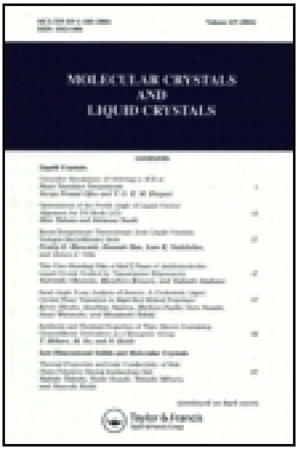

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RAMAN AND ESR MEASUREMENTS IN STAGE-1 $AlCl_3$ GRAPHITE

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Abstract We report Raman and electron spin resonance (ESR) data in stage-1 $AlCl_3$ graphite intercalation compounds (GIC's). The results show that two kind of intercalate species are simultaneously present: Al_2Cl_6 molecules and layers of solid $AlCl_3$.

INTRODUCTION

Although several works have been done on $AlCl_3$ - GIC's, the knowledge about the composition and the in-plane structures of the intercalate layers is still not clear. The structure of solid $AlCl_3$ is similar to those of $FeCl_3$ and $CrCl_3$. All these trichlorides exhibit layer structures with the sequence ...Cl-metal-Cl-Cl-metal-Cl ... , where the chlorine atoms are placed in a close-packing arrangement with different symmetries for each compound. For $AlCl_3$ a distorted cubic close-packing arrangement is found, in which the metal atom occupy two thirds of the octahedral sites between every second layer of chlorine[1]. In the intercalation compounds several works have shown that the chlorine triple-layer structure is conserved for $FeCl_3$ and $CrCl_3$, but it is not clear that this is the case for $AlCl_3$. Behrens et al.[2], using X-ray diffraction, have suggested that $AlCl_3$ - GIC's samples prepared at low Cl_2 pressure (< 17 mbar) and low temperature (< 170 °C), have mainly the solid-like layer structure described above. On the other hand, samples prepared at higher Cl_2 pressure and temperature, consist in an arrangement of Al_2Cl_6 molecules and $AlCl_4^-$ ions.

The purpose of this work is to elucidate the nature of the intercalate layer, using Raman and ESR techniques. The observation of intercalant vibrations in GIC's using non-resonant Raman scattering is very difficult. This is due to the small penetration depth of the incident light on the sample c face and on the other hand, the relative density of intercalant molecules, even for stage 1, is only about 16 mole % or less. Ohana and

Yacoby [3] have shown that it is possible to enhance the Raman intensity of the intercalant species, using polarized light along the **c** axis incident on the **a** face . Under these conditions the light penetrates deeper into the sample (about 10 microns), because direct optical transitions between π bands are forbidden for light polarized parallel to **c** axis. This technique is only successful when the graphite layers are smooth and parallel to each other all the way where the light is focused [3] , and it has been used succesfully only in two cases: stage -1 AsF_5 [3] and stage-2 $SbCl_5$ - GIC's.[4]

EXPERIMENTAL

In order to get a good lateral surface for the Raman measurements, a thin highly oriented pyrolytic graphite (HOPG) sample was first clamped at its two ends an then torn apart by applying a force parallel to the graphite layers. Stage-1 samples were prepared by a two zone intercalation method [5]. The torn sample was placed in the bottleneck of a quartz cell with the **a** face parallel to an optical flat window. Dry Cl_2 was passed over heated aluminum fine powder, forming $AlCl_3$ powder which was deposited on the cooler region of the tube. During the intercalation process the graphite temperature was maintained at about 286 ^{o}C, the $AlCl_3$ at about 235 ^{o}C and the Cl_2 pressure at about 300 torr. For the ESR experiments the intercalant material was prepared as follows; the $Al_{1-x}Cu_x$ ($x \cong 0.1$) alloy was obtained by arc melting the appropriate amounts of each element in argon atmosphere[6]; the alloy was then powdered and the intercalated samples were prepared in the same way and conditions as before. The Cu^{2+}: $AlCl_3$ single crystals were prepared starting from the Cu^{2+}:$AlCl_3$ powder and cooling slowly across the melting point. Good quality hexagonal shaped single crystals were obtained in this way. The Raman spectra was excited using the 514.5 nm argon ion laser line with 50 mW power. The light was focused on the sample **a** face with a cylindrical lens. A back scattering configuration was used, with the incident and scattered beam parallel to the graphite layers. The spectra were obtained using a double monochromator equipped with a thermo-electrically cooled photomultiplier and a photon counting system, interfaced to a PC computer. Since the Raman signal from the intercalants is extremely weak a multi-scan program was used to accumulate the spectra. Noise spikes were eliminated using software. The ESR measurements were carried out in a conventional Varian ESR X-band spectrometer using a 100 KHz room temperature rectangular TE_{102} cavity, adapted for a tail liquid helium dewar.

RESULTS AND DISCUSSION

All the Raman spectra were taken using the scattering configuration described above, with the incident beam polarization parallel and perpendicular to the graphite layers. Using this configuration we looked for the intralayer C-C stretching mode, and found a single E_{2g2} peak at 1635 cm^{-1}, characteristic of pure stage-1 AlCl$_3$- GIC's [5]. The intensity of this peak, for polarized light parallel to the graphite layers ($\mathbf{E} \perp \mathbf{c}$) is about three times stronger than for $\mathbf{E} \parallel \mathbf{c}$ polarization. For $\mathbf{E} \parallel \mathbf{c}$ polarization the graphite mode is forbidden, but due to the high penetration depth of the light and the finite collection angle for the scattered radiation it is still observable.

We show the Raman spectra of the intercalant species in Fig.1. Phonon peaks are observed at 305, 335, 385, 420 and a shoulder at about 171 cm^{-1}. The spectra were recorded with the incident radiation polarized both parallel and perpendicular to the graphite **c** axis, and the Raman peaks are only observed for $\mathbf{E} \parallel \mathbf{c}$ polarization. This result shows that the observed lines come from phonons inside the graphite galleries[3].

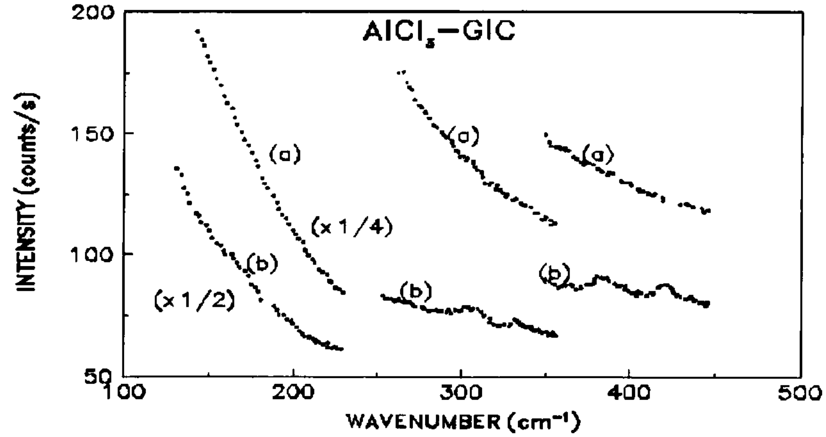

FIGURE 1 Raman spectrum from the **a** face in stage-1 AlCl$_3$ -GIC : a) $\mathbf{E} \perp \mathbf{c}$ and b) $\mathbf{E} \parallel \mathbf{c}$

Single crystals of AlCl$_3$ belong to monoclinic C2/m space group with two molecules in the primitive cell[1], and have accordingly 21 optical phonons distributed as $6A_g + 6B_g + 4A_u + 5B_u$. As we mentioned, only the zz component of the Raman tensor can contribute to the spectra for our scattering configuration , i.e. only A_g modes can be observed inside the graphite galleries. Crystalline $AlCl_3$ has A_g modes at 118, 171, 197, 257, 308 and 391 cm^{-1} [7] . Al_2Cl_6 has D_{2h} molecular symmetry and normal modes of vibration classified as $4A_g + 2B_{1g} + 3B_{2g} + 3B_{3g} + 1A_u + 4B_{1u} + 4B_{2u} + B_{3u}$, with A_g modes observed at 115, 217, 336 and 501 cm^{-1} [8]. On the other hand, $AlCl_4^-$ ions

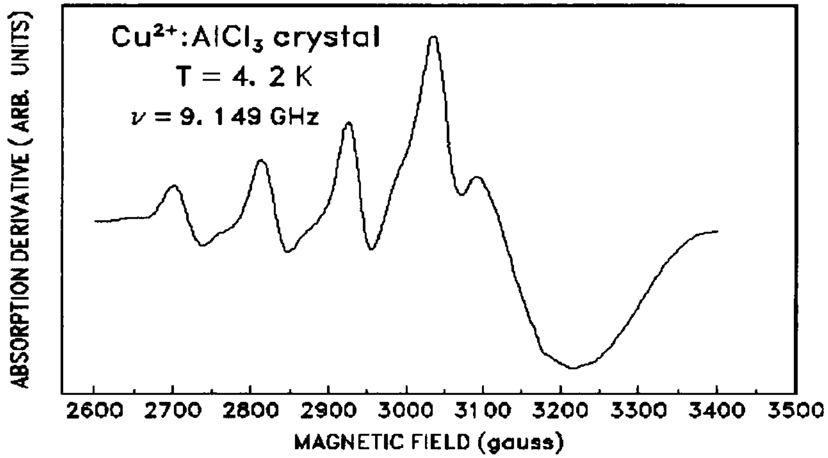

FIGURE 2 ESR spectrum of Cu^{2+} in $AlCl_3$ single crystal.

have tetrahedral symmetry and the nine normal modes are distributed as $1A_1 + 1E + 2F_2$, with the A_1 mode observed at 351 cm^{-1} [9]. A comparison of the observed Raman lines in Fig.1 with the various intercalated species suggested in Ref.2 indicates that the peaks at 171, 305 and 385 cm^{-1} are due to intercalated $AlCl_3$ in a crystalline form. Nevertheless, we failed to observe the line at around 197 cm^{-1}. The 118 cm^{-1} phonon could not be observed probably due to the strong elastic scattering in that region. The peak at 335 cm^{-1} may be associated to the presence of Al_2Cl_6 molecules inside the graphite galleries. The peak at 420 cm^{-1} could not, however, be explained by thhe presence of any of the above species. Nevertheless, this line can be understood if we allows for some distortion of the intercalants, due to the charge transfer between the graphite layers and intercalants. In this case the local C_{2h} and D_{2h} symmetry can be reduced to C_s and C_{2v} for $AlCl_3$ and Al_2Cl_6 respectively. In this case for crystalline

$AlCl_3$ the B_u tensor has zz component in addition to A_g modes, an for molecular Al_2Cl_6 the B_{3u} infrared mode could have zz polarization in addition to the A_{1g} modes. Indeed a B_{3u} mode of Al_2Cl_6 has been observed at 420 cm^{-1} [8], and it could explain the Raman peak at this frequency.

Figure 2 shows the low temperature ESR spectrum of Cu^{2+}: $AlCl_3$ single crystal, for the magnetic field parallel to the tetragonal axis of the distorted chlorine octahedra[1]. For this direction the spectrum shows the maximum hyperfine splitting. The measured ESR parameters are $A_{//}$ = 110 ± 5 gauss and a $g_{//}$ = 2.26 ± 0.01. The broad resonance at g = 2.08 ± 0.02 corresponds to clusters of Cu^{2+} with no hyperfine splitting. Figure 3 shows the low temperature ESR spectrum of Cu^{2+} in $AlCl_3$ stage-1 GIC for the magnetic field along the maximum splitting of the hyperfine lines. The spectrum also shows the conduction electron spin resonance (CESR) of graphite at g = 2.000 ± 0.002 an the Cu^{2+} cluster line at g = 2.06 ± 0.02. It is clear from this spectrum that two sites are observed for the Cu^{2+} ions (labeled A and B in Fig.3).

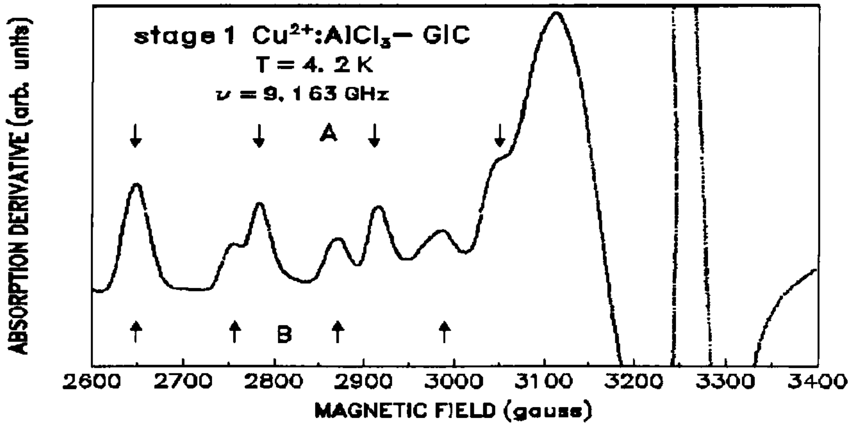

FIGURE 3 ESR spectrum of Cu^{2+} in $AlCl_3$ stage-1 GIC. The arrows indicate the two sites for Cu^{2+} ions (see text).

We found the following ESR parameters for these sites: A = 133 ± 5 , g = 2.28 ± 0.01 for site A and A = 110 ± 5 gauss , g = 2.30 ± 0.01 for site B. The site B, except for a small difference in the g-value, has the same ESR parameters than the one measured for

Cu^{2+} in $AlCl_3$ crystal. Therefore, we identify this site as an intercalation of $AlCl_3$ solid-like layers as discussed in our Raman experiments (see above). The other site (A) , with different hyperfine constant and g-value, should come from another molecular specie, probably Al_2Cl_6 as it was concluded in our Raman experiments.

CONCLUSIONS

In summary we conclude that both Raman and ESR experiments reveal that , under our preparation conditions, the intercalated samples show two coexisting phases: crystalline-like layers of $AlCl_3$ and Al_2Cl_6 molecules.

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