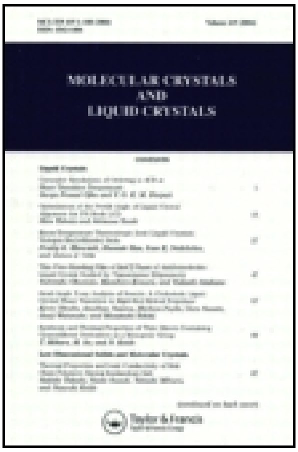

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ANTIFERROMAGNETISM OF IODINE DOPED AlPcF FILM DEPOSITED ON KCl

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Abstract The magnetism of iodine doped fluoro-aluminum phthalocyanine (AlPcF-$I_{0.1}$) film deposited on KCl (100) surface is studied by electron spin resonance (ESR) spectroscopy. An X-ray diffraction study indicates that two distinct phases coexist in the film : In one phase, the AlPcF chains lay parallel to the film plane, and, in the other phase, align perpendicular to the film plane. Both phases exhibit an antiferromagnetic transition at T_c=195±15 K under the pressure of 1 atm, while, at 0 atm, no magnetic transition takes place above 80 K. The g value does not depend on the pressure significantly, indicating that the back charge transfer probability α^2 between $AlPcF^{\ddagger}$ and I_3^- does not have any correlation with T_c.

INTRODUCTION

Antiferromagnetism as well as ferromagnetism is one of the important topics in the study of molecular based materials. We recently found that thin films of fluoro-aluminum[1-3] and fluoro-gallium[4] phthalocyanines (AlPcF and GaPcF) deposited on glass substrates exhibit an interesting antiferromagnetism when doped with electron acceptors : They show a three dimensional antiferromagnetic transition with the maximum transition temperature (T_c) as high as 220 K. Furthermore, the T_c strongly depends on the pressure. For example, in the case of iodine doped AlPcF film, T_c changes from 220 K to 150 K by decreasing the pressure from 1 atm to 0 atm.[3] It has been shown that this pressure dependence originates from a flexible lattice constant in the phthalocyanine crystal.[1]

In the present work, the magnetism of iodine doped AlPcF film deposited on KCl substrate, instead of the glass substrate, is studied by ESR measurement. It is known that AlPcF forms a cofacially-stacked one-dimensional polymer with a $[-Al-F-]_n$ backbone and deposits on the KCl substrate with a different orientation of the polymer axes from that on the glass substrate.[5,6] The purpose of the present study is to elucidate the effect of the different deposition manner on the magnetism.

EXPERIMENTAL

AlPcF was synthesized and purified after a procedure described previously.[3] The purified AlPcF does not have any impurity spins detectable by ESR. Iodine was purchased and was purified by subliming twice at 80°C . KCl single crystal was made by Czochralski method and was annealed at 765°C for 24 hr.

AlPcF film on the KCl (100) surface was prepared by vacuum evaporation in an electric furnace at 390-420°C under the pressure of 10^{-5} Torr. The KCl substrate was heated to 250°C during the evaporation. The film thickness was about 0.5 µm estimated from optical absorption intensity of the film.

Iodine doping was achieved by keeping the AlPcF film with I_2 powder in a vacuum-sealed glass tube at room temperature.[3] Then a part of the doped iodine was evaporated by pumping the film for 5 min. The obtained AlPcF-I_x film is in State II due to the classification used in ref.3, and has a quasi-stationary doping level of $x \sim 0.1$. The film was handled in a glove bag filled with Ar gas.

ESR was measured on a home made X-band apparatus under the pressure of either 0 atm or 1 atm. For the measurement at 0 atm, the sample was sealed into a pumped glass tube, and, for the measurement at 1 atm, the sample tube was connected to a balloon filled with He gas. Details of ESR susceptibility and g-value determinations have been described elsewhere.[3] All the ESR measurements at variable temperature were made by increasing temperature from 77 K.

Cu K_α X-ray diffraction was measured at 1 atm at room temperature on a JEOL DX-GE-E apparatus.

RESULTS AND DISCUSSION

Figure 1 shows an X-ray diffraction pattern of the pristine AlPcF film on KCl substrate. θ denotes the angle between the incident X-ray beam and the film plane. The two peaks at $2\theta=6.9°$ and $24.8°$ are due to the reflections from the AlPcF film and the broad peak at around $2\theta=12°$ from the KCl substrate. The two peaks at $2\theta=6.9°$ and $24.8°$ correspond to the (100) and (001) reflections, respectively, for a tetragonal unit cell of the AlPcF crystal with a=b=12.8 Å and c=3.59 Å.

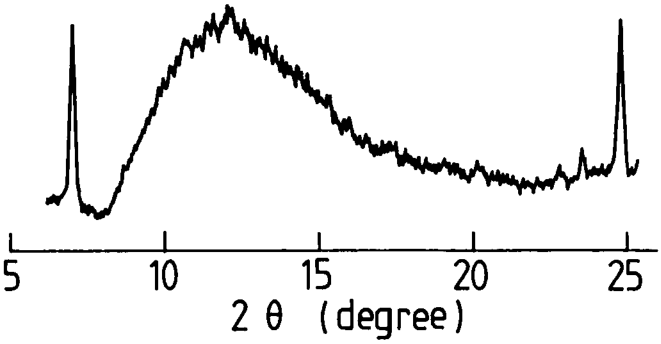

FIGURE 1 Cu-K_α X-ray diffraction pattern of AlPcF film on KCl.

It has been reported that the AlPcF film on glass substrate has only the $2\theta\sim7^\circ$ peak indicating that the polymer chains lay parallel to the glass substrate.[1] The existence of the $2\theta=24.8^\circ$ peak in the present case indicates that a part of the AlPcF polymer chains align perpendicular to the KCl surface. The orientation of the polymer chains is not random, however, because the present diffraction pattern is different from the powder pattern which contains a relatively strong $2\theta\sim15^\circ$ peak[7] coming from the (210) reflection. Thus it is concluded that the AlPcF film on the KCl substrate consists of two distinct phases in which the polymer chains lay parallel (parallel phase) and perpendicular (perpendicular phase) to the film plane.

Figure 2 shows ESR spectra of the AlPcF-$I_{0.1}$ film on the KCl substrate at 0 atm. This ESR signal is attributed to the unpaired spins produced by the charge transfer between the AlPcF and the iodine, because the signal disappears after pumping the film for 15 hr at room temperature to remove the doped iodine. Since the reduced state of the iodine is diamagnetic I_3^- in the present case[3], the detected unpaired spins reside mainly on the AlPcF chains.

It is seen in Figure 2 that the ESR line shape changes depending on the relative angle of the film plane to the static magnetic field H_0. This indicates that the ESR signal has a g anisotropy. It is noted that the present ESR signal is not due to a randomly oriented sample, because the line shape for the randomly oriented sample should not depend on the sample direction relative to H_0.

Each ESR spectrum can be fit by a superposition of two Lorentzian lines as is seen in Figure 2. The *g* value of each of the two Lorentzian components is shown in Figure 3(a) as

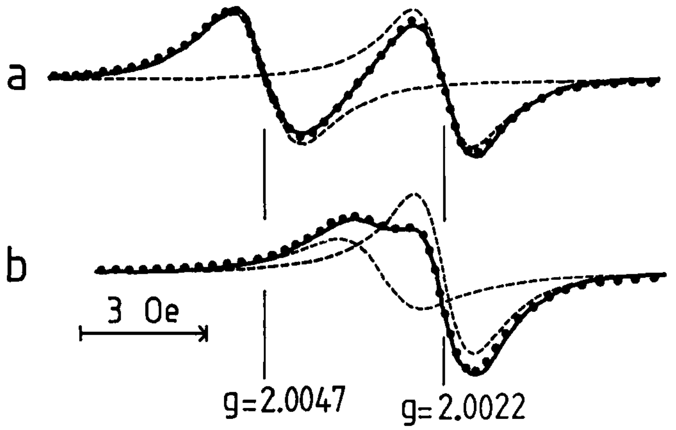

FIGURE 2 ESR spectra of AlPcF-$I_{0.1}$ film on KCl at 0 atm. T=290 K. a : film⊥H_0. b : film//H_0. The dotted curves are calculated ones which are results of two Lorentzian lines' overlap (broken curves).

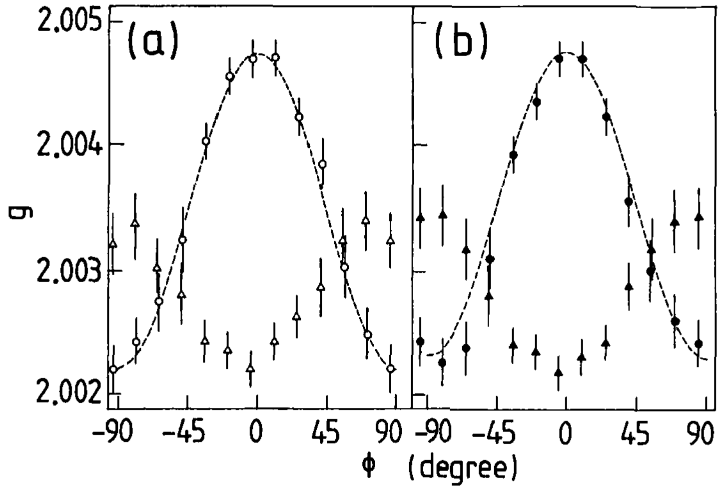

FIGURE 3 Angular dependence of the *g* value of AlPcF-$I_{0.1}$ film on KCl. T=290 K. (a) : at 0 atm. (b) : at 1 atm. △ and ▲ : for parallel phase. ○ and ● for perpendicular phase. The broken curves are theoretical ones calculated from Eq.(1).

a function of the angle ϕ, where ϕ is defined as the angle between H_0 and the vector normal to the film plane, the rotation axis being the [010] direction of the KCl substrate. One of the two components (denoted by ▲ in Figure 3(a)) has the g value and the angular dependence close to those of the previously reported AlPcF-$I_{0.1}$ film on the glass substrate[3] for which the g values were $g(\phi=0^\circ)=2.0022$ and $g(\phi=90^\circ)=2.0036$. This indicates that the component denoted by ▲ in Figure 3(a) originates from the AlPcF chains oriented in the same manner as those in the previous case and is attributed to the parallel phase in which the AlPcF polymer chains lay parallel to and randomly oriented within the film plane. Since the g tensor of the AlPcF-$I_{0.1}$ system is axially symmetric, the relations $g(\phi=0^\circ)=g_\perp$ and $g(\phi=90^\circ)\approx(g_\perp+g_\parallel)/2$ hold for the parallel phase.[3] Using the observed values of $g(\phi=0^\circ)=2.0022$ and $g(\phi=90^\circ)=2.0034$ in Figure 3(a), $g_\parallel\approx2.0046$ and $g_\perp=2.0022$ are obtained.

The other component in Figure 3(a) (denoted by ○) has the g values $g(\phi=0^\circ)\approx2.0048$ and $g(\phi=90^\circ)=2.0022$ which are close to the $g_\parallel$ and the $g_\perp$ values, respectively, estimated above. The angle dependence of the g value is well explained by the relation,

$$g = \sqrt{g_\parallel^2\cos^2\phi + g_\perp^2\sin^2\phi}\,. \tag{1}$$

These results indicates that this component comes from the perpendicular phase in which the AlPcF polymer chains align perpendicular to the film plane.

Thus the ESR result is consistent with the conclusion from the X-ray diffraction study that two phases coexist in the film.

At 1 atm, the similar ESR spectra as those shown in Figure 2 are observed. Each spectrum again consists of two nearly Lorentzian components, and the g value of each component is shown in Figure 3(b). It is seen in Figure 3 that the g value at 1 atm is almost identical with that at 0 atm, and it is concluded that the g value does not depend on the pressure. This is in contrast to the strong pressure dependence of the magnetism which will be presented in the latter part of this section.

The spin susceptibility χ was measured from the ESR signal intensity for each of the two nearly Lorentzian components which correspond to the parallel and the perpendicular phases. The measurement has been done for $\phi=0^\circ$

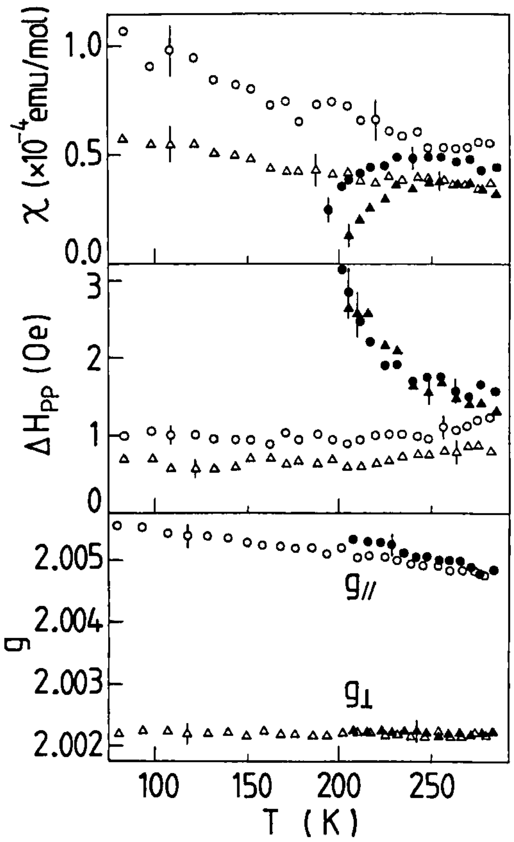

FIGURE 4 ESR susceptibility, peak-to-peak line width and g value of AlPcF-$I_{0.1}$ film on KCl vs. temperature. Film⊥H_0. ▲ : for parallel phase at 1 atm. △ : for parallel phase at 0 atm. ● : for perpendicular phase at 1 atm. ○ : for perpendicular phase at 0 atm.

(or film⊥H_0) because the signals of the two components are well separated in this case as is seen in Figure 2a. Figure 4 shows χ and the peak-to-peak line width ΔH_{pp} vs. temperature for each of the two components under the two pressures at 0 atm and 1 atm. At 1 atm, no ESR signal is observed between 80 and 190 K, and above 190 K the signal similar to the curve a in Figure 2 is observed for both the parallel- and the perpendicular-phase components. As is seen in Figure 4, χ increases steeply as temperature increases from 190 K to 220 K, and at the same time ΔH_{pp} decreases steeply. This indicates that an antiferromagnetic transition takes place at around 200 K.[1] The T_c weakly depends on samples and distributes between

180 and 210 K. At 0 atm, on the other hand, no antiferromagnetic transition takes place above 80 K. This pressure dependence is reversible, i.e. when the sample is kept at 1 atm again, the antiferromagnetic transition takes place at $T_c \approx 200$ K. Comparing with the result for the AlPcF-$I_{0.1}$ film on the glass substrate,[3] the present pressure dependence is even more drastic : In the previous case on the glass substrate the antiferromagnetic transition was observed at both 0 atm and 1 atm with the different transition temperatures of T_c=150 K and 220 K, respectively.

Comparing the magnetisms of the parallel- and the perpendicular-phase components in Figure 4, strong correlation exists between them. The strong correlation has been observed for five independent samples without exception. This indicates that the parallel and the perpendicular phases interact magnetically or mechanically with each other in order to transfer the effect of the pressure applied to the film. The explicit mechanism of the interaction as well as the geometrical arrangement of the two phases is unknown at present.

Figure 4 also shows the g value vs. temperature for film$\perp H_0$. The g value of the parallel-phase component does not depend on temperature, while that of the perpendicular-phase component decreases gradually as temperature increases. As has been discussed in ref.3, the g anisotropy in the AlPcF-$I_{0.1}$ system is due to the back charge transfer between AlPcF† and I_3^-, the latter being the reduced state of the doped iodine.[3] The back charge transfer probability α^2 is defined by,

$$|\Psi\rangle = \sqrt{1-\alpha^2}\,|\mathrm{AlPcF}^{\dagger}\ \mathrm{I}_3^-\rangle + \alpha\,|\mathrm{AlPcF}\quad \mathrm{I}_3\cdot\rangle\ , \tag{2}$$

and the g value of the unpaired spin becomes,[3]

$$g_{\perp} \approx 2\ , \quad g_{/\!/} \approx 2+\alpha^2\cdot[\,g_{/\!/}(\mathrm{I}_3\cdot)\ -2\,]\ , \tag{3}$$

where $g_{/\!/}(I_3\cdot)$ is the $g_{/\!/}$ value of $I_3\cdot$, the exact value of which is unknown but should take a value significantly larger than 2.[3] Since the g value of the parallel-phase component for film$\perp H_0$ is equal to the $g_{\perp}$ value, it should take a constant value near 2, which exactly is observed in Figure 4. The g value of the perpendicular phase for film$\perp H_0$, on the other hand, is equal to the $g_{/\!/}$ value. Assuming that the $g_{/\!/}(I_3\cdot)$ value is temperature independent, the weak temperature dependence of the $g_{/\!/}$ value observed in Figure 4 is ascribed to a weak temperature dependence of α.

Comparing the $g_{\parallel}$ values at 0 atm and at 1 atm in Figure 4, no significant difference is seen between them, in agreement with the result shown in Figure 3. This also agrees with the previous result on the glass substrate.[3] Comparing with the previous $g_{\parallel}$-value measurement, the present measurement is more accurate because of the existence of the perpendicular phase which enables the separate observation of the $g_{\parallel}$ component from the $g_{\perp}$ component, while, in the previous case, the two components overlapped each other. Thus, it has been confirmed by the present unambiguous study that the $g_{\parallel}$ value does not depend on the pressure. Referring Eq.(3), this result indicates that the back charge transfer probability α^2 does not depend on the pressure. Taking the drastic pressure dependence of T_c into account, it is concluded that α^2 does not have any correlation with T_c. This conclusion provides an important information to consider the mechanism of the magnetic interaction in the system as has been discussed in detail in ref.3.

CONCLUSIONS

The AlPcF film on the KCl substrate consists of the parallel and the perpendicular phases. In contrast, the previous AlPcF film on the glass substrate consists of only the parallel phase. The existence of the perpendicular phase permits an accurate observation of the g anisotropy, which leads to a conclusion that the back charge transfer probability between AlPcF^{+} and I_3^- does not have any correlation with the antiferromagnetic transition temperature.

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