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Pressure-induced molecular ordering in $SbCl_5$-intercalated graphite

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A new pressure-induced molecular ordering transition is reported in single-crystal samples of stage-2 $SbCl_5$-intercalated graphite. The transition occurs abruptly at 3 kbar and may be the origin of unexplained electronic anomalies previously discovered in this pressure range.

In the last few years high-pressure techniques have been instrumental in improving our understanding of collective effects in highly anisotropic materials such as layered compounds and one-dimensional conductors. Graphite intercalation compounds (GIC's) constitute an important class of layered materials in which pressure has been found to cause dramatic changes in the physical properties.[1] Of particular interest is the observation that some alkali-metal GIC's reversibly change their "stage," or stacking sequence, under relatively modest applied stress. An important feature of such transitions is that *inter*layer and *intra*layer ordering processes are intimately related through a combination of electrostatic and elastic interactions in the three-dimensional host structure.[2]

The donor-type GIC, KC_{24} (stage 2 at ambient pressure), shows a striking example of a pressure-induced staging instability.[3] The samples transform to a stage 3 sequence at ~ 5 kbar with a concomitant increase in the local intercalant density which preserves the overall stoichiometry. A complex sequence of staging transitions has been reported at still higher pressures in KC_8.[4]

While pressure-induced transitions in the donor GIC's have been the focus of a good deal of research recently, analogous behavior in the acceptor GIC's has so far received little attention. This Brief Report gives the results of applying diamond-anvil x-ray methods to probe the structural behavior of a molecular GIC formed by intercalating natural graphite crystals with $SbCl_5$. Our motivation for choosing this particular compound was the earlier observation of increased splittings in the de Haas-van Alphen spectra[5] at $p \approx 4$ kbar and also unusual changes in the optical reflectivity[6] and electrical resistivity[5] in the same pressure range. Both of these effects are indicative of anomalous electronic behavior induced by high pressure. We find that the anomalies are related not to a staging transition but originate rather in a *molecular ordering transition* driven by the relatively soft *c*-axis compressibility.

The structural behavior of stage-2 $SbCl_5$ GIC was studied as a function of pressure using a Bassett-type[7] diamond-anvil x-ray pressure cell with mineral oil as the pressure transmitting fluid. The stress is essentially hydrostatic at the pressures and temperatures ($T = 296$ K) involved here and was measured using the ruby fluorescence method[8] to a precision of ±0.5 kbar. An x-ray precession camera was used for overall surveys of the diffraction patterns at various pressures up to 14 kbar. Selected features of the diffraction patterns were studied using a computer controlled four-circle offset diffractometer. The x-ray source was a graphite monochromated 12-kW rotating anode (Mo $K\alpha$).

Single-crystal stage 2 samples chosen for this study have been previously well-characterized as to their behavior as a function of temperature and show a quasi-two-dimensional arrangement of the intercalant molecules.[9] This is in contrast to stage-1 samples which are closer in structure to normal three-dimensional solids, albeit of a very complex nature.

It is crucial to the interpretation of the observed behavior, both as a function of temperature and pressure, that there is a coexistence of *two segregated phases* consisting of different molecular species: $SbCl_6^-$ and $SbCl_3$. These are thought to arise from a disproportionation reaction, $3SbCl_5 + 2e^- \rightarrow 2SbCl_6^- + SbCl_3$, of the type first suggested by Bartlett, McQuillan, and Robertson[10] for the metal pentafluoride GIC's. Quantitative evidence for the occurrence of this reaction upon intercalation of graphite with $SbCl_5$ has been obtained from Mössbauer work[11] and from recent x-ray structure factor measurements.[12,9]

The in-plane ordering of these molecular species as a function of *temperature* is discussed in detail in Ref. 9 and we summarize the salient features as follows. At ambient temperature the $SbCl_6^-$ ions form a close packed, commensurate $\sqrt{7}\times\sqrt{7}$ superlattice whereas the minority $SbCl_3$ phase exists as islands of fluid (≥ 100 Å in extent) interspersed in the majority phase. The minority phase is characterized by a series of diffuse x-ray diffraction halos typical of an isotropic liquid. The segregated nature of the two species here is supported by several different experiments including detailed structure factor calculations,[9] and direct observations using high-resolution electron microscopy.[13] The $\sqrt{7}\times\sqrt{7}$ lattice is stable at all temperatures in the range 0–425 K, and for applied pressures up to at least 14 kbar. On cooling the samples at ambient pressure, the $SbCl_3$ phase is found to become ordered for $T \leq 230$ K with a $\sqrt{39}\times\sqrt{39}$ (Ref. 14) epitaxial structure [see Fig. 1(c)]. The latter can be commensurate or slightly incommensurate depending on the exact preparation conditions. It has been suggested[9] that the large periodicity is due to the close packing of $2SbCl_3$ dimers, which are favored at low temperature by the dipole-dipole coupling of the trivalent molecules. The calculated fit of close-packed dimers to the $\sqrt{39}$ periodicity is better than 1%. To summarize, then, the $SbCl_6^-$ ions form a very stable structure which we find to be effectively insensitive to temperature and pressure in the thermodynamic range under consideration here. In what follows, we discuss only the behavior of the minority $SbCl_3$ phase, which is found to depend strongly on both temperature and pressure. We now focus on the structural ordering of the minority phase as a function of pressure, keeping the temperature fixed at ambient.

Figures 1(a) and 1(b) show the in-plane diffraction pattern at a pressure of 4 kbar. This pattern of spots grows out of the first-order diffuse halo abruptly at a pressure of 3

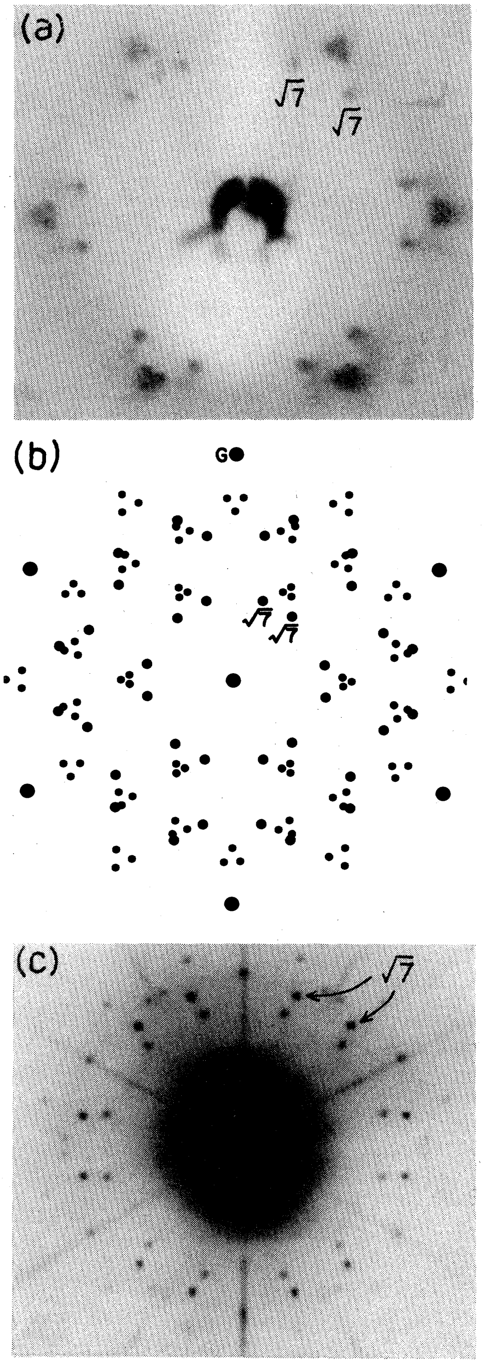

FIG. 1. In-plane x-ray diffraction patterns of a stage-2 $SbCl_5$-intercalated graphite single crystal. (a) At $p=4$ kbar; $T=296$ K. (b) Tracing of high-pressure diffraction pattern, the central part of which is shown in (a). G refers to graphite reciprocal lattice positions and $\sqrt{7}$ to superlattice spots from the $SbCl_6^-$ phase. All other spots are from the ordering of $SbCl_3$ molecules. (c) At $p=0; T=200$ K. [Note: (a) and (c) are on the same scale.]

kbar. Note that the additional spots which appear at this pressure are superposed on the $\sqrt{7}\times\sqrt{7}$ reciprocal lattice of the $SbCl_6^-$ phase. Our interpretation of the high-pressure diffraction pattern is based on the solidification of the $SbCl_3$ islands giving an oblique 2D structure which is not epitaxial with respect to the graphite lattice. The translation vectors of the oblique intercalant structure, inferred from the triangular grouping of spots in the pattern, are shown in Fig. 2. Note that two related configurations are possible. In the first case, shown in Figs. 2(a) and 2(b), one of the translational vectors is orientationally locked to a graphite {100} axis while the other is rotated ±2.25° relative to a {100} axis. In the other configuration [Fig. 2(c)] neither translation vector is locked but is rotated ±2.25° from the respective {100} axes. Referring to Fig. 2, the magnitude of the wave vectors $\vec{a}^*$ and $\vec{b}^*$ is 0.78 Å^{-1}, which is close to $\frac{1}{4}k_G$. However, the 6% misfit relative to the graphite wave vector, k_G, is too large to sustain an epitaxial structure; we see no evidence for structural modulation effects in the high-pressure phase. Superposing the three equivalent orientations of the oblique lattices described above, and adding the $\sqrt{7}\times\sqrt{7}$ reciprocal lattice, the observed diffraction pattern can be reconstructed.

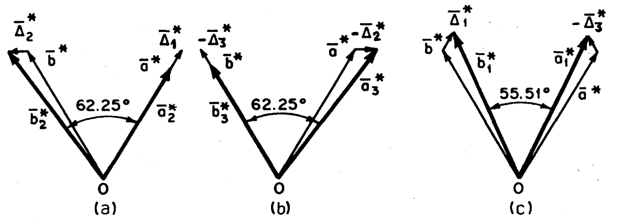

FIG. 2. Reciprocal-lattice vectors (heavy lines) for the two-dimensional oblique lattices derived from Fig. 1(b). (a) and (b): One of the translational vectors locked to a graphite {100} axis. (c) Unlocked case. The vector displacements $\vec{\Delta}_i^*$ are introduced to show the relationship between the oblique lattices and the undistorted hexagonal case ($\vec{a}^*$, $\vec{b}^*$).

We now discuss the kind of in-plane structure that would lead to the diffraction pattern of Fig. 1(b). The fact that the symmetry of the high-pressure arrangement of $SbCl_3$ molecules is oblique and differs from that of the carbon layers suggests that the molecular trigonal axis is no longer normal to the carbon layers as in the low-temperature ordered phase[9] at ambient pressure [see Fig. 3(a)]. Thus, one possible source of this asymmetry could be a tilting of the $SbCl_3$ molecules such that the trigonal axes lie at some angle to the basal plane normal. The gallery spacing at the transition (9.3 Å) imposes a tilt angle, $\phi=31\pm5°$, as shown in Fig. 3(b). This "bridging" configuration is similar to that proposed recently by Boca, Saylors, Smith, and Eklund[12] for the ambient temperature molecular arrangement, although in their case this may be applicable only in an average sense because the $SbCl_3$ molecules are fluidlike at $T\geqslant 230$ K.[9]

Further compression beyond the onset of the transition

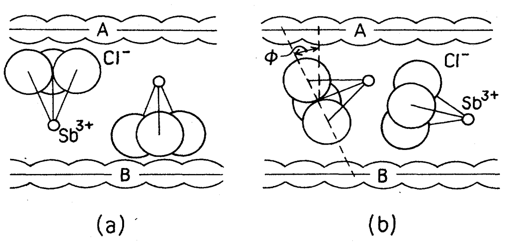

FIG. 3. Orientation of $SbCl_3$ molecules at (a) low temperature, ambient pressure, (b) high pressure, ambient temperature. Note the A/B conformation of the graphite layers.

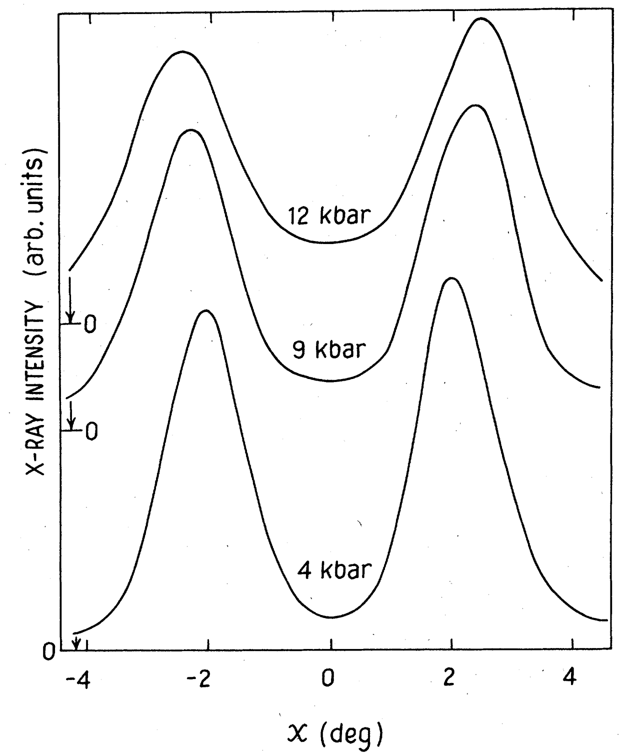

FIG. 4. Azimuthal diffractometer scans through the two spots closest to the $\sqrt{7}$ reflections in Fig. 1(b). The displacement of the peaks from the position $\chi = 0$ [the graphite {110} axis for this group of spots] gives the oblique angle of the unit cell. Note: for clarity, the zeros of the intensity scale for each pressure have been shifted.

(see Fig. 4) leads to a progressive increase of the oblique angle of the unit cell which is consistent with an increasing tilt, ϕ, as the gallery is compressed $[(1/c)(dc/dp) = 3.11 \times 10^{-3}$ kbar$^{-1}]$. It is interesting that the peaks shown in Fig. 4 broaden noticeably at the higher pressures. We have checked that this is not due to sample damage and note that the $\sqrt{7}$ peak widths remain constant with pressure. The effect may be a precursor to a further reorientational transition at still higher pressures. We see no evidence for a staging transition up to $p \approx 14$ kbar. The large gallery spacing implies that considerable elastic energies would be involved in such an instability. Thus, one would expect staging transitions at somewhat higher pressures than in the alkali-metal GIC's.

In conclusion, our results suggest that a molecular orientational ordering transition is responsible for the anomalous electronic behavior previously reported in high-pressure studies of $SbCl_5$ graphite. In particular, the large, negative pressure coefficient of the in-plane resistivity measured[5] in the range $0 < p < 4$ kbar may result from the onset of a more ordered high-pressure phase. An intriguing aspect of the new transition reported here is that the ordered phase induced by pressure is of a qualitatively different nature than the superlattice ordering encountered solely by reducing the temperature. The complex behavior associated with the molecular degrees of freedom in acceptor GIC's may provide access to a wide variety of novel molecular ordering phenomena.

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[1] R. Clarke and C. Uher, Adv. Phys. (to be published).

[2] S. A. Safran and D. R. Hamman, Phys. Rev. Lett. **42**, 1410 (1979); D. P. DiVincenzo and E. J. Mele, Phys. Rev. B **25**, 7822 (1982); G. Kirczenow, Phys. Rev. Lett. **52**, 437 (1984).

[3] R. Clarke, N. Wada, and S. A. Solin, Phys. Rev. Lett. **44**, 1616 (1980).

[4] C. D. Fuerst, J. E. Fischer, J. D. Axe, J. B. Hastings, and D. B. McWhan, Phys. Rev. Lett. **50**, 357 (1983).

[5] Y. Iye, O. Takahashi, S. Tanuma, K. Tsuji, and S. Minomura, J. Phys. Soc. Jpn. **51**, 475 (1982).

[6] K. Syassen (unpublished).

[7] L. Merrill and W. A. Bassett, Rev. Sci. Instrum. **45**, 290 (1974).

[8] G. J. Piermarini, S. Block, and J. D. Barnett, J. Appl. Phys. **44**, 5377 (1973).

[9] R. Clarke and H. Homma, in *Intercalated Graphite,* edited by M. S. Dresselhaus, G. Dresselhaus, J. E. Fischer, and M. J. Moran (Elsevier, New York, 1983), pp. 3–8; H. Homma, Ph.D. thesis, University of Michigan, 1984.

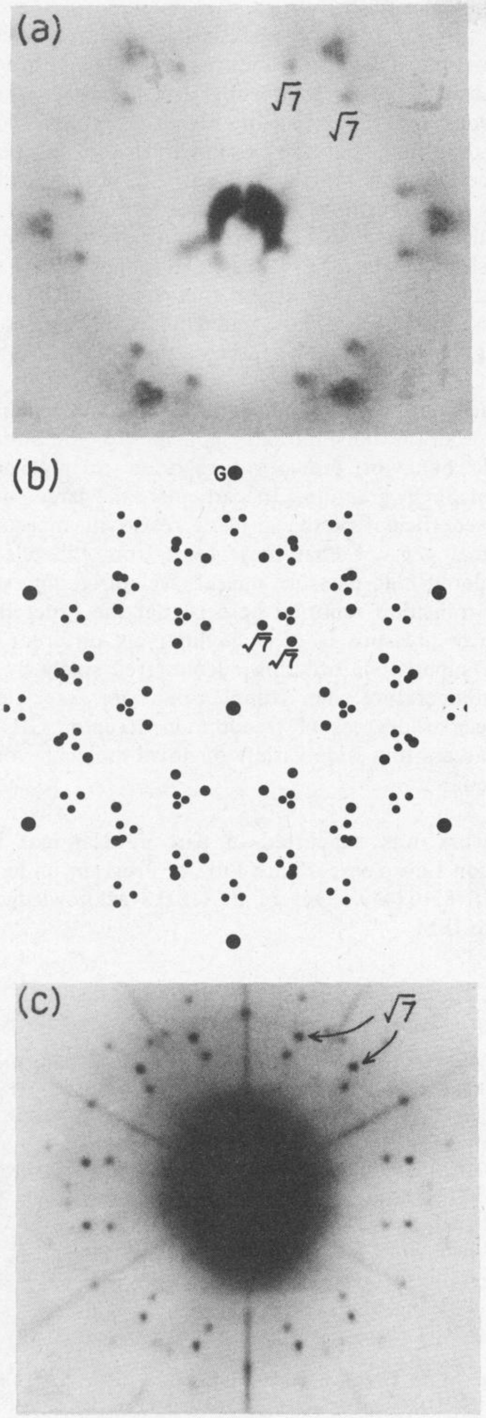
[10] N. Bartlett, B. McQuillan, and A. S. Robertson, Mater. Res. Bull. **13**, 1259 (1978).

[11] P. Boolchand, W. J. Bresser, D. McDaniel, K. Sisson, V. Yeh, and P. C. Eklund, Solid State Commun. **40**, 1049 (1981).

[12] M. H. Boca, M. L. Saylors, D. S. Smith, and P. C. Eklund, Synth. Met. **6**, 39 (1983).

[13] D. M. Hwang and S. A. Solin, Bull. Am. Phys. Soc. **29**, 293 (1984).

[14] G. Timp, M. S. Dresselhaus, L. Salamanca-Riba, A. Erbil, L. W. Hobbs, G. Dresselhaus, P. C. Eklund, and Y. Iye, Phys. Rev. B **26**, 2323 (1982).



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