X-Ray Study of Single Crystal Stage 4 $MoCl_5$-Graphite Intercalation Compound

P.C. Chow, M. Suzuki and H. Zabel
Department of Physics and Materials Research Laboratory,
University of Illinois at Urbana-Champaign,
Urbana, Illinois 61801

Introduction

The graphite intercalation compounds (GIC's) with metal pentahalide MX_5 (M = As, Sb, Mo, ... ; X = Cl, F) form a class of materials in which the chemical reaction occuring upon intercalation of MX_5 compounds into the graphite host gives rise to the formation of several chemical species. The in-plane structure of the intercalant layer in MX_5-GIC's seems to be very different from that of the pristine MX_5 compounds.

So far there have been only a few detailed studies on the in-plane structures of MX_5-GIC's. Those are X-ray and electron diffraction experiments[1-4] of the metal-chlorides MCl_5-GIC (M = Sb, Mo). The pristine MCl_5 compounds form two types of molecular lattices[5] in which the molecules are independent ($SbCl_5$) or associated in pairs by co-ordinate links (Mo_2Cl_{10}).[5]

In the present paper we report[10] the results of an X-ray scattering study on stage 4 $MoCl_5$-GIC in the temperature range between 300 K and 730 K. It is important to clarify the in-plane structure of $MoCl_5$-GIC, in order to establish a unified picture of the in-plane ordering in MCl_5-GIC's. We will show that the intercalant layer is composed of two kinds of species at 300 K and that these species undergo two structural phase transitions at T_{cl} = 511 K and T_{cu} = 583 K.

Experimental

The sample was prepared by heating a mixture of powdered $MoCl_5$ and a single crystal of Kish graphite (SCKG)[5] inside the Pyrex glass ampoule sealed in vacuum. The reaction was continued at 480°C for about 15 days. The chemical composition was determined as $C_{45.5}MoCl_5$ from weight uptake.

Result and Discussion

Figure 1 shows a schematic diagram of the in-plane diffraction pattern of stage 4 $MoCl_5$-GIC at 300 K. Two sets of Bragg spots were observed; I (A, C, D, E, M, J, N) and II (B, K, L, P). The Bragg spots belonging to species I appear at $\{\vec{G} \pm \vec{Q}\}$, where $\{\vec{G}\}$ and $\{\vec{Q}\}$ are the

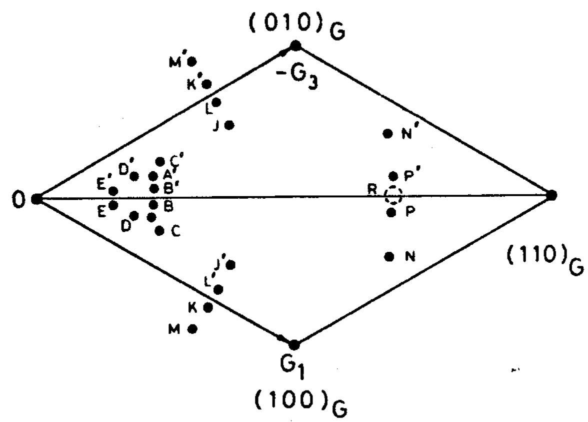

Fig.1 Schematic drawing of Bragg spots in the reciprocal lattice plane at 300 K. The points A', B', ... with the points A, B, ... are symmetric.

sets of graphite- and the intercalant (species I)-reciprocal lattice vectors; $\vec{OA} = \vec{Q}_1$, $\vec{OC} = \vec{G}_2 - 3\vec{Q}_2$, $\vec{OD} = \vec{G}_1 - \vec{Q}_1 + \vec{Q}_2$, $\vec{OE} = 2\vec{G}_1 - \vec{G}_2 - 2\vec{Q}_1 + 5\vec{Q}_2$, $\vec{OM} = \vec{Q}_1 - \vec{Q}_2$, $\vec{OJ} = \vec{Q}_1 - \vec{Q}_3$ and $\vec{ON} = 3\vec{Q}_1$, where $|\vec{Q}_1| = 1.185$ Å^{-1}, $|\vec{G}_1| = 2.95$ Å^{-1} and $\theta = 21.9°$ (the rotation angle between $\vec{G}_1$ and $\vec{Q}_1$). The strain associated with the misfit of species I in the intercalant layer with respect to the graphite layers gives rise to a static distortion wave (SDW) which manifests itself in the appearance of reflections at $\{\vec{G} \pm \vec{Q}\}$.

The Bragg spots belonging to species II appear at $\{\vec{K}\}$, where $\{\vec{K}\}$ are the sets of the intercalant (species II)-reciprocal lattice vectors, $\vec{OB} = \vec{K}_1$, $\vec{OK} = \vec{K}_1 - \vec{K}_2$, $\vec{OL} = \vec{K}_1 - \vec{K}_3$ and $\vec{OP} = 3\vec{K}_1$, where $|\vec{K}_1| = |\vec{Q}_1|$ and $\phi = 27.4°$ (the rotation angle between $\vec{K}_1$ and $\vec{G}_1$). No satellite reflections at $\{\vec{G} \pm \vec{K}\}$ were observed. Thus the intercalant layer is composed of two species, I and II, which may correspond to the dimer phase and the hexagonal phase, respectively, according to Johnson.[4] However, the 6-fold symmetry of $\{\vec{Q}\}$ in the reciprocal lattice plane indicates that the in-plane structure of species I has a different symmetry from the dimer phase.

Figure 2 shows the temperature variation of the peak intensity of the Bragg spot at the point N ($c^* = 0$). A structural phase transition occurs at $T_{cl} = 511 \pm 5$ K. On approaching T_{cl} from the low temperature side, the Bragg spot at N rapidly shifts to the point R (see Fig.1) on the circle of radius $|\vec{ON}|$ centered at the origin, with the peak intensity decreasing. The Bragg spot at P also shifts to R. Thus the in-plane structure above T_{cl} can be described by species III with the fundamental wave vector $|\vec{q}_1| = |\vec{G}_1|$ and $\psi = 30°$ (the rotation angle between $\vec{q}_1$ and $\vec{G}_1$).

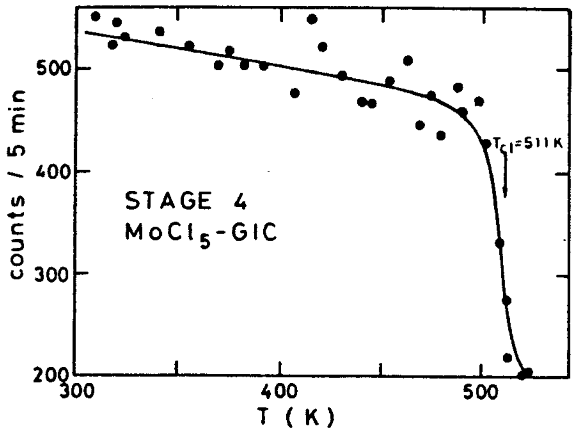

Fig.2 Temperature variation of the Bragg peak intensity at N.

With further temperature increase, the peak intensity of the Bragg spot at R gradually decreases and is reduced to zero at $T_{cu} = 583 \pm 5$ K, which may coincide with the melting temperature of this compound.

In summary, stage 4 $MoCl_5$-GIC undergoes two structural phase transitions at $T_{cl} = 511$ K, from the low temperature phase with co-existence of species I and II to the intermediate phase with species III, and at $T_{cu} = 583$ K, probably to a disordered liquid phase.

References

1. G. Timp, M.S. Dresselhaus, L. Salamanca-Riba, A. Erbil, L.W. Hobbs, G. Dresselhaus, P.C. Eklund and Y. Iye, Phys. Rev. B26, 2323 (1982).
2. R. Clarke, M. Elzinga, J.N. Gray, H. Homma, D.T. Morelli and C. Uher, Phys. Rev. B26, 5250 (1982).
3. M. Suzuki, R. Inada, H. Ikeda, S. Tanuma, K. Suzuki and M. Ichihara, J. Phys. Soc. Jpn. 53, 3052 (1984).
4. A.W.S. Johnson, Acta Cryst. 23, 770 (1967).
5. A. Hérold, in Physics and Chemistry of Materials with Layered Structures, (edited by F. Levy), vol. 6, p.323, Reidel, Dordrecht (1980).
6. M. Suzuki, K. Suzuki, M. Ichihara and A. Furukawa, unpublished.