Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Anomalous Transport Properties of Graphite-$CoCl_2$

L. Piraux [a] [b]

[a] Unité de Physico-Chimie et de Physique des Matériaux, place Croix du Sud 1, B-1348, Louvain-la-Neuve, Belgium

[b] Research Associate of the National Fund for Scientific Research, (Belgium)

Version of record first published: 23 Oct 2006.

To cite this article: L. Piraux (1994): Anomalous Transport Properties of Graphite-$CoCl_2$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 67-74

To link to this article: http://dx.doi.org/10.1080/10587259408051668

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 67–74
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

ANOMALOUS TRANSPORT PROPERTIES OF GRAPHITE-$CoCl_2$

L. PIRAUX *
Unité de Physico-Chimie et de Physique des Matériaux, place Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium

Abstract A comparison is made between the anomalies in the resistivity of $CoCl_2$-GIC's below the Néel temperature and that of metallic antiferromagnets and magnetic multilayers. Special emphasis is given on the ingredients required for the observation of the anomalous electrical transport properties in these magnetic systems.

INTRODUCTION

The most remarkable feature of the resistivity of stage-1 $CoCl_2$-GIC's [1,2] is the sudden increase in the resistivity as the temperature is lowered below the Néel temperature T_N (Fig.1a). Such phenomena have been observed in resistivity measurements with the current perpendicular [1,2] (ρ_a) or parallel [3] (ρ_c) to the c-axis. To date, resistivity increases not greater than 10% have been reported for stage-1 compounds. The same anomalous resistivity behavior has been observed in other stage-1 magnetic acceptor GIC's which exhibit an antiferromagnetic order stacking (along the c-axis) of ferromagnetic spin planes such as $NiCl_2$-GIC's [4] and $CoCl_2$-GIC's diluted with $MgCl_2$ [5].

Though a similar jump in resistivity at T_N has been observed in stage-2 $CoCl_2$-GIC's [2,6] (Fig.1b) in both ρ_a and ρ_c measurements, the results are still controversial since a decrease in the in-plane resistivity of ~1% was initially reported by Yeh and coworkers [1]. The origin of this discrepancy is not yet understood. Regarding the magnitude of the effect, the situation is also confusing since an increase in ρ_a smaller than 1% was found by Kinany and coworkers [2] while a giant jump in ρ_a, in excess of 50%, was reported by Pernot and Vangelisti [6]. An anomalous increase of the resistivity of the same functional form as that observed in stage-1 and stage-2 compounds was also reported [7] in a bi-intercalation compound C-$CoCl_2$-C-$AlCl_3$ below T~10K (Fig.1c). Surprisingly, the increase in ρ_a observed on this particular sample was as large as ~35%.

In this work, we compare the anomalies observed in the transport properties of $CoCl_2$-GIC's around T_N with those reported in various metallic antiferromagnets as well as in magnetic metallic multilayers which likewise exhibit an antiferromagnetic interlayer exchange coupling.

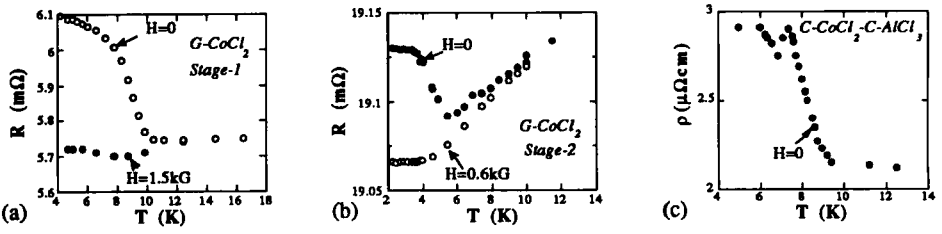

Fig.1 : Low temperature variation of the in-plane resistance of stage-1 (a) and stage-2 (b) $CoCl_2$-GIC's in zero magnetic field and under an external field, as indicated; (c) in-plane resistivity vs temperature at H=0 for a bi-intercalation compound C-$CoCl_2$-C-$AlCl_3$ (from ref. 7).

COMPARISON WITH METALLIC ANTIFERROMAGNETS

An anomalous behavior of the resistivity similar to that observed for $CoCl_2$-GIC's has been seen in several antiferromagnet systems including transition metals (Cr, α-Mn) [8,9], rare-earth metals (Dy, Er) [10,11] and some intermetallics (URu_2Si_2, UNi_2Si_2) [12,13]. However, in these systems, the sharp rise in resistivity just below T_N is followed by a maximum and by a rapid decrease as the temperature is lowered. Fig.2a illustrates the anomalous resistivity behavior around T_N for single-crystal URu_2Si_2.

The theoretical model used with some success in explaining this phenomenon involves two competing mechanisms [14]. One is the formation of energy gaps on the Fermi surface which decreases the effective number of conduction electrons when the gaps appear in the conduction band and consequently increases the resistivity. The gapping effect results from magnetic ordering with a periodicity larger than that of the lattice, giving rise to new Brillouin zone boundaries perpendicular to the c-axis. In these materials, the c-axis refers to the direction along which the additional magnetic periodicity takes place. Hall-effect measurements performed on intermetallic compounds confirmed such changes in the effective number of conduction electrons just below the transition temperature [15]. In a previous model [16], it was stated that, for $CoCl_2$-GIC's, the Fermi-surface effect also affects the scattering of the conduction electrons in both in-plane and c-axis directions due to a smaller effective screening of the charged impurities in the antiferromagnetic phase which enhances the electron scattering.

In the second mechanism, an exchange interaction between the localized spins $\underline{I}$ and conduction electron spins $\underline{s}$ of the type $\Gamma\underline{s}.\underline{I}$ gives rise to spin disorder scattering. The reduction of the spin fluctuations as the temperature is lowered below T_N leads to a decrease in the resistivity.

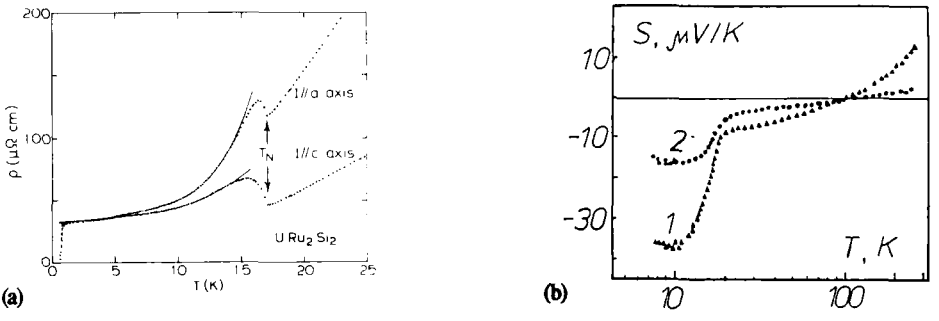

Fig.2 : Anomalies in the resistivity (a) and thermoelectric power (b) around the antiferromagnetic transition temperature T_N for single-crystal URu_2Si_2 (from refs. 12 and 20); the curves 1 and 2 in (b) refer to measurements with the heat current parallel and perpendicular to the c-axis respectively.

In general, the gapping of the Fermi surface only influences electrical transport along the c-axis [14]. As a matter of fact, the anomalous increase of the resistivity below T_N is marked for the c-direction in the above mentioned antiferromagnets, whereas for the perpendicular direction the anomaly is strongly reduced in magnitude or is even not observed as for Er, UNi_2Ge_2, ... In these solids, an abrupt decrease in resistivity with decreasing temperature below T_N is observed [11,13]. Such an anisotropy in the resistivity behavior in the vicinity of T_N is not observed in stage-1 $CoCl_2$-GIC's since a sharp increase in resistivity of comparable magnitude has been reported along the two directions [1-3]. However, it is premature to draw any conclusion from this observation because of the highly anisotropic electronic structure of acceptor GIC's and since the mechanisms responsible for the electrical transport along the c-axis are not yet understood.

One of the most important ingredients associated with the formation of energy gaps on the Fermi surface is the ***long-range coherence of the antiferromagnetic ordering***. Neutron scattering measurements have shown that long-range antiferromagnetic order along the c-axis (>100 Å) exists in stage-1 $CoCl_2$-GIC's [17]. In the second stage [18], the correlation length is considerably reduced (20-30 Å). This striking difference between stage-1 $CoCl_2$-GIC's and higher stage compounds has been invoked by Yeh and coworkers [1] to explain the contrasting resistivity behavior observed between stage-1 and stage-2 compounds. According to this interpretation, the Fermi surface modification effect is about one order of magnitude larger than the spin disorder effect in stage-1 $CoCl_2$-GIC's, giving rise to a net increase of resistivity at T_N. The Fermi surface modification effect is not apparent in stage-2 $CoCl_2$-GIC's due to a much smaller magnetic coherence distance along the c-axis, giving rise to an abrupt decrease in resistivity of about 1% below T_N due to spin fluctuations. However, this model is not consistent with the

small increase in ρ_a (as small as 0.3%) reported by Kinany and coworkers [2,19] on several stage-2 compounds and the results of c-axis resistivity measurements given in ref.7. Because of the short antiferromagnetic correlation length in the bi-intercalation compound C-$CoCl_2$-C-$AlCl_3$, the Fermi-surface modification effect should be considerably reduced. In addition, since the period of the spin arrangement in bi-intercalation compounds is much larger than in stage-1 and stage-2 compounds, gaps should be closer to the Brillouin zone boundaries so that the anomalies in the resistivity should be less marked. This is not consistent with the observation of the large jump in resistivity shown in Fig.1c.

The magnitude of the resistivity jump at T_N likely depends on the low-T value of ρ_a. For a given stage, this might explain the puzzling results reported to date since it was found that $CoCl_2$-GIC's give far more variable and sample-dependent in-plane resistivities than most other metal chloride-GIC's [7].

In metallic antiferromagnets, the thermoelectric power S was found to be sensitive to modifications in the Fermi surface and scattering mechanisms at the antiferromagnetic ordering temperature [8,20]. To illustrate this point, the anomalies in the thermoelectric power near $T=T_N$ for URu_2Si_2 [20] are shown in Fig.2b. In contrast, no marqued anomalies in the thermoelectric power of first stage $CoCl_2$-GIC's [19] have been observed at T_N as shown in the S(T) and dS/dT curves (Fig.3a-b) though a small increase in slope in the S(T) curve seems to appear. However, it is likely that this enhancement in the thermoelectric power around T~10K corresponds to the onset of the phonon-drag contribution, as observed in most low-stage acceptor GIC's [21].

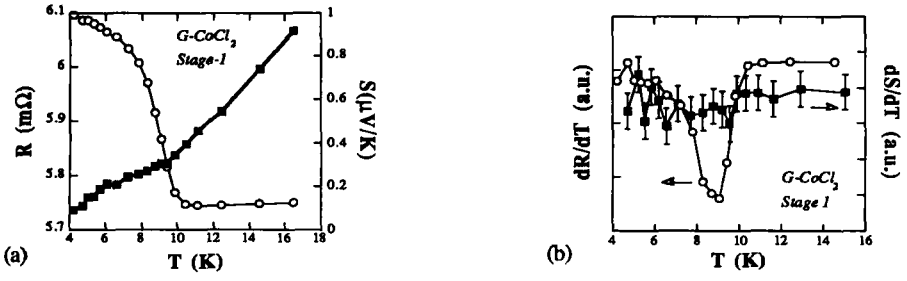

Fig.3 : (a) Variation of the in-plane resistivity and thermoelectric power with temperature near the antiferromagnetic transition temperature for a stage-1 graphite-$CoCl_2$; (b) dR/dT and dS/dT vs T curves.

In conclusion, it seems that the theoretical model used in explaining the striking resistivity behavior and anomalies in the thermoelectric power just below T_N in usual metallic antiferromagnets does not reproduce the general features of the resistivity and thermoelectric power just below T_N in $CoCl_2$-GIC's. Experimental evidence in support of

partial gapping of the Fermi surface below the transition temperature in $CoCl_2$-GIC's is still lacking. In particular, no modification of the Fermi surface below T_N was clearly identified in the experimental investigation of two properties which usually depend sensitively on the electronic structure, specifically the thermoelectric power and Shubnikov-de Haas effect [22]. Further information on the hypothetical change in the Fermi surface and associated reduction in the effective number of conduction charge carriers in $CoCl_2$-GIC's might be obtained from Hall-effect measurements around T_N.

COMPARISON WITH MAGNETIC MULTILAYERS

The application of a strong enough magnetic field - usually parallel to the $CoCl_2$ layer - suppresses the anomalous increase in resistivity below T_N (Fig.1a-b), giving rise to a negative magnetoresistance. It was found that magnetic fields of about 0.1T and 0.03T are sufficient to completely quench the anomalies in stage-1 and stage-2 compounds respectively [1,2]. The effect of a magnetic field is to overcome the antiferromagnetic coupling and to force the magnetic moments of all ferromagnetic $CoCl_2$ layers to lie in a direction parallel to the applied field. As shown in Fig.4a, the magnitude of the negative magnetoresistance observed on stage-1 and stage-2 $CoCl_2$-GIC's is relatively small (the largest value reported to date does not exceed ~10%). However, owing to the fact that a resistivity increase in zero magnetic field of several tens of percent has been observed below T_N in a stage-2 compound [6] and in a bi-intercalation compound C-$CoCl_2$-C-$AlCl_3$ [7], we may anticipate that very large negative magnetoresistances are expected in these compounds. Further investigation of the low-temperature resistivity of $CoCl_2$-GIC's should help to clarify the situation.

Such experimental observation bears some ressemblance with the ***"giant magnetoresistance effect"*** observed in metallic magnetic multilayers (Fig.4a-b) [23]. These multilayers are made by the orderly deposition of alternating ultra-thin films of ferromagnetic (Fe, Co, ...) and non-magnetic metals (Cu, Ag, Ru, Cr, ...). In these multilayers, the magnetization is usually in the plane of the layers. The last four years have seen increasing interest in the magnetic properties and magnetotransport properties of these multilayers. Oscillatory magnetic exchange coupling, i.e. oscillations between ferromagnetic and antiferromagnetic coupling as a function of the non-magnetic layer thickness, have been discovered [24]. The period of oscillations is much larger than predicted by the RKKY model and depends on the nature of the non-magnetic layer and its orientation. Measurements of the resistivity in applied fields of antiferromagnetically coupled multilayers have led to the observation of giant magnetoresistance effects [23]. The

resistivity drops by a few percent (as in Co/Ru) up to several tens of percent (as in Fe/Cr or Co/Cu) when the magnetic field is sufficiently large to overcome the antiferromagnetic coupling between the neighbour magnetic layers.

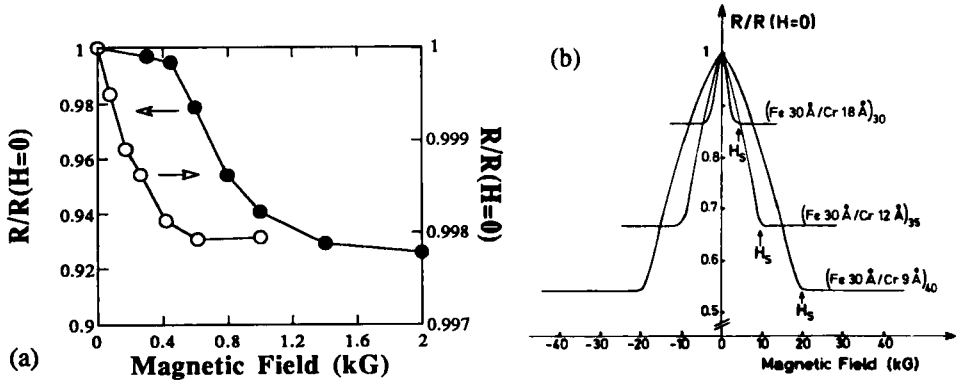

Fig.4 : (a) Magnetic field dependence of the resistance of stage-1 (●) and stage-2 (o) $CoCl_2$-GIC's below T_N; (b) Change of the resistance in applied external magnetic fields for Fe/Cr magnetic multilayers (from ref. 23).

The giant magnetoresistance has been explained on the basis of the ***two-current model*** widely used for ferromagnetic transition metals such as Fe, Co or Ni. In the absence of spin-flipping processes, the current is carried by the spin ↑ and spin ↓ electrons in two independent channels. The two currents can be different because the d↑ and d↓ densities of states at the Fermi level are different so the s to d scattering rates will be different for spin ↑ and spin ↓ conduction electrons. The present understanding of the giant magnetoresistance in magnetic multilayers is based on ***spin-dependent scattering*** at interfaces between the magnetic and non-magnetic layers and, to a lesser extent, within the magnetic layers . The thickness of the layers must be less than the mean free path of the conduction electrons. The spin-dependent scattering changes as the magnetic field reorients the magnetic layers, producing a different resistance for antiparallel and parallel magnetic arrangements. The resistance is less for the parallel configuration than for the antiparallel configuration and this difference accounts for the giant magnetoresistance effect. Recently, giant magnetoresistance has been observed in granular solids containing magnetic particles [25]. In these granular solids, the moments of the ferromagnetic particles are randomly oriented in zero magnetic field. This is the high resistivity state. When a magnetic field is applied, the moments of the individual particles align, giving rise to a decrease in resistivity. It has been proposed that the origin of the giant magnetoresistance for these systems is similar to that for magnetic multilayers, i.e. based on spin-dependent

scattering at the interface between the magnetic particles and the non-magnetic metallic matrix.

In $CoCl_2$-GIC's, the changes in resistivity as the relative orientation of successive magnetic layers is modified by the application of a magnetic field is similar to that observed in magnetic multilayers. In both magnetic systems, negative magnetoresistance is observed though in $CoCl_2$-GIC's the values reported to date do not exceed 10%.

According to the analysis given in Refs 1 and 16, the magnetic scattering in $CoCl_2$-GIC's can be described in terms of a modified s-d model in which a complicated exchange coupling mechanism occurs between the π conduction electrons and the magnetic d electrons of the cobalt ions separated by the chlorine layers. Alternatively, one might envisage an extreme s-d model where the π electrons are scattered by the magnetic atoms through π-d hybridization weakened by the large separation between the spins and the π electrons and by the intervening chlorine layers. Because of the π-d hybridization, the d-levels of the cobalt ions are broadened to form ***"virtual bound states"*** as introduced by Friedel [26] for magnetic transition-metal impurity systems. This picture has been further extended and described formally by Anderson [27]. In this approach, the asymmetry between the spin $\uparrow$ and spin $\downarrow$ d-levels leads to spin-dependent scattering which is the fundamental mechanism producing the giant magnetoresistance effect in magnetic multilayers and granular systems.

Finally, it should be mentioned that evidence for superposition of intercalate band and graphitic π-band at the Fermi level was recently found in stage-1 $AuCl_3$-GIC [28]. The presence of such "localized" states at the Fermi energy might also account for the unusually large in-plane resistivity of this compound invoking interband scattering.

ACKNOWLEDGEMENT

I would like to thank Prof. M. S. Dresselhaus and Drs. G. Dresselhaus and S. Flandrois for useful discussions and careful reading of the manuscript prior publication. This work was carried out under the financial support of the programme "Action de Recherche Concertée" sponsored by the "DGESR de la Communauté Française de Belgique".

REFERENCES

* Research Associate of the National Fund for Scientific Research (Belgium).
1. N. C. Yeh, K. Sugihara, M. S. Dresselhaus and G. Dresselhaus, Phys. Rev. B40, 622 (1989)
2. M. Kinany-Alaoui, L. Piraux, V. Bayot, J. P. Issi, P. Pernot and R. Vangelisti, Synthetic Metals 34, 537 (1989)
3. J. T. Nicholls and G. Dresselhaus, J. Phys. : Condensed Matter 2, 8391 (1990)
4. J. T. Nicholls, J. S. Speck and G. Dresselhaus, Phys. Rev. B39, 10047 (1989)

5. J. T. Nicholls and G. Dresselhaus, Phys. Rev. B41, 9744 (1990)
6. P. Pernot and R. Vangelisti, Z. Naturforsch. 44b, 761 (1989)
7. E. McRae, A. Herold, M. Lelaurain, J. F. Mareche, A. Perignon, P. Pernot and R. Vangelisti, Extended Abstracts of the Symposium on Graphite Intercalation Compounds at the Materials Research Society Meeting, Boston, edited by M. Endo, M. S. Dresselhaus and G. Dresselhaus (Materials Research Society Press, Pittsburgh, 1988), p.105
8. A. L. Trego and A. R. Mackintosh, Phys. Rev. 166, 495 (1968)
9. G. T. Meaden, Electrical Resistance of Metals (New York : Plenum, 1965)
10. S. Legvold, F. H. Spedding and P. M. Hall, Phys. Rev. 117, 971 (1960); R. A. Craven and R. D. Parks, Phys. Rev. Lett. 31, 383 (1973)
11. S. Legvold, F. H. Spedding and R. W. Green, Phys. Rev. 122, 827 (1961)
12. T. T. M. Palstra, A. A. Menovsky and J. A. Mydosh, Phys. Rev. B33, 6527 (1986)
13. Y. B. Ning, J. D. Garett and W. R. Datars, J. Phys. : Condens. Matter. 4, 9995 (1992)
14. H. Miwa, Prog. Theor. Phys. 29, 47 (1963); R. J. Elliott and F. A. Wedgwood, Proc. Phys. Soc. 81, 846 (1963)
15. J. Schoenes, C. Schonenberger, J. J. M. Franse and A. A. Menovsky, Phys. Rev. B35, 5375 (1987)
16. K. Sugihara, N. C. Yeh, M. S. Dresselhaus and G. Dresselhaus, Phys. Rev. B39, 4577 (1989)
17. H. Ikeda, Y. Endoh and S. Mitsuda, J. Phys. Soc. Jpn. 54, 3232 (1985)
18. D. G. Wiesler, M. Suzuki and H. Zabel, Phys. Rev. B36, 7051 (1987)
19. M. Kinany-Alaoui, PhD thesis, Louvain-la-Neuve, Belgium (1989)
20. F. G. Aliev, V. Kovachik, V. V. Moshchalkov, V. V. Pryadum, N. E. Alekseevskii, A. V. Mitin, N. Agrait, S. Vieira and R. Villar, J. Low Temp. Phys. 85, 359 (1991)
21. J. P. Issi in Graphite Intercalation Compounds II : Transport and Electronic Properties, edited by H. Zabel and S. A. Solin - Springer Series in Materials Science 18 (Springer-Verlag, Berlin, 1992), p.195
22. G. Dresselhaus in ref. 21, p.292
23. M. N. Baibich et al, Phys. Rev. Lett. 61, 2472 (1988); G. Binasch et al, Phys. Rev. B39, 4828 (1989)
24. S. S. P. Parkin, N. More and K. P. Roche, Phys. Rev. Lett. 64, 2304 (1990)
25. A. E. Berkowitz et al, Phys. Rev. Lett. 68, 3745 (1992); J. Q. Xiao et al, Phys. Rev. Lett. 68, 3749 (1992)
26. J. Friedel, Can. J. Phys. 34, 1190 (1956)
27. P. W. Anderson, Phys. Rev. 124, 41 (1961)
28. T. Ishii, Y. Komatsu, K. Suzuki T. Enoki, A. Ugawa, K. Yakushi and S. Bandow, Proceeding of this conference