Evidence for Reentrant Structural-Phase Transition in DCNQI–Cu System

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Recently the unique physical properties of the $(R_1,R_2$-DCNQI$)_2$Cu systems (R_1,R_2-DCNQI = 2,5-disubstituted *N,N'*-dicyanoquinonediimine; R_1, R_2 = CH_3, CH_3O, Cl, Br,...) have attracted a considerable interest.[1] The mixed-valency of Cu ($Cu^{1.3+}$) suggests that the highest 3d orbitals of Cu must be located near the Fermi level of the $2p\pi$ metal electrons of DCNQIs, forming the $p\pi$–d mixing bands.[2,3] This is an important new aspect in the field of the molecular metals and opens a possibility to design new types of molecular conducting systems where conduction electrons and magnetic ions coexist. In this report, we present the general pressure–temperature (P–T) phase diagram of the DCNQI–Cu systems and give evidence for the reentrant structural phase transition coupled with the reentrant metal–insulator–metal (M–I–M) transition.

We have recently proposed the P–T phase diagram of $(R_1,R_2$-DCNQI$)_2$Cu.[4] In order to explain briefly the unique nature of the reentrant transition and the motivation of the present study, the simplified general P–T phase diagram is introduced (Figure 1), where P is "effective pressure", $P = P_0$ (applied pressure) – P_c (critical pressure). The critical pressure P_c, above which the metal instability appears, depends on the substituents R_1 and R_2. The approximate P_c values of some typical DCNQI–Cu systems are as follows:[4] (DMe-DCNQI$)_2$Cu, 100 bar; (DMeO-DCNQI$)_2$Cu, 6 kbar; (MeBr-DCNQI$)_2$Cu, –3 kbar; (MeCl-DCNQI$)_2$Cu, –5, kbar. The negative P_c means that the system undergoes a metal–insulator (M–I) transition at atmospheric pressure. The P–T phase diagram can be divided into three regions: (1) negative pressure region (region I), where the system is metallic down to very low temperature, (2) high-pressure region (region II), where the system exhibits a M–I transition at T_{MI} and an antiferromagnetic (AF) transition at low temperature ($T_{AF} \approx 10$ K), and (3) low-pressure region (region III), where reentrant transition takes place. In this paper, we present the X-ray evidence of the reentrant structural phase transition in region III.

In the metallic state, the DCNQI molecules are stacked regularly. The valence of Cu is fluctuating, taking the average valence of +1.3.[4–6] In region II, the metallic state becomes unstable at T_{MI}, where the valence of Cu is fixed in either +1 or +2.[7–10] The threefold structure, coupled with the charge ordering in Cu sites (Cu^{2+} Cu^{+} Cu^{+} ...), has been observed below T_{MI} of every system in region II.[4] The metal instability can be induced also by allowing the system[11] or by the deuteration of DCNQI.[12]

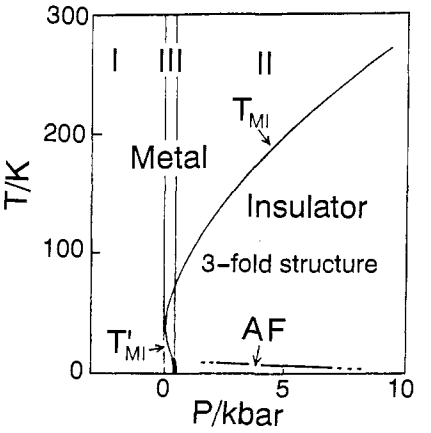

Figure 1. Schematic phase diagram of the DCNQI–Cu system.

Since the metal instability is coupled with the appearance of the magnetic ions (Cu^{2+}), the reentrant transition in region III will become unique. The localized spin associated with Cu^{2+} will make its appearance below T_{MI} and will disappear again below T'_{MI} (Figure 1).[4] Thus, the system seems to undergo a reentrant transition analogous to that of the so-called dense Kondo system. In this context, it should be mentioned that Nishio et al. have reported the large enhancement of low-temperature specific heat in region III.[13] However, until quite recently, there seemed to be some doubt about the credibility of the reentrant resistivity behavior, because except for the experimental results obtained by using the helium gas pressure technique,[14] there seems to be a large ambiguity about the precision in the reported resistivity data.[15] It was suspected that the inhomogeneous distribution of the pressure or the inhomogeneous mixing ratio in the alloy system[4,15] might be responsible for such a phenomenon. However, the very sharp reentrant resistivity transition of the deuterated (DMe-DCNQI$)_2$Cu system observed recently has brushed off such a suspicion.[16,17] Thus, one of the main problems of this unique molecular conducting system remaining to be clarified is the possibility of the reentrant structure change being associated with the appearance and disappearance of the localized magnetic moments of Cu^{2+}. In order to make clear this point, monochromatic Laue photographs were examined. Two needle crystals of the alloy system based on undeuterated and fully deuterated DMe-DCNQI molecules, $[(\text{DMe-DCNQI}(h_8))_{1-x}(\text{DMe-DCNQI}(d_8))_x]_2$Cu ($x \approx 0.29$ (sample A) and 0.26 (sample B)), were

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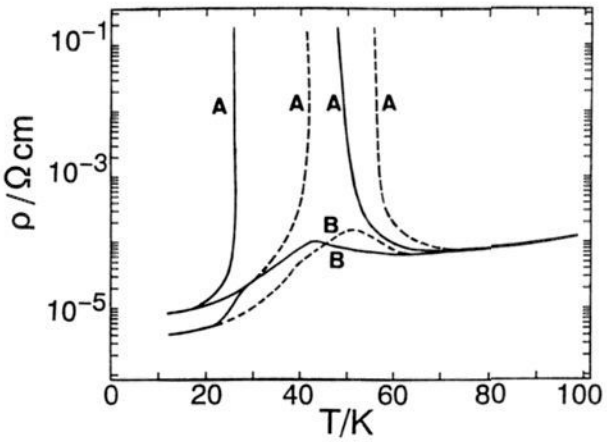

Figure 2. Reentrant resistivity behavior of $[(DMe\text{-}DCNQI\text{-}(h_8))_{1-x}(DMe\text{-}DCNQI(d_8))_x]_2Cu$ (A, $x \approx 0.29$; B, $x = 0.26$). Solid and broken lines are the resistivity changes in the cooling and heating cycles, respectively.

used after their resistivities were measured which had been done along the needle axes of the crystals by the standard four-probe method. As shown in Figure 2, the crystals exhibited the reentrant resistivity transitions with hysteresis.[16] The x value was estimated from the relation between T_{MI} (or T'_{MI}) and x ($T - x$ phase diagram of $[(DMe\text{-}DCNQI(h_8))_{1-x}(DMe\text{-}DCNQI(d_8))_x]_2Cu$) determined recently.[16] In the cooling cycle, sample A showed a resistivity jump at 50 K and a drop at 25 K. The resistivity drop was extremely large (the order of 10^9), while the resistivity anomaly of sample B was small. A closed-cycle helium refrigerator, T-2000 Cryo Controller (TRI Research, Inc.), and a MAC rotating anode-type X-ray generator (Mo, 18 kW) with graphite monochromater were used (λ(Mo Kα) = 0.7107 Å). The exposure time was 40–70 h. The needle crystals (samples A and B) were fixed on the cold head of the helium refrigirator by silver conducting paint with their needle axes almost perpendicular to the incident X-ray beam. X-ray diffraction photographs were taken with cylindrically bent films (Kodak Scientific Imaging Film (Cat. 153 2340)). In the case of the sample A, the threefold superlattice spots characteristic of the insulating state of the DCNQI–Cu system were observed at the temperature range of 50–25 K in the cooling process (insulating state) (Figure 3) and disappeared again below 20 K (metallic state). This is definite evidence of the structural reentrant transition of DCNQI–Cu system. Similar threefold X-ray diffraction patterns below T_{MI} were first observed in $(MeCl\text{–}DCNQI)_2Cu$ by us[2] and Moret[18] several years ago. Interestingly, the threefold spots observed at 28 K in the cooling process (insulating state) could not be observed at the same temperature in the heating process (low-temperature metallic state), which is consistent with the hysteresis of the resistivity (Figure 2). It was surprising that clear threefold reflections were observed at 45–27 K in sample B, indicating that the magnetic ions (Cu^{2+}) appear at T_{MI} and disappear below

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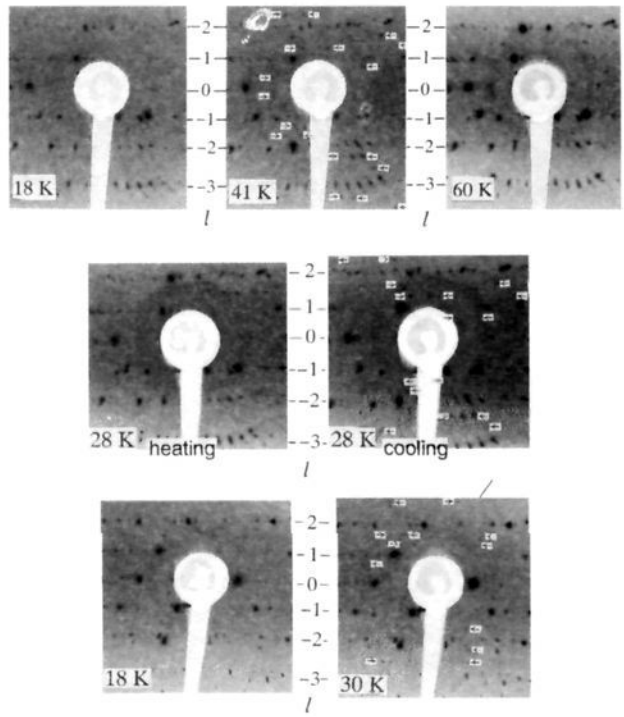

Figure 3. X-ray diffraction photographs. (Top) X-ray photographs of the crystal A in the cooling process. (Middle) Diffraction patterns of the crystal A at 28 K in the cooling and heating cycles. (Bottom) Diffraction patterns of the sample B in the cooling process. Arrows indicate the diffraction spots showing the appearance of the threefold structure. Reflections at the middle of the layer lines (l = 2 to approximately –3) are originated from the diffraction of X-ray with a half-wavelength of λ(Mo Kα).

T'_{MI} even in the system with only a small resistivity anomaly. These results are consistent with the recent observation of the reentrant susceptibility behavior in $[(DMe\text{-}DCNQI(h_8))_{1-x}\text{-}(DMe\text{-}DCNQI(d_8))_x]_2Cu$.[16]

It has been pointed out that the coupling between the periodical lattice distortion and the CDW instability of the DCNQI stack is essential for the metal instability.[2,3,11] Although the underlying mechanism appears to be different, the reentrant structural transition associated with the redisappearance of magnetic ions Cu^{2+} shows that a unique transition seemingly analogous to that of the heavy electron compound takes place in this molecular conducting system.[4,6] It should be noted that the threefold spots are somewhat diffuse, which suggests that the long-range order of the threefold lattice distortion is incomplete in region III. The regular structure in the low-temperature reentrant metallic state and the threefold structure of the insulating phase require the existence of the phase boundary separating regions II and III at low temperatures (the bold line in T'_{MI} (see Figure 1)), which agrees well with the phase diagram of $[(DMe\text{-}DCNQI\text{-}(h_8))_{1-x}(DMe\text{-}DCNQI(d_8))_x]_2Cu$ determined recently.[16]