the TEM technique. Figures 5(a) and 5(b) show, respectively, the SAED patterns with the electron incidence parallel to the [0001] direction at 300 K and 100 K for $SrCu_{4-x}P_2$. It is clear that the patterns are the same above and below T_p, except for the variations of the spot brightness intensity. No noticeable change in the crystal structures in the space group occurs. In previous work on $EuAg_4As_2$, a similar phase transition has also been observed,[6] where a superlattice structure emerges below T_p in the x-ray diffraction precession study. Here, this transition in $SrCu_{4-x}P_2$ should not arise from structural phase transition or CDW, but is due to the subtle lattice changes, as shown in Fig. 4(c). A similar transition was also observed in $EuCu_4As_2$[4] and $SrAg_4As_2$.[33] Convergent beam electron diffraction (CBED) or scanning tunneling mi-

croscope (STM) measurements are helpful in determining the underlying physics of the unique T_p transition in $SrCu_{4-x}P_2$.

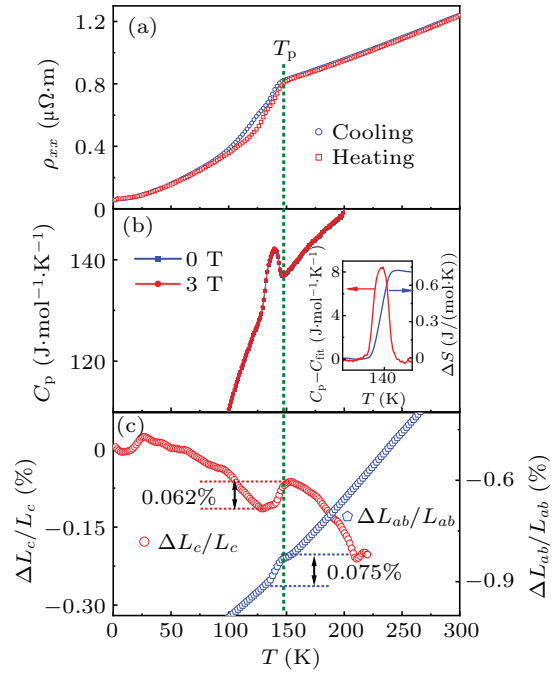


Fig. 4. (a) The temperature-dependent resistivity under cooling (blue line) and heating (red line) processes for $SrCu_{4-x}P_2$. (b) The temperature-dependent specific heat capacity (C_p) curves at $H = 0$ T, 3 T near T_p in $SrCu_{4-x}P_2$. The inset shows the heat capacity by subtracting the background and transition entropy in the transition region. (c) Thermal expansion of lattice parameters along the c-axis and in the ab plane in $SrCu_{4-x}P_2$.

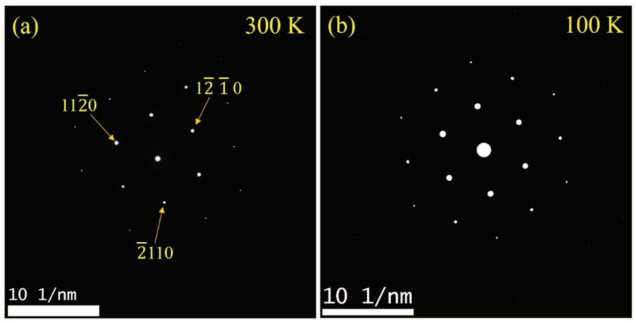


Fig. 5. (a) and (b) The SAED patterns of $SrCu_{4-x}P_2$ taken along the zone axis [0001] at 300 K and 100 K, respectively.

In conclusion, we performed systematical investigation of $SrCu_{4-x}P_2$ single crystals. Large non-saturating LMR was observed, which should originate from the disorder caused by Cu deficiency. A phase transition was observed at $T_p \sim 140$ K, with anomalies in resistivity and heat capacity. The thermal expansion measurements and structural characterization proved that there are only subtle lattice parameter changes near T_p. Our measurements demonstrate that the transition of $SrCu_{4-x}P_2$ does not endure any type of magnetic or crystal structural changes, but is likely associated with structural distortion.

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