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ON THE ROLE OF CLOSELY PLACED EXCITED STATES IN THE ANOMALOUS BEHAVIOUR OF THE SPIN SYSTEM Fe^{3+} IN GaAs

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The observation of anomalous behaviour of the paramagnetic Fe^{3+} centre in GaAs at low concentration studied by EPR is reported. Two lines of this $S = 5/2$ spin system, belonging to the $M_S = -5/2 \leftrightarrow -3/2$ and $M_S = -3/2 \leftrightarrow -1/2$ transitions, respectively, show anomalously large intensities. Dependencies of spectra versus microwave power and frequency, modulation frequency and phase, concentration of centres and temperature show differences from the ordinary spectra. It is argued that this effect is due to electric-quadrupole and -dipole excitation, which processes are effective additional to the magnetic-dipole excitation mechanism. The contribution of the orbital momentum from closely placed excited states makes this mechanism possible for ions in orbital singlet ground states.

1 Introduction

The well-known electron paramagnetic resonance (EPR) spectrum of Fe^{3+} ions in gallium arsenide has shown anomalous behaviour as observed in a set of GaAs samples at low temperatures, containing small concentrations of iron impurity ($\approx 10^{15}$ cm^{-3}). The anomalous spectrum consisted of two lines corresponding to the transitions $-5/2 \leftrightarrow -3/2$ and $-3/2 \leftrightarrow -1/2$ with $\Delta M_S = 1$. The spectrum showed cubic symmetry of the centres and was satisfactorily described by the spin Hamiltonian for the case of centres in the $^6S_{5/2}$ state

$$\mathcal{H} = g\mu_B \boldsymbol{B}\cdot\boldsymbol{S} + \mathcal{H}_c, \tag{1}$$

where

$$\mathcal{H}_c = (a/6)[S_x{}^4 + S_y{}^4 + S_z{}^4 - (1/5)S(S+1)(3S^2+3S-1)], \tag{2}$$

with $g = 2.046$ and $a = 340\times10^{-4}$ cm^{-1}.

Since the anomalous behaviour of the spectrum could not be explained by magnetic-dipole transitions we will give the suggestion about excitation of the spectrum by the electrical component of the microwave field in the cavity. An important argument in favour of the suggestion appears to be the fact that the intensity of the signal was reduced only to one half when shifting the sample away from the centre of the cylindrical cavity to half of the radius. The electric field in this position has a maximum value and the magnetic field is negligibly small; transitions are caused by the electrical component of the microwave field. In the centre of the cavity the electrical effect can be comparable to the displaced position for samples with a large value of the dielectric constant ϵ_r, because the electric field of the microwaves in the centre of the cavity has preferentially a tangential component but for a sample displaced from the centre a normal component, which is reduced ϵ_r times in comparison with the tangential component inside the sample. This follows from the boundary conditions for the components of the electric field. In case when the paramagnetic centre has electric-dipole or multipole-moment transitions caused by the electric component of the electromagnetic wave it must be observed even when the sample with large value of ϵ_r (e.g., $\epsilon_r = 10.9$ for GaAs) is placed in the centre of the EPR resonator.

In the crystal-field approximation for impurities in ^{6}S states electrical effects must be weakly observable in the ground state because it has only small contributions of orbital moment from higher-lying excited states ^{4}G, ^{4}F, ^{4}D and ^{4}P. The contribution of the orbital moment in the ground state is estimated by the fine-structure parameter a and the departure of the g factor from its free-electron value. According to calculations done in the crystal-field approximation when taking into account ^{4}G, ^{4}F, ^{4}D and ^{4}P states [1,2] above the ground state, and also spin-orbit and electrostatic interactions, $a = 0.2\times10^{-4}$ cm^{-1} for Fe^{3+} which is substantially below the value obtained experimentally. Calculations of the g factor in the framework of this model [3,4] also give a smaller departure from $g = 2.0023$ compared to $g = 2.046$ for Fe^{3+} in GaAs. Since the fine-structure parameters and the effect observed by us require a substantially larger contribution of the orbitally degenerated ground state, we assume that the behaviour of the Fe^{3+}-spin system described here has the same nature and that more closely placed orbitally degenerated excited states must be involved in the considerations. In the present work the main experimental results are given, in which the anomalous excitation spectrum is displayed, and also a possible explanation is given.

2 Experimental Results

EPR spectra were studied on X- and K-band spectrometers with cylindrical TE_{011} resonators, tuned to observe the dispersion signal. Investigations were done on six semi-insulating (LEC) gallium arsenide samples prepared under different conditions. In the samples 1, 4, 5 and 6, iron was introduced by diffusion at 650 °C (24 hours), 750 °C (24 hours), 860 °C (18 hours) and 1100 °C (42 hours), respectively. Samples 2 and 3 were not doped with iron, but sample 3 was subjected to thermal treatment at 1180 °C for 2 hours. The concentration of iron was increasing from sample 1 to sample 6: $N_{Fe} \approx 10^{17}$ cm^{-3} for sample 6, $\approx 10^{15}$ cm^{-3} for sample 5, $<10^{13}$ cm^{-3} for samples 1, 2, 3 and 4.

EPR spectra consisting of only two lines were observed for the samples 2 and 3. In sample 1, probably due to a low concentration of centres, a spectrum was not discovered. For the samples 4 and 5 the spectra consisted of five lines but the intensity

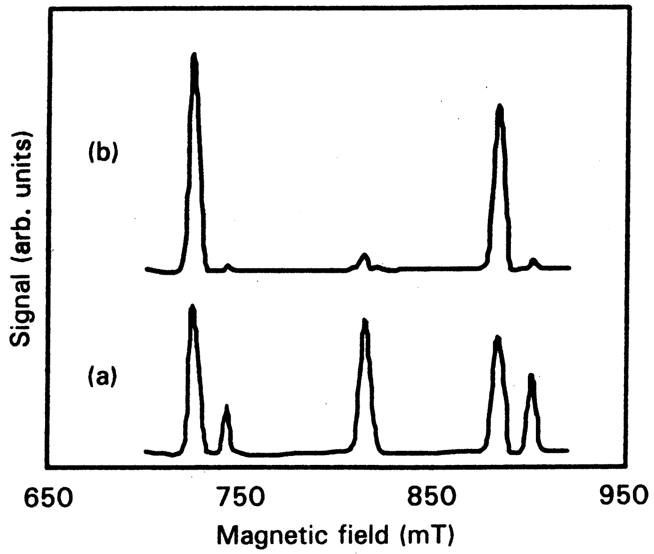

Figure 1: EPR spectrum for sample 6 (a) and 5 (b); $T = 4.2$ K, $\boldsymbol{B} \parallel [100]$, $\nu = 23.285$ GHz, power attenuation 20 dB. The intensity for sample 5 is multiplied by a factor 5.

of two of them was substantially higher than that of the others. The anomalous effect was not demonstrated by sample 6. Spectra as observed for the samples 5 and 6 are depicted in figure 1. From the angular dependence of the positions of the lines in the EPR spectrum, shown in figure 2, it is seen that the lines follow the well-known pattern of the Fe^{3+} in GaAs, with S=5/2; the lines with anomalous intensity are identified as the $-5/2 \leftrightarrow -3/2$ and $-3/2 \leftrightarrow -1/2$ transitions. The dependence of the intensity of the lines in the spectrum on the power of the microwave field in the cavity was investigated. The dependence for sample 5 is shown in figure 3. As is seen for the transitions $-5/2 \leftrightarrow -3/2$ and $-3/2 \leftrightarrow -1/2$ it is linear (at low power, i.e., below saturation) and for the other transitions the intensities are proportional to the square root of the power. For the samples 2 and 3 the intensities of the two observable transitions also depend linearly on microwave power. The angular dependence of the intensities of the lines for the transitions with anomalous behaviour in the EPR spectrum differed considerably from the dependence for the case of magnetic-dipole transitions [5]. Recording of spectra at different temperatures has shown that the lines corresponding to excitation by the E-wave reduces in intensity faster than the lines corresponding to the usual transitions in the interval of temperatures from 4.2 to 10 K.

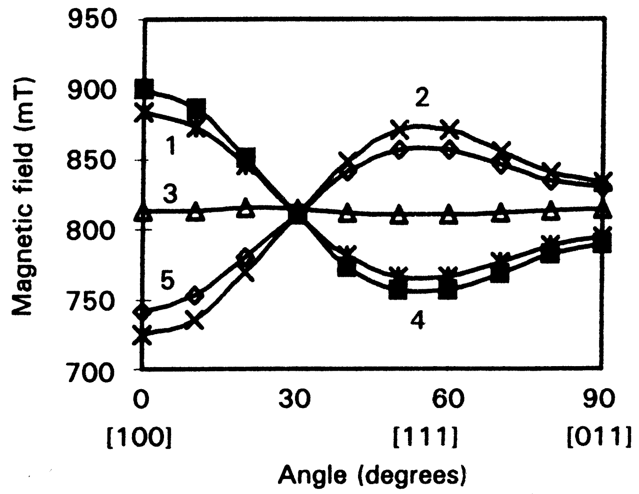

Figure 2: Angular dependence of the EPR spectra in samples 2, 4, 5 and 6. Curve 1: $M_s = -5/2 \leftrightarrow -3/2$; 2: $M_s = -3/2 \leftrightarrow -1/2$; 3: $M_s = -1/2 \leftrightarrow +1/2$; 4: $M_s = +1/2 \leftrightarrow +3/2$; 5: $M_s = +3/2 \leftrightarrow +5/2$.

3 Discussion of Results

The excitation of spectra by the electrical component of the wave in the EPR experiment is known for centres in Si [6] and in GaAs [7]. For all centres studied in mentioned works only electric-dipole transitions were considered for which the perturbation Hamiltonian was given by

$$\mathcal{H}_p = E_1[b\mu_B(J_xB_z+J_zB_x)+c(J_xJ_z+J_zJ_x)], \tag{3}$$

where x, y, and z are the cubic axes and E_1 is parallel to the y axis. The linear dependence of the signal on power, as observed in our case, cannot be satisfactorily described by magnetic-dipole or electric-dipole transitions and requires terms quadratically on the field in the perturbation spin Hamiltonian. Thus, it is suggested to assume that electrical quadrupole perturbation of the spin system in addition to the dipole mechanisms, is the reason for the observed transition spectrum of the Fe^{3+} in GaAs at low concentrations of iron. The Hamiltonian of the perturbation can in this case be written in the form

$$\mathcal{H}_p = E_1^2[b'\mu_B(J_xB_z+J_zB_x)+c'(J_xJ_z+J_zJ_x)], \tag{4}$$

where the coefficients b, c, b' and c' depend on the admixture of orbital momentum in the ground state and are substantially bigger for centres with orbitally degenerated ground state, as was observed for the dipole mechanism in Ref. 6.

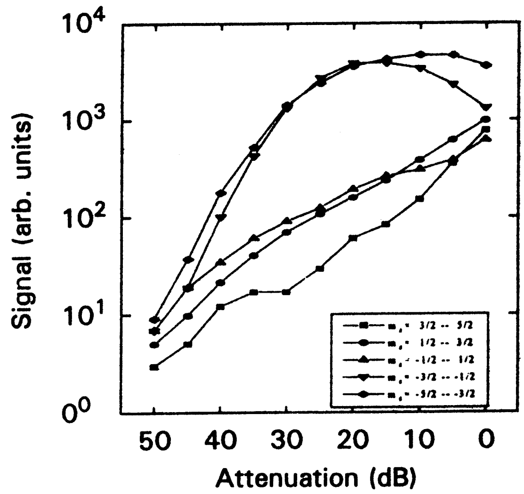

Figure 3: Dependence of the dispersion signal intensity of sample 5 on microwave power; $T = 4.2$ K, $B \parallel [100]$, $f_m = 183.3$ Hz. Sample placed in centre of resonator.

As was already mentioned above, the ^4P state which is closest to the ground state, connected with it by spin-orbit interaction and separated by about 1 eV from the ground state can give only negligible contribution to the parameters b, c and b', c'. Admixture of momentum from ligands in case when the central atom is in singlet orbital ground state is also not big [8]. If one uses experimentally found parameters a and g for Fe^{3+} in GaAs and tries to estimate the value of energy of the excited state with respect to the ground state, using the scheme of calculation [1,2] that would satisfy the experimental parameters a and g, the energy would be reduced to the value 0.1 eV. This value is substantially lower than the energy of the ^4P state above the ^6S ground state.

Therefore, one can assume that admixture of orbital momentum in the ground state ^6S of the Fe^{3+} ion in GaAs must come from excited states that are situated at closer energetical distance from the ground state and connected with it by spin-orbit interaction. Such additional excited states one can interprete as the state of a bound hole excited from 3d shell. Those excitations were observed in Calorimetric Absorption Spectroscopy (CAS) [9] and interpreted as bound excitons at the isoelectronic Fe^{3+} ion (Fe^{3+},X) and bound hole to a negatively charged Fe^{2+} centre (Fe^{2+}, e^+), and also observed by EPR [10] as a thermal excitation of the Fe^{3+} system with energy much smaller than the ionization energy. In both cases the excited states have an orbital degeneracy and may give a contribution of orbital momentum in the ground state.

The excited and ground states in this case correspond to configurations ($3d^6$+h) and $3d^5$ and sets of quantum numbers J=5/2, S=3/2, L=1 and J=5/2, S=5/2, L=0, respectively. The operator of the spin-orbit interaction will have matrix elements between these states which are different from zero, therefore the contribution of orbital momentum from them will be substantially higher than from the ^{4}P state. The wave function of the ground state can in this case be presented as

$$|J,M_J\rangle=|G,M_s\rangle+c^0|0,M_s'\rangle+c^1|1,M_s'-1\rangle+c^{-1}|-1,M_s'+1\rangle, \qquad (5)$$

where J=5/2 and M_J=M_L+M_S=5/2, 3/2, 1/2. $|G,M_s\rangle$ corresponds to the ground state, and the remaining terms correspond to an excited state; the coefficients c^0, c^1, and c^{-1} have the following values:

$$c^0 = 0, \qquad (6a)$$

$$c^1 = (1/2)\sqrt{2}\lambda[S(S+1)-M_S'(M_S'-1)]^{1/2}/[W(0,M_S')-W(1,M_S'-1)], \qquad (6b)$$

$$c^{-1} = (1/2)\sqrt{2}\lambda[S(S+1)-M_S'(M_S'+1)]^{1/2}/[W(0,M_S')-W(-1,M_S'+1)]. \qquad (6c)$$

From these expressions it follows, in particular, that the probability of ΔM=1 transitions is proportional to $\lambda^2/(\Delta W)^2$ and is higher than the probability of ΔM=2 transitions which are proportional to $\lambda^4/(\Delta W)^4$, in agreement with experimental observations.

Consequently, the anomalous behaviour of the EPR spectrum of the Fe^{3+} in GaAs can be connected with electric-quadrupole excitation of the spectrum which occurs in addition to the electric-dipole and magnetic-dipole excitation mechanisms. The contribution of the orbital momentum from the closely placed excited states makes this mechanism possible for ions in orbital singlet ground states. At the same time, it will give the explanation for the values of the g factor and the zero-field splitting constant a.

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