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Electron spin resonance of FeVO$_4$

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We report on electron spin resonance (ESR) investigations of a FeVO$_4$ single crystal. Temperature and angular dependences of ESR resonance positions were measured and calculated in temperature range of 35 – 100 K. The spectra show rich angular dependences of the linewidth, the shape and the resonance field. They consist of a single broad line with asymmetric distortion. Due to the low symmetry of the crystal lattice this distortion can be explained by taking into account the influence of non diagonal dynamic susceptibility.

Keywords: *electron spin resonance; X-band, FeVO$_4$; single crystal; susceptibility*

1. Introduction

FeVO$_4$ is a low symmetry magnetic system undergoing antiferromagnetic phase transition at T$_N$ = 20 K. The crystal structure is triclinic with space group P$\bar{1}$, with lattice parameters a = 0.6719 nm, b = 0.8060 nm, c = 0.9254 nm, α = 96.65°, β = 106.57°, γ = 101.60° [1]. It has also high-pressure metastable phases FeVO$_4$–II, crystallizing in orthorhombic *Cmcm* system, FeVO$_4$–III, crystallizing in orthorhombic *Pbcn* system and FeVO$_4$–IV, crystallizing in monoclinic wolframite *P2/C* system [2]. The FeVO$_4$ structure consists of double bent chains of six edges surrounding six iron atoms. Two of the three independent polyhedra are distorted FeO$_6$ octahedra and the other is a distorted FeO$_5$ trigonal bipiramid. It contains also three VO$_4$ tetrahedra.

FeVO$_4$ shows catalytic behavior [3, 4], moreover, it may be an excellent lithium insertion host applied for positive electrode materials of lithium batteries [5]. ESR properties resulting from the ESR linewidth of the ESR spectrum of FeVO$_4$ were analyzed in [6, 7]. They were analyzed in a temperature range of 77 – 650 K [6] and in a

range of 20 – 200 K [7], using powdered samples of cylindrical shape.

In the paper we analyze all possible temperature dependences of the ESR lines measured for FeVO$_4$ single crystal in a temperature range of 35 – 100 K. Moreover, angular dependencies are analyzed for all crystallographic planes at low (27 K, 35 K) and higher (300 K) temperatures. The study of the magnetic properties can help to understand the catalytic mechanism.

2. Experimental

Single crystals of FeVO$_4$ were grown in the Institute of Physics, Szczecin University of Technology, by a standard melt method described previously in [1]. A mixture of high-purity reagents of Fe$_2$O$_3$ (4N) and V$_2$O$_5$ (4N) in molar ratio 1:2 was packed into a platinum crucible and then the crucible was put into a homemade electric furnace with an adjustable temperature gradient. The furnace was heated up to 975 °C and kept at the temperature for 6 h to ensure that the solution melted completely and homogeneously. Next, the furnace was cooled slowly down to 650 °C at a rate of 8 °C/h while keeping at a constant temperature several times, and then cooled down to room temperature at a rate of about 100 °C/h.

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V_2O_5 excess was removed from the crucible rinsing up the crystals with hot nitric acid. With this procedure, dark red crystals were obtained by mechanical separation from the crucible. The obtained crystals were investigated by X-ray powder diffraction technique. It was found that all peaks in the XRD pattern can be indexed with the triclinic system and identified to diffraction peaks from $FeVO_4$ (Ref: ICSD Code 10329). No impurity phases were detected.

The obtained crystals were oriented using X-ray diffractometer. The maximum size of the investigated samples was as large as $2 \times 1.5 \times 1$ mm.

ESR spectra were recorded using Bruker E 500 X-band spectrometer ($\nu \sim 9.43$ GHz) with 100 kHz field modulation equipped with Oxford flow cryostat for measurements at temperatures from 300 K down to 4 K. Due to triclinic symmetry of the crystal, angular measurements were performed at orthogonal system axes a, b_1, c^*, where b_1 lies in ab plane and is orthogonal to the a axis.

3. Results and discussion

ESR spectra of the investigated $FeVO_4$ single crystal for several temperatures, from 35 to 100 K, are presented in Fig. 1. As one can see mainly single broad asymmetric lines are observed, consistent with high Fe^{3+} ions concentration and the concomitant dipole-dipole and exchange interactions causing exchange narrowing of the dipolar broadened ESR line. The shape of each line is very well established from Eq. (1). At the Neel temperature, ~ 20 K, the resonance line strongly broadens and disappears due to opening of the antiferromagnetic excitation gap.

Walczak et al. [6] have found the same features of EPR lines registered for powdered $FeVO_4$ samples. They have observed departure of the lines from Lorentzian shape at lower temperatures. The asymmetry of the lines they assigned to two nonequivalent positions occupied by iron ions in the crystal structure of $FeVO_4$.

In Fig. 2 we present ESR magnetic susceptibility, χ, calculated as double integral of the measured ESR signal (a), product of the double inte-
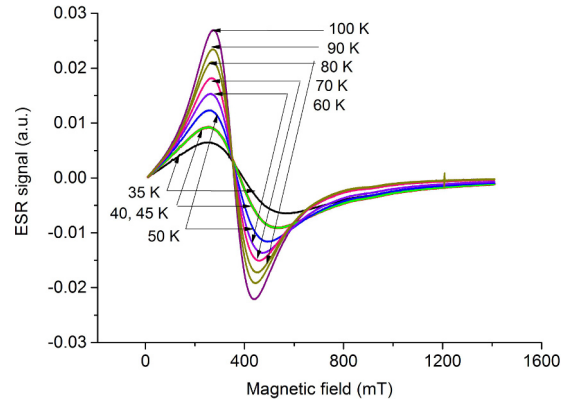

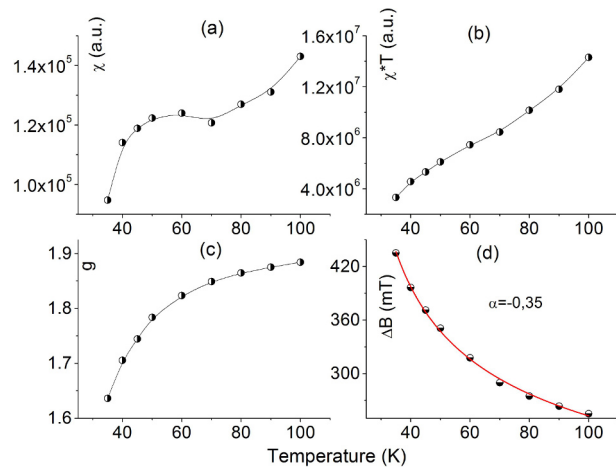Fig. 1. ESR signal for several temperatures from 35 K to 100 K.

Fig. 2. Temperature dependences of the integral intensity (a), product of the intensity and a temperature (b), g-factor (c) and the ESR linewidth; solid line (d).

gral and a temperature, χ^*T, being usually proportional to a square root of magnetic moment (b), g-factor (c), and the linewidth, ΔB, of the ESR lines (d), versus temperature. As one can see from the figure, magnetic susceptibility versus temperature shows nonmonotonic increase, varying in two regions: 35 – 70 K and 70 – 100 K (a), with a broad maximum at about 60 K. It well agrees with magnetic susceptibility measurements [8] only in the range of 35 – 70 K. The discrepancy between ESR and magnetic susceptibility dependence observed for temperatures higher than 70 K may result from the difference in the methodology of both experi-

ments. In case of ESR measurements only a part of total Fe ions could be detected. Such shape of the ESR and magnetic susceptibility in the temperature range of 35 – 70 K, suggests predominance of one-dimensional antiferromagnetic interactions in the Fe–O chains running along c axis, very similarly as in a case of $FeVO_4$–II polymorph [8]. Magnetic interactions in this crystal, analyzed in the temperature range of 35 – 100 K, reveal mainly antiferromagnetic like behavior, what could be deduced from the slope of the χ*T product (b).

Spectroscopic g-factor versus temperature dependence suggests the presence of internal magnetic fields in the crystal. It monotonically increases from g $\sim$ 1.65 for 35 K to g $\sim$ 1.9 for 100 K. The g-factor, measured for powdered samples by Walczak et al. [6] in a temperature range of 77 – 650 K, was constant versus temperature and equal to 1.970(1). It differs significantly from the values recorded for a single crystal sample at low temperatures, where we observed an influence of some internal magnetic fields, and, only slightly from the values obtained at higher temperatures.

Only temperature dependence of the linewidth is more clear (d), which exponentially decreases with increasing temperature, indicating the shortening of the lattice relaxation time. The value of the ESR linewidth is extremely large, changing from 435 mT at 35 K to 255 mT at 100 K. At a low temperature, T $<$ 50 K, where the exchange coupling between the Fe^{3+} ions became stronger, the spin-spin relaxation time decreases with the decrease of temperature and hence, a sudden increase of the linewidth is observed. It is indicative for an onset of a magnetic ordering which yields strong internal fields and therefore inhomogeneous line broadening effects. Walczak et al. [6] have reported that ESR linewidth measured for powder sample is well described by Huber's theory [9]. As one can see from Fig. 2d the ESR linewidth recorded for a single crystal behaves similarly. The critical exponent $\alpha = -0.35$ for a single crystal, and $\alpha = -0.33$ for a powder sample [6]. The latter agrees very well with the one predicted for the sample by Kawasaki theory [10]. The theory assumes that the dominant spin-spin interaction is of Heisenberg type and that

the dipole-dipole interaction is the only source of anisotropy which can be treated as a small perturbation. So, they concluded that both Huber and Kawasaki theories enough good describe magnetic properties of $FeVO_4$.

Bojanowski et al. [7] have found that the ESR linewidth reveals some deviation between 200 K and 42 K, described by the model of Dorman and Jaccarino [11]. It suggests that in this temperature range the ratio of dipolar to exchange energy changes continuously. Below 42 K the ESR linewidth manifests the critical behavior more intensively.

Taking the above into account one can conclude that the origin of the lines is not clear and needs further investigations. From Moessbauer data [1] we can expect that the main line is due to Fe^{3+} ions. We fitted the ESR signal according to the following equation [12]:

$$\frac{d}{dH}P_{abs} \approx \frac{d}{dH}\left(\frac{\Delta H + b(H - H_{res})}{(H - H_{res})^2 + \Delta H^2} + \frac{\Delta H + b(H + H_{res})}{(H + H_{res})^2 + \Delta H^2}\right) \quad (1)$$

where H is the applied magnetic field, b describes the asymmetry of ESR line. Such asymmetric lines shapes are usually observed in metals, because of skin effect [12]. A second reason for the asymmetry arises from the influence of non diagonal elements of the dynamic susceptibility, which are characteristic of low symmetry magnets [13, 14]. Due to the large linewidth we took into account both circular components of the line at $+H$ and $-H$, respectively.

Fig. 3, 4 and 5 show the full angular dependence of the linewidth, resonance field and b parameter, respectively, for two temperatures: 300 K and 27 K (35 K).

When the magnetic field rotates in (b_1c^*) plane the sine angular dependence of $\Delta H(\theta)$ is observed. When the magnetic field rotates around the *a* axis, the angular dependence of $\Delta H(\theta)$ can be described as $A + B(1 + \cos^2\theta)$.

Similar angular dependence as ΔH has b parameter. It suggests that there is a strong correlation between asymmetry of the line and the width. Neg-
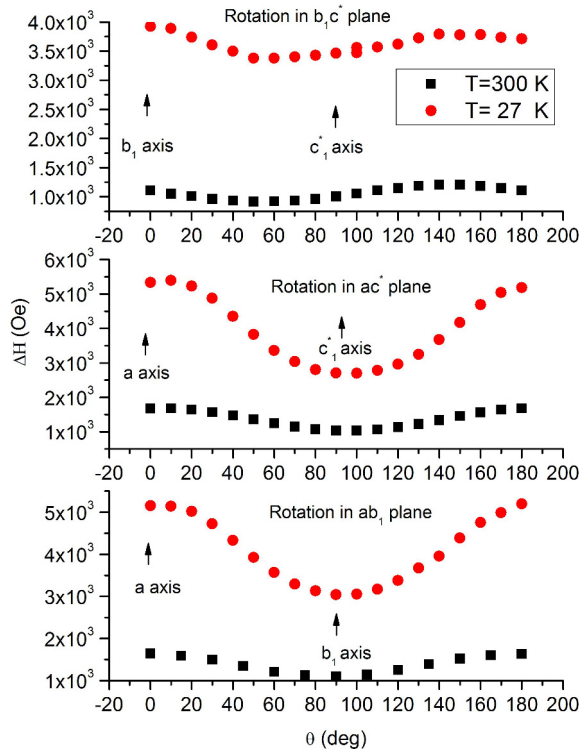
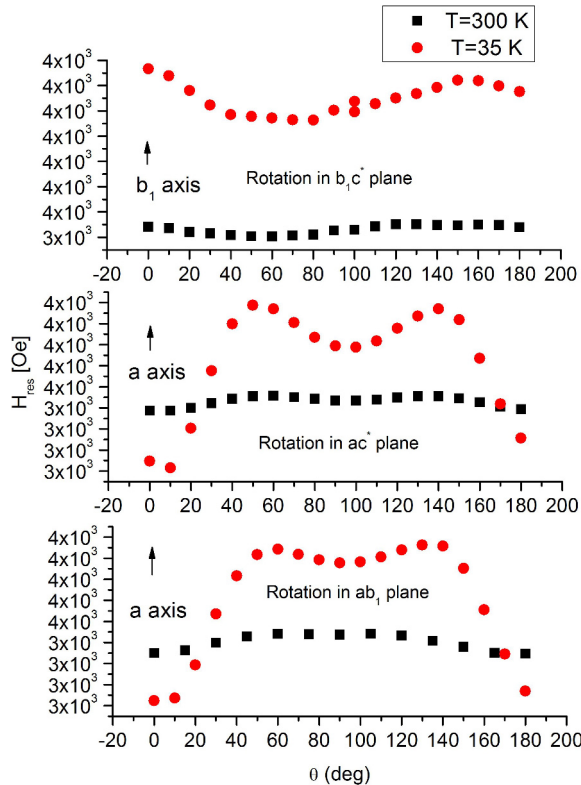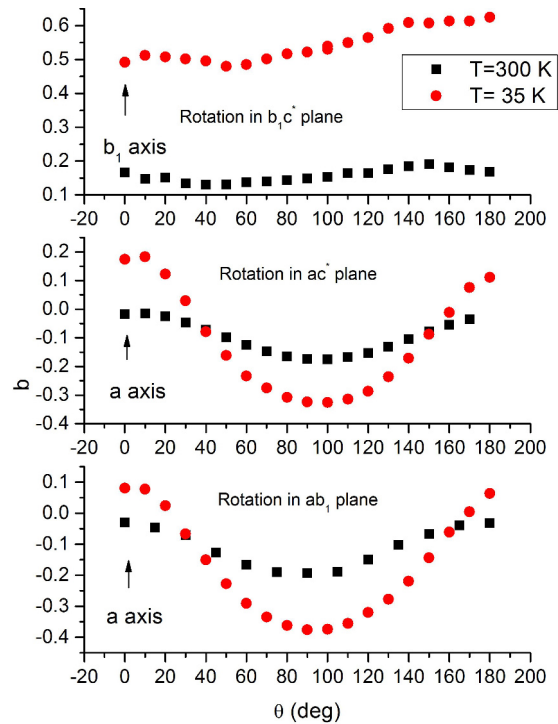Fig. 3. Angular dependence of the linewidth.

Fig. 4. Angular dependence of the resonance field.

ative values of this parameter at some orientations cannot be understood in terms of the skin effect. Hence, the asymmetry has to be ascribed to the influence of non diagonal elements of the dynamic susceptibility.

The anisotropy of the resonance field exhibits angular dependence being different than previously observed for e.g. ΔH. When the magnetic field rotates around the a axis the angular dependence $H_{res}(\theta)$ has a characteristic M shape which was previously reported for La$_{1-x}$Sr$_x$MnO$_3$ compound by Deisenhofer et al. [15]. The shape seems to be an artificial effect connected with not so well defined baseline due to the large linewidth.

Fig. 5. Angular dependence of the ratio absorption/dispersion (parameter b in Eq. 1).

4. Conclusions

ESR spectrum of the investigated FeVO$_4$ single crystal contains mainly single broad asymmetric lines. The asymmetry of the main line appears to be due to non diagonal elements of the dynamic susceptibility. The behavior of the ΔH and b pa-

rameter observed in the angular dependences, being very similar to each other, suggest that there is a strong correlation between asymmetry of the line and the width. In case of resonance field, however, when the magnetic field rotates around the *a* axis the angular dependence $H_{res}(\theta)$ has a characteristic M shape, which was previously reported in [15].

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