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---子計畫六：含有鈣鈦礦結構的釕基 $RuA_2RCu_2O_y$ 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-032-023

執行期限：89年08月01日至90年9月30日

主持人：林大欽　助理教授　執行機關：淡江大學物理系

計畫參與人員：楊世綱, 許世杰　(淡江大學物理系碩士班學生)

一、中文摘要

我們有系統地研究了鋁摻雜 $RuSr_2GdCu_2O_8$(Ru-1212)鐵磁超導體的磁電傳輸性質、磁學性質與拉曼光譜。實驗的結果顯示在高磁場下此系統的零電阻溫度(T_{c0})並不隨著磁場的升高往低溫移動，意味著此系統的磁通動力學行為與高溫超導銅氧化物迥然不同。當T<100 K時，Ru-1212系統具有正磁阻，磁阻在磁場為2T附近有一極大值。當T>100 K時，系統的磁阻變為負的，磁阻值在磁有序溫度附近最大。這代表著銅氧平面上載子與釕氧平面上自旋的散射機制決定系統反常磁電阻的行為。另一方面，磁學性質的測量顯示Ru-1212系統中釕的價數是混合的，大約55%的釕是五價，而45%的釕是四價的，此結果與X光吸收光譜的結果是一致的。拉曼光譜的實驗數據顯示和連接Ru-O八面體與Cu-O八面體的頂點氧原子的聲子振動峰值隨著鋁參雜量的增加急遽降低，這代表著頂點氧原子是Ru-1212系統銅*3d*與釕t_{2g}軌道雜化效應所誘發電荷轉移機制的媒介。

關鍵詞：鐵磁超導體，磁通動力學行為，軌道雜化，頂點氧原子，電荷轉移

Abstract

Magnetoresistance (MR), magnetic susceptibility and Raman spectra of Al-doped ferromagnetic superconductor $Ru_{1-x}Al_xSr_2GdCu_2O_8$ (Ru-1212) with x = 0.0-0.15 have been investigated. The temperature dependence of the resistance for Ru-1212 in different magnetic fields shows that the zero-resistance temperature (T_{c0}) shifts toward lower temperatures dramatically at low fields, while slowly at high fields. The observed results indicate that the vortex dynamics of Ru-1212 might be intrinsically different from that of the other high-T_c cuprates. When T > 100 K, the MR of the Ru-1212 is negative. However, the MR displays a positive peak at field of 2 T and becomes negative at high fields when T < 100 K. These anomalous features suggest that the exchange interaction between the carriers in CuO_2 planes and the spins in RuO_2 layers dominates the magneto-transport properties of the Ru-1212 system. Magnetic studies show that the effective moment of Ru is about 3.15 μ_B, indicating the Ru valence in the Ru-1212 is a mixture of 55% of Ru^{5+} and 45% of Ru^{4+}. The intensity of Raman shift at 659 cm^{-1}, assigned as an A_{1g} (apical oxygen O_4) phonon mode, weakens substantially with increasing Al content suggesting that the apical oxygen is responsible for charge transfer between Cu-*3d* and Ru-t_{2g} bands. More interestingly, a line around 550 cm^{-1} was observed in the Al-doped compounds, indicative of a significant spin-phonon interaction induced by Al doping.

Keywords: ferromagnetic superconductor, vortex dynamics, hybridization, apical oxygen, 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, which is much less than the estimated value of 0.4 holes/Cu obtained from bond valence sum. 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. Therefore, it is worthwhile to investigate the following issues. (1) Is vortex dynamics of Ru-1212 intrinsically different from that of other high–T_c cuprates? (2) Is the valence of Ru mixed? (3) How are active phonon modes of Ru-1212 modified by introducing excess holes in RuO_2 planes as result of doping? To address these issues, we have investigated the interaction between the transport carriers and the ferromagnetic Ru moments by magneto-transport property measurements. In addition to that, the temperature dependences of magnetic susceptibility and Raman spectra of underdoped $Ru_{1-x}Al_xSr_2GdCu_2O_8$ with x=0.0-0.2. were systematically studied.

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. 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/parallel to current direction were applied for magneto-transport measurements. The Raman data were obtained on powder samples using 514.5-nm line of an Ar-ion laser. The incident light and the scattered light were both vertically polarized.

三、結果與討論

Figure 1 shows the temperature dependence of the resistance for $RuSr_2GdCu_2O_8$ measured in magnetic fields up to 6 T. As can be seen in Fig. 1, the superconducting onset temperature (T_c) hardly has any change as field increases, indicating that superconductivity in the Ru-1212 is a quasi-2D in nature. The transition width becomes broader as field increases. This behavior was observed in the both cases of current perpendicular to field and current parallel to field, which can be understood in the framework of spontaneous vortex phase. More interestingly, zero-resistance temperature (T_{c0}) shifts toward low temperatures at low fields.

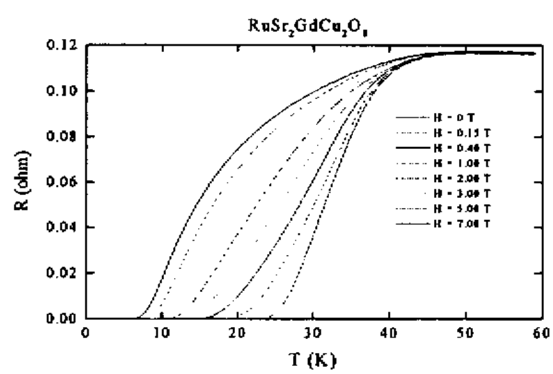

FIG. 1. Resistance as a function of temperature at various magnetic fields for

$RuSr_2GdCu_2O_8$.

However, the T_{c0} decreases slowly with increasing field in the range of 7 T. The observed behavior seems to indicate that a field-induced change of the magnetic structure has a strong influence on the superconducting state of Ru-1212. Furthermore, the intriguing vortex dynamics, intimately related to how magnetic structure is modified to fit the superconducting state, is still an open issue. A magnetic-temperature phase diagram can be obtained by extracting $T_{c0}(H)$ from Fig. 1.$H_{c2}(T)$ can be fitted into an expression of $H_{c2}(T) = 25(1-T/T_c)^{1.65}$ with $H_{c2}(0) = 25$ T.

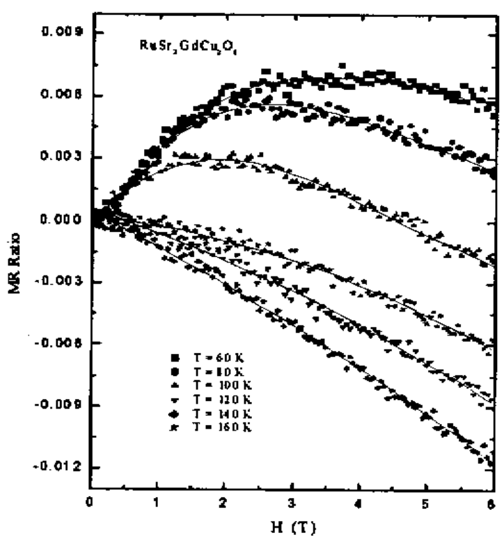

FIG. 2. The field dependence of the MR at various temperatures for $RuSr_2GdCu_2O_8$.

The magnetoresistance as a function of applied field at various temperatures for Ru-1212 is shown in Fig. 2. The MR is positive at temperatures below 120 K. More importantly, the MR exhibits a peak at fields of 2 T, but it becomes negative again at high fields. On the contrary, the MR is negative at temperature above 120 K and is proportional to the square of the applied field well above T_M (magnetic ordering temperature of Ru moment in RuO_2 planes). It is believed that the negative MR arises from the freezing out spin-disorder scattering as the Ru moments align along the direction of applied field. Based upon this model, a value of 30 meV for the exchange interaction between the carriers in the CuO_2 planes and the Ru spins in RuO_2 planes is deduced. It should be noted that the value is of the order of the superconducting energy gap. Therefore, it is expected to have a significant effect on the superconducting properties as indicated in Fig. 1.

Figure 3 shows the temperature dependence of the MR for $Ru_{1-x}Al_xSr_2GdCu_2O_8$ with x = 0.0-0.15 in field of 5 T. As shown in Fig. 4, a maximum negative MR occurs at T_M, and the absolute value of the MR decreases monotonically away from T_M. This result strongly suggest that the magneto-transport properties of Ru-1212 is dominated by the exchange interaction between the carriers in the CuO_2 planes and the Ru spins in RuO_2 planes. However, it is not well understood at this moment that why such a large exchange interaction doesn't affect superconductivity.

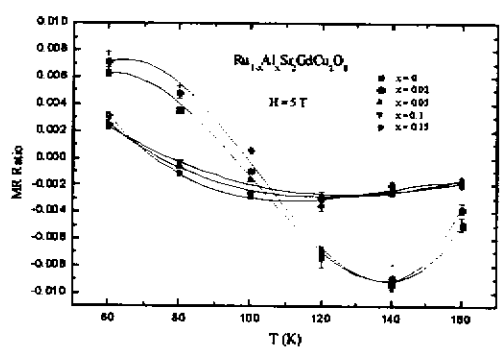

FIG. 3. The MR as a function of the temperature at field of 5 T for $Ru_{1-x}Al_xSr_2GdCu_2O_8$ with x = 0.0-0.15.

Now let's turn to magnetic properties of Ru-1212. The temperature dependence of the inverse molar magnetic susceptibility for $RuSr_2GdCu_2O_8$ is shown in Fig. 4. Apparently, a linear behavior is observed at temperature above 200 K. It turns out that the experimental data $\chi(T)$ can be fitted into $\chi_{Ru}(T) + \chi_{Gd}(T) + \chi_0$, where $\chi_{Ru}(T) = C_1/T-135$

is Curie-Weiss term from Ru moments with T_{curie} of 135 K ，$\chi_{Gd}(T) = C_2/T$ is Curie term from Gd moments and χ_0 is a temperature-independent term. After putting appropriate values of C_2 and χ_0 in the previous expression, C_1 can be deducted curve fitting. The effective magnetic moment of $\mu_{eff}(Ru)$ ~3.15 μ_B in Ru-1212 can be obtained from C_1. This value does not correspond to any of theoretical values for a single valence state of Ru ions, either high or low spin. If mixed valence is assumed, the measured effective moment would be compatible with (a) 55% of Ru^{5+} (S= 1/2) and 45% of Ru^{4+} (S= 2). (b) 31% of Ru^{5+} (S=3/2) and 69% of Ru^{4+} (S=1). The former estimation is consistent with the values determined by XANES techniques.

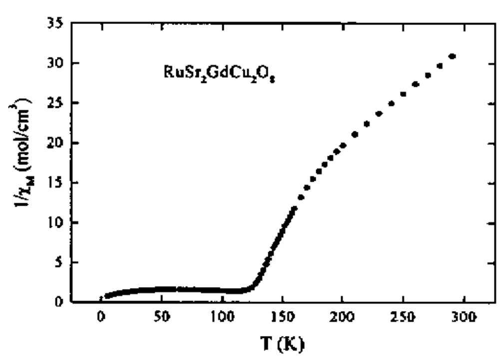

FIG. 4. The temperature of the inverse magnetic molar susceptibility for $RuSr_2GdCu_2O_8$.

Figure 5 shows polarized Raman spectra of $Ru_{1-x}Al_xSr_2GdCu_2O_8$ with x = 0.0-0.15. The intensity of Raman shift at 659 cm^{-1}, assigned as an A_{1g} (apical oxygen O_4) phonon mode, weakens substantially with increasing Al content suggesting that the effective valence of O_4 varies as doping level changes. Since the Cu-O layers are connected by perovskite $SrRuO_3$ layers through the apical oxygen atoms, the apical oxygen is responsible for charge transfer between Cu-*3d* and Ru-t_{2g} bands. More interestingly, a line around 550 cm^{-1} was observed in the Al-doped compounds, indicative of a significant spin-phonon interaction induced by Al doping.

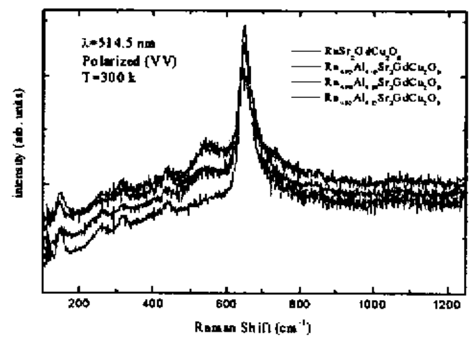

FIG. 5. Raman spectra of Al-doped Ru-1212.

四、計劃成果自評

our detailed study on magneto-transport, magnetic and Raman scattering properties of Al-doped Ru-1212 has found several distinct features. First of all, the intriguing field dependence of T_{co} really suggests that the vortex dynamics of Ru-1212 is quite different from that of high-T_c cuprates. Moreover, the origin of the positive MR at temperature below T_M is an interesting issue for further investigations. Secondly, the valence of Ru is mixed which allows us to tune the system from underdoped to overdoped region by simple doping in RuO_2 planes. Thirdly, magnetic fluctuation and structural instability induced by Al doping have a profound influence on charge transfer between Cu-*3d* and Ru-t_{2g} orbitals. We certainly believe that the obtained results really shed a light on understanding of the underlying mechanism associated with coexistence of ferromagnetism and superconductivity in underdoped hybrid ruthenate-cuprate $RuSr_2GdCu_2O_8$.

五、參考文獻

[1] L. Bauernfeind *et al.*, Physica C **254**, 151 (1991).

[2] I. Felner *et al.*, Physica C **311**,163 (1999).

[3] C. Bernhard *et al.*, Phys. Rev. B **59**, 14099 (1999).