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NOVEL MAGNETISM AND SUPERCONDUCTIVITY IN A Ru-BASED DOUBLE PEROVSKITE*

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We report the observations, using magnetic susceptibility and specific heat measurements, of the coexistence of superconductivity and magnetic ordering at low temperatures in the Cu-doping double perovskites $Sr_2ARu_{1-x}Cu_xO_6$, with A = Y or Ho, and $x < 0.2$. The observed striking features can be understood in terms of a plausible theoretical model based on the double exchange mechanism, which occurs indirectly via Ru^{5+} spin coupling to itinerant electrons hopping from one Ru site to another.

1. Introduction

In recent years there is renewed interest in the magnetic materials that involve double exchange interaction due to the observations of colossal magnetoresistance effect in several perovskites. Most reports in the literature focus on the problems that deal with the important issue of how the magnetic order and the magnetoresistance correlate concerning the transport properties, both experimentally and theoretically. Recently, a systematic study has demonstrated the coexistence of superconductivity and magnetic ordering at lower temperature in the double perovskite structure[1] $Sr_2Y(Ru_{1-x}Cu_x)O_6$ system.[2] The observation of a superconducting transition temperature T_c as high as 50 K in a system without CuO_2 planes is quite remarkable. The observed striking features, both magnetic and electrical,

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can be understood in terms of a plausible theoretical model based on the double exchange mechanism,[3] which occurs indirectly via Ru^{5+} spin coupling to itinerant electrons hopping from one Ru site to another. It opens up a new direction to search for new high-temperature superconductors. More importantly, it provides valuable clues to understand the nature of superconductivity in the oxide system.

The results of resistive measurements[2] on $Sr_2YRu_{1-x}Cu_xO_6$ exhibit a broad transition with a width of $\sim$ 20 K. It raises a question whether the unexpectedly high superconducting transition arises from the presence of a second phase that may be related to the cuprate superconductor, such as the YSCO-123 phase. It is well known that specific heat measurements give a direct measure whether the observed phase transition is a bulk one in addition to the important electronic and lattice dynamic information. In an attempt to identify the origin of superconductivity observed in $Sr_2Y(Ru_{1-x}Cu_x)O_6$, we have carefully prepared single-phase samples and measured their specific heat at low temperatures. We observed unambiguously two pronounced specific jumps at almost the same temperatures as those for superconducting and magnetic order temperatures, observed by magnetic susceptibility measurements, in the samples doped with Cu. On the other hand, only a rather broad peak was seen in the parent compound, which is an antiferromagnetic insulator. These results are consistent, semi-quantitatively, with a detailed theoretical calculation of the magnetic specific heat based on the double exchange model.[4]

2. Experimental

Polycrystalline samples of $Sr_2YRu_{1-x}Cu_xO_6$ with $0 < x < 0.15$ were prepared by the standard solid-state reaction method. Stoichiometric starting powders of $SrCO_3$, Y_2O_3, RuO_2 and CuO were thoroughly mixed, then calcined at 1000°C for several days in air. Subsequently, the reacted powder was ground and pressed into a pellet, then sintered at 1380°C in a mixture gas of 70% O_2 and 30% Ar for 12 hours. Structural characterization was carried out by SEM equipped with EDX analyzer and high-resolution powder X-ray diffraction technique to confirm the samples with 2116 stoichiometry and phase homogeneity. The resistive measurements were made by the conventional four-probe technique. An ac calorimeter using small sample bolometer technique. The measurements were carried out in a He^3 cryostat in a field up to 9 Tesla.

3. Results and Discussion

All samples examined in the present study were single phase characterized by both X-ray and neutron powder-diffraction. The temperature dependence of resistivity for a typical $Sr_2YRu_{0.9}Cu_{0.1}O_6$ sample is shown in Fig. 1. It clearly demonstrates the superconducting transition with $T_c \sim 30$ K exhibiting zero resistance. Figure 2 displays the magnetic susceptibility of three samples in the temperature range from 5 K to 60 K. After Cu-doping, the sample shows unambiguously the existence of superconducting transitions, especially in zero-field-cool (ZFC) data, which show

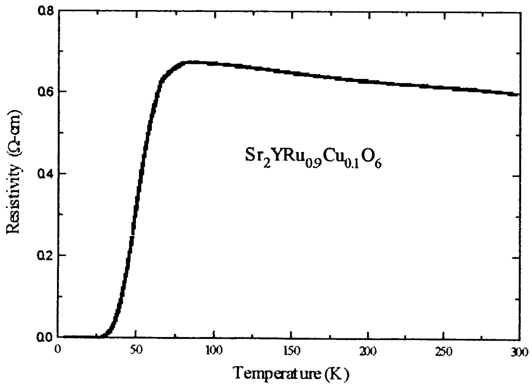

Fig. 1. Temperature dependence of resistivity of $Sr_2YRu_{0.9}Cu_{0.1}O_{6-\delta}$.

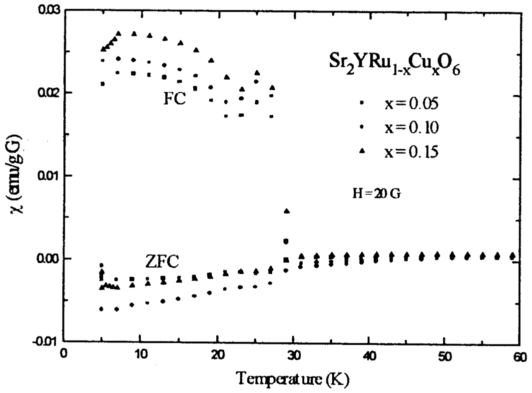

Fig. 2. Zero-filed-cool (ZFC) and field-cool (FC) susceptibility of $Sr_2YRu_{1-x}Cu_xO_6$.

clearly a diamagnetic response that corresponds to at least 8% in volume of the bulk sample. We define the onset of this diamagnetic response as the superconducting transition temperature T_c. Nonetheless, the field-cool (FC) data exhibit the presence of an additional order at a temperature, T_m, which is slightly lower than T_c. Recent low field rf conductivity measurements[5] provide further confirmation the existence of superconductivity in these samples.

Specific heat measurements[6] were conducted on samples with different concentrations of Cu, and the result of a 7% Cu sample is shown in Fig. 3. The key features of the specific heat data can be summarized as the following:

(1) The parent compound shows a broad peak with an onset temperature at 26 K, which is the same as that of the magnetic transition. The temperature dependence of the specific heat below the broad peak can be best fit with T^3.
(2) Two sharp peaks are observed in the Cu-doped samples. The first peak appears at the same temperature as T_c, while the second peak occurs at the same

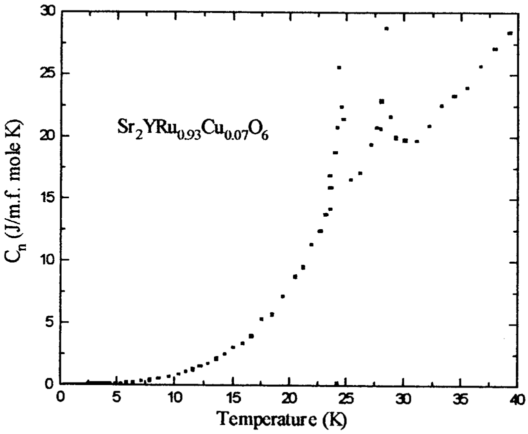

Fig. 3. Specific heat of $Sr_2YRu_{0.93}Cu_{0.07}O_6$.

temperature as T_m observed in the FC magnetic susceptibility measurement. Except the two sharp peaks, there appears to have much less specific heat below the ordering temperature in the doped sample compared with that of the parent compound, though its temperature dependence can still be fit to T^3 relation.

(3) In the presence of magnetic field, the first specific heat peak of the doped samples slightly enhanced, whereas the second peak remains essentially unchanged with an external field as high as 7 Tesla.

To gain a qualitative understanding of the observed feature a model[4] was constructed by considering a cubic lattice with Ru^{+5} and Y^{+3} at the face-center sites and octahedral sites, Sr^{+2} at tetragonal sites and O^{-2} in the middle of Y-Ru bonds. The outer electronic configuration of a Ru^{+5} is $4d^3$ with total spin $S = 3/2$ in accord with Hund's rule. It is conceivable that the orbital wave functions of the three outer electrons correspond to a closed shell of T_2 and the antiferromagnetic exchange is isotropic. When the system is doped with Cu itinerant holes are created. An effective ferromagnetic coupling among Ru spins is introduced through the double exchange mechanism proposed by Zener,[3] Anderson and Hasegawa.[3] Furthermore, the approximate cubic symmetry of the magnetic coupling is offset by the holes and the anisotropy may become stronger.

The effective magnetic Hamiltonian has been treated with molecular field approximation (MFA).[7] Two parameters, the antiferromagnetic exchange J; and the double exchange b, are essential to determine the magnetic properties. For the parent compound, $b = 0$, Monte Carlo simulation[4] gave rise to a pronounced peak in the specific heat. However, considering the possible random occupations of Ru and Y ions at face-center sites and octahedral sites, Monte Carlo study with a fraction of spins removed randomly is performed. The peak is greatly depressed and broadened, consistent with the observed results on the parent compound.

At low-T, the specific heat comes from both the magnons and phonons. At high temperatures, the magnetic contribution drops rapidly and the phonon contribution dominates. A lower limit of the Debye temperature, $T_{\mathrm{D}} = 380$ K has been extracted from the high temperature data of the specific heat on the assumption that the phonon contribution is insensitive to the doping. A reasonable agreement between specific heat data ($T < T_{\mathrm{N}}/5$) and the theoretical estimation can be achieved with $J = 2.06$ meV, and the ratio between intralayer exchange to interlayer exchange $J'/J = 0.95$, for $\mathrm{Sr_2YRuO_6}$. This ratio is consistent with the approximate cubic symmetry and the J value is not too far off from the MC estimation.

Extensive Monte Carlo simulations were performed for the phase diagram specified by the model Hamiltonian.[4] The phase diagram is found in qualitative agreement with the MFA calculation.[7] For a given strength of the interlayer double exchange two magnetic orders are encountered as the temperature is lowered: either (1) antiferromagnetic order ($T_1 < T < T_{\mathrm{N}}$) followed by canting ($T < T_1$) or (2) ferromagnetic order ($T_1 < T < T_{\mathrm{C}}$) followed by canting ($T < T_1$). The Monte Carlo results on T_{N}, T_{C} and T_1 are all considerably lower than that of MFA. The two-peak structure of the magnetic contribution to the specific heat obtained from the Monte Carlo simulation is consistent with the observed results. The observed closeness of two peaks in temperature and the shift of the higher temperature one under an external magnetic field for the doped sample $\mathrm{Sr_2Y(Ru_{0.93}Cu_{0.07})O_6}$ indicates that we are in case (2) and near the boundary between case (1) and (2). The peak at the lower temperature is then driven by AF order, and therefore insensitive to the field, as observed.

The existence of a canting magnetic order in a system involving double-exchange remains a controversial issue both experimentally and theoretically. Our recent neutron powder diffraction experiments[8] show the existence of an antiferromagnetic order below 28 K. But the data does not give unambiguously the existence of an additional transition or crossover to another magnetic phase at lower temperature. Our results clearly show the coexistence of superconductivity and magnetism in the 2116 double perovskites. The superconducting transition temperature is of the same order as that of the magnetic order and the superconductivity is likely to be with p-wave symmetry. This is consistent with the presence of a canting magnetic order, which originates from the coexistence of an antiferromagnetic order and ferromagnetic order. The spin fluctuation of the former may provide the necessary attraction and the spin polarization of the band from the latter makes equal spin pairing likely. It is noted that de Gennes in 1987[9] suggested a similar mechanism for the cuprate superconductors.

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