RRPA89070248 (4.P)

行政院國家科學委員會專題研究計畫成果報告

高溫超導機制及新穎材料之研究---子計畫四：含有鈣鈦礦結構 $RuA_2RCu_2O_y$ 系統物性研究(A = Ca, Sr, and Ba；R = lanthanides)

An investigation of physical properties of Ru-based $RuA_2RCu_2O_y$ with perovskite related structure (A = Ca, Sr, and Ba；R = lanthanides)

計劃編號：NSC 89-2112-M-032-012

執行期限：88年08月01日至89年10月31日

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一、中文摘要

我們有系統地研究了鋁摻雜 $RuSr_2GdCu_2O_8$ 鐵磁超導體的磁電傳輸性質與磁學性質。樣品的超導轉變溫度隨著鋁摻雜量增加而遞增；當鋁摻雜量超過20%時，超導轉變溫度隨著鋁摻雜量增加而遞減。實驗的結果顯示了銅 $3d$ 與釕 t_{2g} 的軌道雜化效應(交換交互作用)隨著鋁摻雜量的增加變得較不顯著，導致了銅 $3d$ 與氧 $2p$ 軌域之間的電荷轉移，使得銅氧平面上的電洞數目增加，超導轉變溫度因而增加。另一方面，磁學性質的測量顯示了樣品的鐵磁轉變溫度則隨著鋁摻雜量的增加而單調遞減，同時低場的磁化率於30 K附近有一谷狀的異常現象，而高場的磁化率則在低溫出現類鐵磁性的平滑趨勢。這代表著鋁的摻雜對釕氧平面上的鐵磁耦合強度有著相當程度的抑制，然而對於釕氧平面間的弱反鐵磁性並沒有顯著的改變。

關鍵詞：鐵磁超導體，軌道雜化，電荷轉移

Abstract

Electrical and magnetic properties of ferromagnetic superconductor $Ru_{1-x}Al_xSr_2GdCu_2O_8$ with x = 0.0-0.2 have been investigated. The superconducting transition temperature (T_c) of Al-doping Ru-1212 samples increases with increasing Al content up to 20%, and then decreases with increasing doping level. It suggests that hybridization (exchange interaction) between Cu-$3d$ and Ru-t_{2g} becomes less pronounced in the Al-doped samples, leading to a charge transfer between Cu-$3d$ and O-$2p$ bands. As a result, excess holes induced by Al-doping would be in the CuO_2 planes. Magnetic studies show that magnetic ordering temperature (T_{Curie}) of Ru sublattice decreases significantly as Al content increases. In addition to that, low-field M(T) shows a peak feature indicating the dominant low-field magnetic order is antiferromagnetic, whereas high-field M(T) exhibits a rounding structure suggesting the dominant high-field magnetic order is ferromagnetic.

Keywords: ferromagnetic superconductor, hybridization, charge transfer

二、緣由與目的

A novel superconductor where superconductivity and atomic ferromagnetism uniformly coexist in a microscopic has recently been found in the hybrid ruthenate-cuprate compound $RuSr_2GdCu_2O_8$ (Ru-1212).[1-2] A variety of physical measurements, in particular zero-field muon spin rotation experiments,[3] have demonstrated that the material is microscopically uniform with no evidence for spatial phase separation of superconducting and magnetic regions. This compound provides an unprecedented opportunity for studying superconductivity and magnetism. Ru-1212 is found to be oxygen stoichiometric, and the doping of the CuO_2 planes necessary to induce superconductivity arises from overlap of the minority spin Ru-t_{2g} and the Cu-$3d$ bands. Transport measurements show that the CuO_2 planes are underdoped with 0.1 holes/Cu,[4] which is much less than the estimated value of 0.4 holes/Cu obtained from bond valence sum.[5] This discrepancy seems to suggest that a large proportion of the holes in the copper oxide layers are trapped or strongly scattered by the ferromagnetic Ru moments. Furthermore, a powder neutron-diffraction study on Ru-1212 and a magnetization study on $RuSr_2EuCu_2O_8$ have recently found evidence for low-field antiferromagnetic order in all directions in the RuO_2 planes with the Ru moments aligned along the *c*-axis and spin canting along the *ab*-plane direction..[6-7] Therefore, it is interesting to investigate the following issues. (1)Can superconducting transition temperature of Ru-1212 be increased by appropriate doping? (2) What is the correlation between superconducting transition temperature and ferromagnetic ordering temperature as a function of doping level? (3) Does the low-field antiferromagnetic order survive as the doping level changes? To address these issues, we have attempted to substitute Ru by nonmagnetic Al, which has similar ionic radius to Ru and fewer valences comparing with Ru. In this report, we have systematically studied the temperature dependences of magnetic susceptibility and resistance of underdoped polycrystalline $Ru_{1-x}Al_xSr_2GdCu_2O_8$ with x=0.0-0.2. The observed results suggest that exchange interaction between holes in the CuO_2 planes and Ru spins in the RuO_2 layers plays a significant role in localizing holes in the CuO_2 planes.

The samples investigated were prepared by the solid-state reaction method. Stoichiometric powders of Gd_2O_3, $SrCO_3$, RuO_2, CuO and Al_2O_3 were ground thoroughly and calcined at 960 °C in air for 36 h, followed by annealing at 1100 °C in N_2, then at 1055 °C, 1060 °C in flowing oxygen. The structure was determined by X-ray diffraction. The final product was annealed at 500 ℃ for 24 hours in O_2 to get a single-phase compound. Magnetic susceptibility was measured by using a SQUID magnetometer. Resistivity measurements were performed using a conventional four-probe method. External magnetic fields up to 6 T perpendicular to current direction were applied for magneto-transport measurements.

三、結果與討論

Figure 1 shows the temperature dependence of the resistance (normalized to room temperature value) for $Ru_{1-x}Al_xSr_2GdCu_2O_8$ with x = 0.0-0.15. As can be seen in Fig. 1, the superconducting onset temperature (T_c) increases from 35 K at x = 0.0 to 56 K at x = 0.15 and falls thereafter. In addition, the normal-state resistance becomes more metallic in character as T_c increases. The results seem to indicate that the hole concentration in the CuO_2 planes increases with increasing Al content. However, it should be noted that T_c suppression in higher Al-doping samples is not due to the overdoping effect since the normal-state resistance of the samples exhibits a semi-conducting behavior. This might be caused by the local disorder in the RuO_2 planes as a result of doping.

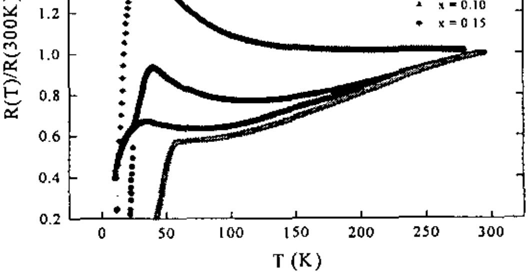

FIG. 1 The temperature dependence of the resistance for $Ru_{1-x}Al_xSr_2GdCu_2O_8$.

The temperature dependence of the magnetic susceptibility for Ru_{1-}

${}_{x}Al_xSr_2GdCu_2O_8$ with x = 0.0-0.15 is shown in Fig. 2. Apparently, the ferromagnetic ordering temperature (T_{curie}) is drastically reduced from 135 K at x = 0.0 to 95 K at x = 0.15. To establish whether the ferromagnetic order is associated with Ru moments or Gd moments, the inverse molar magnetic susceptibility as a function of temperature is analyzed. It turns out that the experimental data $\chi(T)$ can be fitted into $A_1/(T-135) + A_2/T$, where $A_1/(T-135)$ is Curie-Weiss term from Ru moments with T_{curie} of 135 K and A_2/T is Curie term from Gd moments. The magnetic moment μ_1 = 1.1 μ_B and μ_2 = 7.6 μ_B can be deducted from A_1 and A_2, respectively. These two values are in good agreement with the expected moment of a free Gd^{3+} and a Ru^{5+} in the low-spin state. Therefore, the magnetic ordering temperature T_{Curie} is attributed to ferromagnetism of Ru in the ruthenate layers.

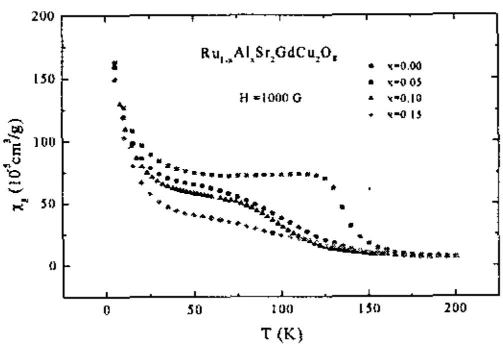

FIG. 2 Magnetic susceptibility as a function of temperature for $Ru_{1-x}Al_xSr_2GdCu_2O_8$ in an applied magnetic field of 1000 G.

The T_c and T_{curie} versus Al content are plotted in Fig. 3. The Al substitution not only modifies the electronic properties of CuO_2 planes, it also suppresses the itinerant electron ferromagnetism of the RuO_2 planes. The increases in conductivity and superconductivity as well as the decrease in the ferromagnetic Ru moment strongly suggest that some holes are localized or scattered in the CuO_2 planes due to strong hybridization between Cu-*3d* and Ru-t_{2g} orbitals, whereas pair breaking within the superconducting state of the CuO_2 planes is possibly caused by the ferromagnetism in the RuO_2 planes. This could result from slight canting of the Ru moments due to disorder of the rotations and tilts of the RuO_6 octahedra or the presence of out-of-plane low-lying spin wave excitation. As doping level increases, the spin wave excitation might be highly suppressed and the hybridization effect might be less significant as well. It is the reason that superconducting onset temperature increases substantially with lower Al doping.

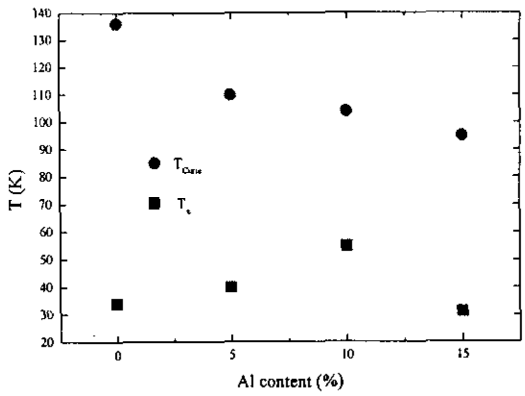

FIG. 3 Variation of T_{curie} and T_c with Al content.

Figure 4 plots the temperature dependence of the zero-field-cooled magnetic susceptibility $\chi(T)$ for $Ru_{0.9}Al_{0.1}Sr_2GdCu_2O_8$ under various magnetic fields. As shown in Fig. 4, the low-field $\chi(T)$ and high-field $\chi(T)$ have different features below 55 K. The low-field $\chi(T)$ has a local minim around 25 K and exhibits a peak structure around 50 K, whereas the high-field $\chi(T)$ keep increasing at lower temperatures. A zero-field-cooled peak is not expected in a ferromagnetic compound.[8-9] In fact, a peak in the ZFC $\chi(T)$ near the magnetic ordering temperature is observed in antiferromagnetic compounds. Thus, the observed data suggest that the dominant low-field magnetic order is antimagnetic, consistent with the neutron-diffraction study on $RuSr_2GdCu_2O_8$. The disappearance of the peak with increasing magnetic field may be related to the spin-reorientation or containing a significant ferromagnetic component in the high field regime. In any case, although the Al-doping weaken the ferromagnetism, it doesn't change the subtle magnetic structure of Ru moments very much. The intriguing magnetic properties of Ru-1212 indeed deserve further detailed investigations.

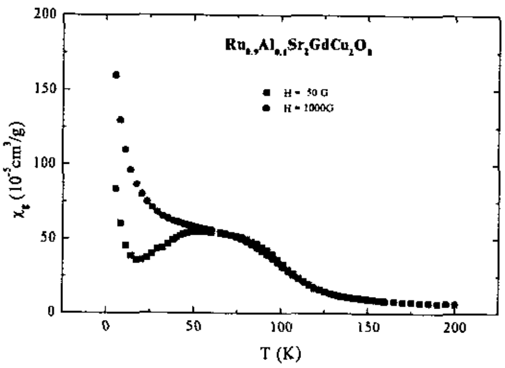

FIG. 4 The temperature dependence of the χ(T) for $Ru_{0.9}Al_{0.1}Sr_2GdCu_2O_8$ under various magnetic fields.

Finally, let's discuss transport properties a little bit. It has been found experimentally that normal-state resistance of underdoped cuprate deviates from linear behavior at a characteristic temperature T* which is a signature of spin-gap opening. The Ru-1212 system appears to have similar feature. A possible spin-gap characteristic temperature decreases from 275 K to 260 K as doping level increases from 0.0 to 0.1 as shown in Fig.1 and 5. Therefore, the Al-doping really

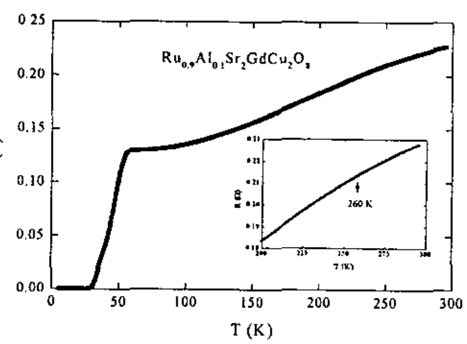

FIG. 5 Resistance as a function of temperature for $Ru_{0.9}Al_{0.1}Sr_2GdCu_2O_8$. The inset shows resistance deviates from linear at 260 K.

moves system away from underdoped regime. How the spin-gap feature manifests itself in the Ru-1212 system is a worthwhile issue to study in the near future.

四、計劃成果自評

In summary, our detailed systematic study on electrical and magnetic properties of the $Ru_{1-x}Al_xSr_2GdCu_2O_8$ with x = 0.0-0.2 reveals that the enhancement of superconductivity by Al-doping is closely associated with the hybridization between Cu-*3d* and Ru-t_{2g} orbital, which consequently causes the localization of mobile holes. This hybridization effect has been suppressed by Al-doping. As a result, it induces a charge transfer between Cu-*3d* and O-*2p* bands. In addition, the magnetic structure of the Ru moments persists in the presence of Al-doping. Furthermore, It appears that a possible spin-gap characteristic temperature decreases from 275 K to 260 K as doping level increases from 0.0 to 0.1. We certainly believe that the obtained results really shine a light on understanding of the physical properties of underdoped ferromagnetic rutheno-cuprate $RuSr_2GdCu_2O_8$.

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