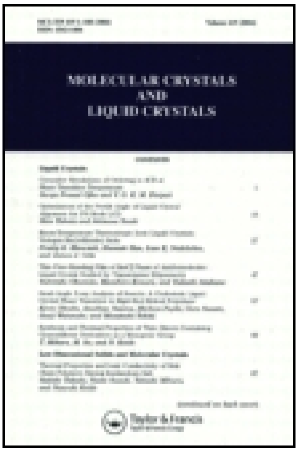

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FERROMAGNETIC RESONANCE IN *p*-NPNN BELOW 1 K

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Abstract The Electron Spin Resonance in ferromagnetic β-*p*-NPNN (T_c = 0.6 K) has been studied for the spherically shaped samples down to 0.4 K. It is shown that the demagnetization effect is particularly important to understand the results both in paramagnetic and ferromagnetic states . The ESR measurements for the shaped samples down to 1 K reveal the completely different g-value temperature dependence from those for the unshaped samples due to the shape demagnetization effect. The resonance line shapes along *a*- and *c*-axes become rapidly asymmetric from 2K and below, indicating the existence of anisotropic relaxation process in the ferromagnetic state. It is shown that the sharp resonance g-shift exists at the ferromagnetic transition temperature in the magneic field along *b*. Such a shift had been unidentified in the early studies due to the aspheric sample shape. These results can be ascribed to the anisotropic susceptibility due to the low dimensionality of the system. The magnetic resonance below 1 K can be understood as the ferromagnetic resonance with the *b*-axis as the easy axis .

INTRODUCTION

The β-phase *p*-NPNN is one of the well known and well studied molecular ferromagnet among others.[1] In spite of the much effort the low temperature spin structure has not yet been established. One of the reasons is its low T_c (0.6K) which makes the study difficult. One of the contradicting results among the researchers has been the direction of the ferromagnetic easy axis. An early ESR result has suggested the a-axis to be the special axis because a large positive g-shift has been observed along this axis.. But a different experiment using μSR technique has suggested the spontaneous magnetization at zero field along the b-axis, and therefore the easy axis to be along the b-axis.[3] As the ESR measurement has been reported only down to 2 K, we started the ESR measurement down to 0.4 K to study the paramagnetic and ferromagnetic resonance.[4] In the course of study, we noticed that the g-shift is in accord with the shape demagnetization effect for the as grown samples (long needle), and reported the preliminary results on this system.

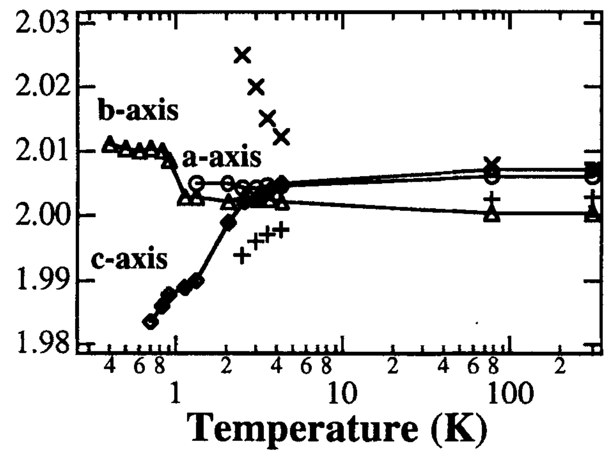


FIGURE 1 The g-value of the paramagnetic resonance above 1 K and ferromagnetic resonance below. The x and + indicate the result of Turek (Ref.2) for a and b axes respectively.

We have shown that the g-shift is actually dependent on the sample shape, and therefore we can intentionally make the g-shift along the a-axis to be negative making a flat shaped sample. Therefore, it is exclusively important to make a completely spherical sample to understand the magnetism of this system. Though the fact is well known from the study of inorganic ferromagnetism, it is fairly a difficult task in organic systems. Firstly it is very difficult to make a big crystal which is twining free, and secondly it easily breaks along the cleavage plane during the shaping process, and lastly it is difficult to keep track the direction of the crystal axis during the experiment because the sample appropriate to study ferromagnetic resonance should be sufficiently small (< 1 mm diameter). In this paper, we show a first report which can be considered free from the demagnetization effect.

EXPERIMENTAL

The as grown *p*-NPNN crystals are mechanically ground to a nearly spherical shape at first. And next, the crystal was shaped using solvent under the microscope. We have obtained several spherical samples with different size. We used 0.7 mm diameter sphere in this study. Though the sphere has a small pit on the surface, it seems that the demagnetization effect is nearly suppressed considering the paramagnetic resonance as is discussed below. The crystal axes are determined using the four-circle X-ray diffractometer of the X-ray Laboratory at Okayama University. The ESR measurement has been performed using home-made reflection-type ESR spectrometer. We can perform ESR measurements approximately down to 0.4 K using a double walled quartz dewar inserted into the TE_{102}

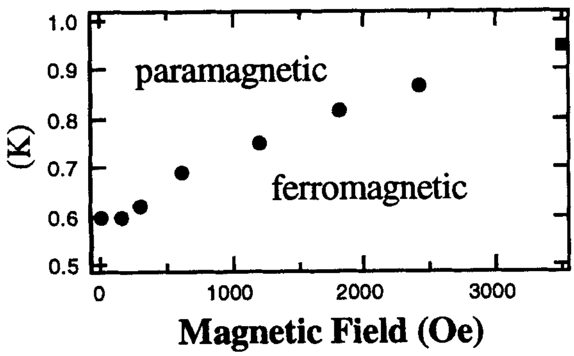


FIGURE 2 The temperatures of the specific heat peaks (dots) in the fields by Nakazawa's data (Ref.1) and the extraporated Tc (square) for the field in the X-band ESR.

mode X-band cavity. Microwave is transmitted through a coaxial cable, therefore the sensitivity of the spectrometer is not so good compared with the commercial one. Samples are directly immersed in liquid ^{3}He below 2K, and the temperature is determined by the vapor pressure (MKS Baratron). The first derivative of the absorption was obtained using the 60 Hz field modulation. The resonance field is determined using a Hall sensor calibrated by the NMR magnetometer. The resonance frequency is determined using the wave-meter, therefore the accuracy of the g-factor is limited to the four orders of magnitude. As the sample is small, the signal to noise ratios at the room temperature and liquid N_2 temperature are not so good.

RESULTS OF PARAMAGNETIC RESONANCE

The ESR results for g-values for the field along the principal axes are shown in Figure 1. The system above 1 K is considered in paramagnetic phase as can be seen from the result of Nakazawa *et al.*[1] (Figure 2). The specific heat shows sharp anomaly at zero field. The system is in the ferromagnetic phase below the temperature at the peak. But the peak becomes broad and shifts to the higher temperatures in the magnetic field. It means that the ferromagnetic short range order increases from the higher temperatures. The paramagnetic resonance result by Turek[2] is also shown in Figure 1. It is seen from the figure that there exist little g-shift for the shaped sample down to 4 K in contrast to the unshaped results. The new and impressive result is the fairly rapid shifts below 4 K along c-axis and the sharp shift below 1 K along the b-axis. We should be careful because the resonance line shape becomes asymmetric along a- and c-axes below 1 K, and it makes difficult to decide the resonance points correctly.

RESULTS OF FERROMAGNETIC RESONANCE

Figure 3 shows the resonance line shapes along *a*-, *b*-, and *c*-axes. In the paper reported earlier, the ferromagnetic resonance was hysteretic for the upward and downward field sweep along the *a*- and *c*-axes[4]. This can be ascribed to the so called 'foldover' effect known in the ferromagnetic resonance[5]. This mainly takes place due to the demagnetization effect in conjunction with the large excitation using a high power micro- wave. The results shown in Figure 3 do not show hysteretic behavior, therefore the effect of the shape demagnetization is also clear in the ferromagnetic state. The reason of the asymmetric resonance line shape is not clear at present. In our experimental condition, the microwave power is rather low. Probably the reason why we observe such effect is due to the anisotropy effect from the low dimensionality of the system as discussed later. As can be seen from the figure, the line shape along the *b*-axis shows normal behavior expected in the ferromagnetic resonance. As discussed earlier, [4] this may be due to the fact that the easy axis is along the *b*-axis. The subsidiary resonance line arises from the magnetostatic modes due to the inhomogeneous excitation of the $k = 0$ modes. It should be noted the line shape along the c-axis is broadened, and clearly shifted from the paramagnetic line.

DISCUSSIONS

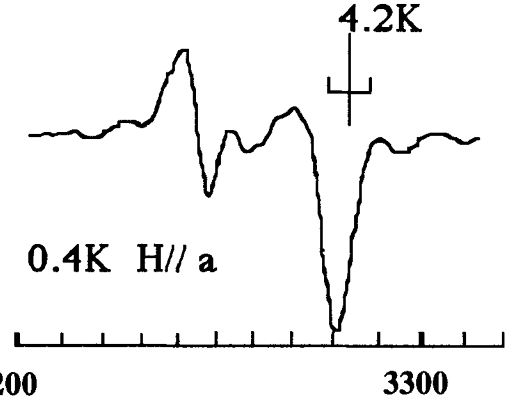
Low Dimensionality

The ESR result of spherically shaped crystal has shown that nearly no g-shift exists along *a*- and *b*-axes, and fairly large negative g-shift along *c*-axis. This means that the spin is contracted along *c*-axis. The shift along *c*-axis starts from the temperature substantially higher than the transition temperature in the magnetic field. The resonance line shape becomes asymmetric in this temperature regime. These results suggest that the susceptibility along the c-direction decreases above the ferromagnetic transition temperature. It is probably due to the low dimensional nature of the system and the effect of short range order in this temperature range. The system is considered to be two-dimensional in the *ab* plane just above the transition temperature. These behaviors are in accord with the behavior of the specific heat which shows the broad maximum in the magnetic field.

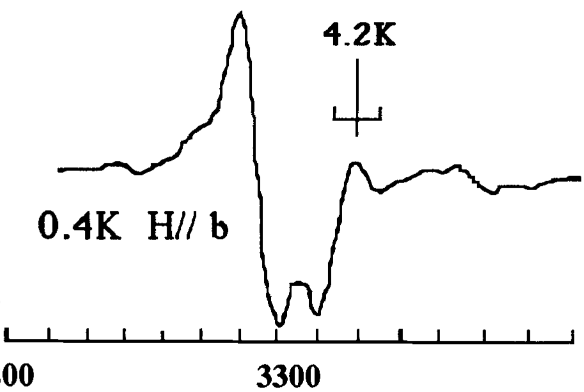
Easy Axis in the Ordered State

The resonance along the *b*-axis shows a clear shift at the temperature corresponding to the peak of the specific heat in the field. The main resonance along the *a*-axis becomes asymmetric and it is difficult to follow the exact resonance point along the *a*-axis. The behavior suggests that the easy saturation of resonance line along *a*-axis and the appearance of the anisotropy field along *b*-axis. The asymmetric line shape along the c-direction also indicates that the spins easily deviates from the field direction due to the resonance. The effect explains the foldover effect for the aspheric samples. The asymmetric line shape is due to the saturation of the resonance line. The normal line shape can be recovered if we place samples at the very low microwave field. Therefore it seems that a very anisotropic relaxation process exists in the ferromagnetic state.

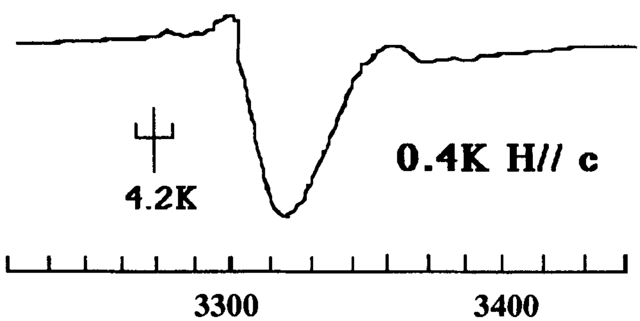
We can conclude that we have observed ferromagnetic resonance in β-p-NPNN system for the first time for the spherically shaped samples. The importance of the shape demagnetization effect indicates unambiguously the ferromagnetic nature of



(a) The resonance line shape along the a-axis at 0.4 K. The main line is totally asymmetric. The paramagnetic resonance point at 4.2 K is indicated with peak to peak width.



(b) The resonance line shape along the b-axis at 0.4 K. The asymmetry is low in this direction. The 4.2 K point is also indicated.



(c) The resonance line shape along the c-axis at 0.4 K. The most anisotropic line shape is obtained and the resonance line broadens along this direction. The 4.2 K point is clearly lower than the ferromagnetic resonance.

FIGURE 3 The Ferromagnetic resonance line shapes along a, b, and c axes.

this system. A fairly clear transition from paramagnetic to ferromagnetic state is observed. The resonance above the transition temperature can be understood as the 2-dimensional behavior. The peculiar line shapes can be understand as the system to be low dimensional spin system, therefore to have anisotropic relaxation. The anisotropy of the resonance clearly indicates that the easy axis is along the *b*-axis This conclusion is supported by the dipolar anisotropy energy. The origin and mechanism of the nonlinear line shape at the low microwave power level should be investigated further.

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