Magnetic Study of Metal-Insulator-Metal Transitions in (DMe-DCNQI-\(\alpha,\alpha'-d_2\))\(\textsubscript{2}Cu\)

Masafumi TAMURA, Hiroshi SAWA, Shuji AONUMA, Reizo KATO and Minoru KINOSHITA

The Institute for Solid State Physics, The University of Tokyo, Roppongi 7-22-1, Minato-ku, Tokyo 106

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Temperature dependence of magnetic susceptibility of Cu salt of DMe-DCNQI-\(\alpha,\alpha'-d_2\) has been investigated over the temperature range of the metal-insulator-metal (M-I-M) reentrant transition. The insulating phase of this salt has been revealed to exhibit the same temperature dependence of susceptibility as that of the insulator phase of (DMe-DCNQI-\(d_2\))\(\textsubscript{2}Cu\), which shows only a M-I transition. In the reentrant metallic phase, there is no sizable enhancement of susceptibility such as expected from the specific heat enhancement.

\[ \text{DCNQI, copper, deuterium, magnetic susceptibility, molecular conductor, reentrant metal-insulator transition} \]

(DMe-DCNQI)\(\textsubscript{2}Cu\), where DMe-DCNQI is 2,5-dimethyl-N,N'-dicynoquinonediimine, retains metallic conductivity down to very low temperature.\(^1\)\(^-\)\(^4\) The crystal of (DMe-DCNQI)\(\textsubscript{2}Cu\) is tetragonal, in which DMe-DCNQI molecules form one-dimensional columns along the c-axis.\(^1\)\(^-\)\(^3\) These columns are interconnected by mixed-valence Cu ions,\(^2,3,5,6\) which are tetrahedrally coordinated by the terminal N atoms of DMe-DCNQIs. The three-dimensionality thus introduced is considered to stabilize the metallic state of the system. (DMe-DCNQI)\(\textsubscript{2}Cu\) exhibits a metal-insulator (M-I) transition under pressure.\(^7\) The transition temperature increases with increasing pressure.\(^7,8\) The appearance of a reentrant transition at lower pressures is peculiar;\(^9\) the system undergoes the M-I transition at \(T = T_{c1}\) and reenters the metallic phase at \(T = T_{c2}\), which is lower than \(T_{c1}\). Both the transitions are first-order. A similar effect has been observed at ambient pressure for the alloyed systems, (DMe-DCNQI)\(\textsubscript{2-x}(\text{MeBr-DCNQI})_\text{xCu}\), where MeBr-DCNQI is 2-bromo-5-methyl-DCNQI.\(^6\) Enhancement of electronic specific heat\(^9\) and \(T^2\) dependence of resistivity\(^6\) have been reported for the reentrant metallic state of such alloyed systems. Much attention is paid to this phenomenon because of the possibility of electron mass enhancement suggested in connection with the close situation of Cu-3d states near the Fermi level.\(^2,3,5,6,9\) Recently, Fukuyama\(^10\) proposed that the reentrant metallic state results from the classical-quantum crossover of the tunneling of rotational motion of the methyl group.

The reentrant transition in (DMe-DCNQI)\(\textsubscript{2}Cu\) appears only within a rather narrow pressure range, from about 100 bars to 250 bars.\(^8\) This has limited experimental activity on the reentrant phenomenon. However, the recent discovery of the giant reentrant transitions in Cu salt of selectively deuterated DMe-DCNQI,\(^11\) e.g., (DMe-DCNQI-\(\alpha,\alpha'-d_2\))\(\textsubscript{2}Cu\) (or DMe-DCNQI-\(d_2\))[1,1:0] after the nomenclature defined in ref. 11; see Formula 1.), which were made following the discovery of deuteration-induced M-I transition,\(^12\) has entirely changed this situation. These deuteration effects have been explained in terms of “chemical pressure” due to the secondary isotope effect.\(^11,13\) Fine tuning of effective internal pressure without alloying has thus become possible by this technique; now the reentrant behavior can be explored in detail at ambient pressure. The series of deuterated (DMe-DCNQI)\(\textsubscript{2}Cu\) can be classified into three groups at ambient pressure; Group I is metal-
lic over the entire temperature range, Group II undergoes the M-I transition, and Group III exhibits the giant reentrant transitions.\textsuperscript{11} As regards the magnetic properties of the system, the following is so far known.\textsuperscript{14-16} i) The susceptibility (\(\chi\)) is small and almost temperature-independent in the metallic phase above \(T_{c1}\). ii) Below \(T_{c1}\), \(\chi\) of the \(d_8\) salt (Group II) follows the Curie-Weiss law, with the Curie constant corresponding to 1/3 mol of \(\text{Cu}^{2+}\), which is consistent with the localized threefold arrangement of \(\text{Cu}^{2+}\) along the \(c\)-axis.\textsuperscript{2,6} iii) The \(d_8\) salt undergoes an antiferromagnetic transition accompanied by weak ferromagnetism at about 8 K.\textsuperscript{15} We have carried out the magnetic study of the Group III systems, in order to answer the following two questions. Is there any difference between the insulating phase of Group III and that of Group II? Can we observe susceptibility enhancement in the reentrant metallic phase of Group III? This paper reports the results for the case of (DMeo-DNCQI-\(d_2\)[1,1;0])\(_2\)Cu.

Single crystals of (DMeo-DNCQI-\(d_2\)[1,1;0])\(_2\)Cu were prepared from CuI and DMeo-DNCQI-\(d_2\)[1,1;0] by a diffusion method in an acetonitrile solution. A bundle of about 30 pieces of the single crystal (13.1 mg), softly sandwiched by a small amount of quartz wool, was held in a bag (about 6 \(\times\) 6 \(\times\) 1.5 mm\(^3\)) made of transparent film (FUJI XEROX No. V515). The effect of stress on the crystals or the effect of rapid changes in volume due to the first-order transitions during the measurements was minimized in this way.* Magnetizations and magnetic susceptibilities were measured for this specimen by a Quantum Design MPMS SQUID magnetometer. The reentrant behavior of each crystal was confirmed by four-probe resistivity measurements. The paramagnetic susceptibilities (\(\chi_p\)) were estimated by subtracting the blank (the bag and quartz wool) data and diamagnetic susceptibility, \(-1.95 \times 10^{-4}\) emu/mol,\textsuperscript{14} which was calculated by use of Pascal's law from the susceptibilities of DMeo-DNCQI and Cu\(^+\), \(-9.15 \times 10^{-5}\) emu/mol and \(-1.2 \times 10^{-5}\) emu/mol, respectively.

The temperature dependence of \(\chi_p\) of (DMeo-DNCQI-\(d_2\)[1,1;0])\(_2\)Cu for magnetic fields parallel and perpendicular to the \(c\)-axis (noted as \(H//c\) and \(H\perp c\), respectively) is shown in Fig. 1, together with that of (DMeo-DNCQI-\(d_8\))\(_2\)Cu for comparison. The reentrant behavior is obvious. In the insulating phase, \(\chi_p\) of the \(d_2\)[1,1;0] salt coincides with that of the \(d_8\) salt. The reentrant metallic phase shows almost the same \(\chi_p\) as those of the undeuterated \(h\) salt (Group I) and in the high-temperature metallic phases of the three groups.

A strong overcooling effect often appeared during the measurements, as anticipated for a first-order transition at considerably low temperature. Inhomogeneity due to overcooling, which refers to small portions of samples quenched above the transitions, reduces \(\chi\) of the insulating phase, and raises \(\chi\) of the reentrant metallic phase. The peculiar behavior of \(\chi_p\) of the \(d_2\)[1,1;0] salt reported in our previous paper\textsuperscript{16} is the one strongly affected by the overcooling. The volume change measured by X-ray diffraction has also indicated that the system exhibits incomplete transition.\textsuperscript{16} We found that this can be sufficiently removed by annealing of samples. For example, a cooling from 20 K (the insulating state) to 7 K in 40 minutes yielded a large \(\chi\) value, which decayed at 7 K in the following several hours, accompanied by the weak ferromagnetism very similar to that reported for the \(d_8\) salt. After an overnight anneal at around 15 K, \(\chi\) approaches almost the same value as that of the high-tem-

* In the course of this study, it is recognized that a finely crushed portion of the sample gives rise to paramagnetic susceptibility which increases with decreasing temperature down to 1.8 K. The susceptibility does not necessarily follow the simple Curie law. This contribution obscures the intrinsic one of the single crystals and, therefore, should be removed as completely as possible.
temperature metallic phase. The results given in Fig. 1 were recorded in this way. It is also recognized that \( \chi \) during the transitions varies slightly with the cooling or warming rate of the measurements.

The \( \chi_p \) values between 30 K and 50 K in the insulating phase can be well reproduced by the Curie-Weiss law, \( \chi_p = C/(T - \theta) \), with \( \theta = -14 \) K and \( C = 0.18 \) emu K mol\(^{-1} \) for \( H//c \) and \( C = 0.14 \) emu K mol\(^{-1} \) for \( H \perp c \). The anisotropy of \( \chi_p \) is ascribable to the anisotropy of the \( g \)-factor. The values of the Curie constant, \( C \), agree with those expected for 1/3 mol of Cu\(^{2+} \): \( S = 1/2 \) spins with \( g(H//c) = 2.41 \) and \( g(H \perp c) = 2.08 \).\(^3 \) This leads us to the conclusion that the Cu\(^{2+} \) ions in the insulating phase retain substantially the same electronic state over Group II and Group III. It is now evident that the anomalous magnetic properties previously reported for the \( h \) salt\(^5,17,18 \) can be interpreted as a result of the coexistence of Group II- and III-type behavior introduced probably by weak inhomogeneous stress on the sample.

In our previous paper,\(^16 \) the possibility of spin fluctuation in the insulating phase of Group III was proposed on the basis of the observation of diffuse X-ray scattering and the Seeming depression of susceptibility, which is now revealed to be a result of the overcooling effect. There is no need to introduce such a consideration, in light of the above conclusion. The possibility of the reduction of Cu\(^{2+} \) magnetic moment in the case of a small \( \pi-d \) charge transfer gap is pointed out by Fukuyama.\(^19 \) Such a reduction is not observed in the present case. It follows that the gap is so large that the localized Cu\(^{2+} \) spins retain almost a pure \( 3d \) character.

The susceptibility of the reentrant metallic phase is of special interest, because of the reported enhancement of electronic contribution in the specific heat, \( \gamma T \).\(^2,9 \) Such enhancement is usually related to the enhancement of the density of states, or enhanced mass, of the conduction electrons. If this is the case, \( \chi \) should be enhanced as well as \( \gamma \). Although \( \chi_p \) in the reentrant metallic phase is slightly larger than that in the high-tempera-

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* Even after an overnight anneal at 15 K, there appeared small remanent magnetization due to the weak ferromagnetism, which amounts typically to a few percent of that of the \( d_6 \) salt. When the, sample was subjected to stress, appreciable enhancement of the remanent magnetization was detected. The temperature dependence of the magnetization of this component is substantially the same as that of the \( d_6 \) salt.

** Recently, enhancement of \( \gamma \) to about 70 mJ K\(^{-2} \) mol\(^{-1} \) in the reentrant metallic phase, was also observed for an alloy system, (DMe-DCNQI-\( h \))\(_{2-}\)(DMe-DCNQI-\( d_6 \)), Cu, and for a series of Cu salts of selectively deuterated DMe-DCNQI.\(^20 \)
ture metallic phase, there is no sizable enhancement of $\chi_p$ in the reentrant state. Therefore, the present result seems to conflict with this picture.

It has been recognized that linear temperature dependence of the specific heat is a common feature of disordered systems, e.g., spin glasses, $^{21}$ and non-stoichiometric vanadium bronzes. $^{22}$ This feature has been shown to be due to low-lying excitations as a result of tunneling between randomly distributed states. $^{23,24}$ The strong overcooling effect, which is capable of introducing randomness into the sample, suggests that such a disorder-induced contribution is responsible for the enhancement of $\gamma$. Improved studies taking account of this possibility are desired, in order to clarify the origin of the anomalous specific heat.

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References

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