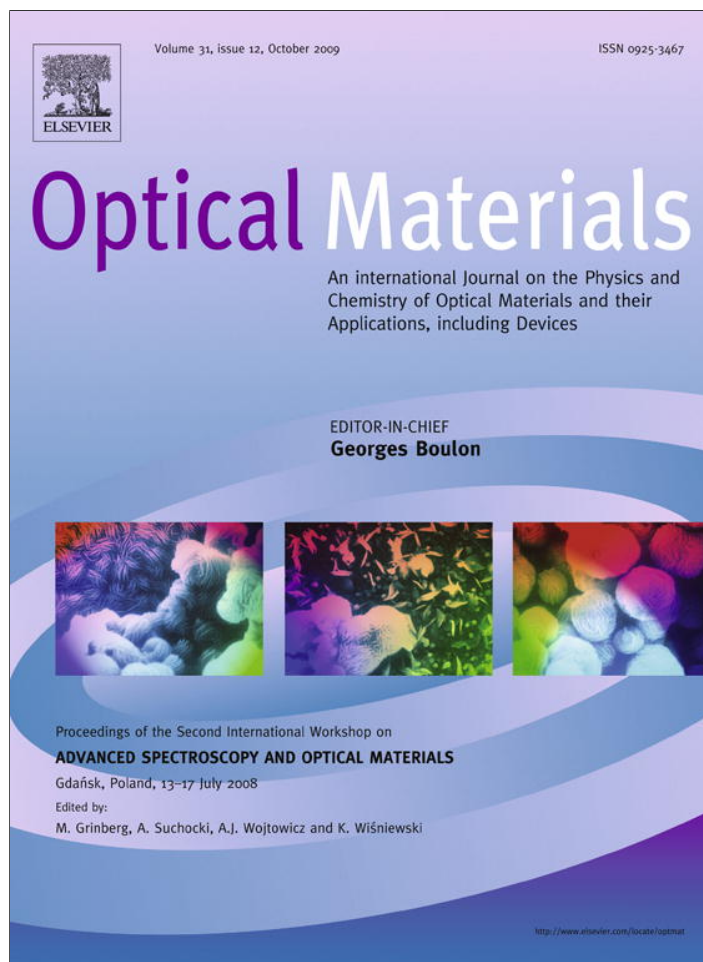


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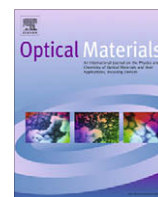


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EPR and vibrational studies of $\text{YVO}_4:\text{Tm}^{3+}$, Yb^{3+} single crystal

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ABSTRACT

A well oriented YVO_4 single crystal, with 5% Yb^{3+} and 2% Tm^{3+} nominal doping, was investigated using the Raman and EPR techniques.

The EPR measurements suggest that Yb^{3+} ions occupy eight-coordinated Y^{3+} sites forming bisdisphenoids of the D_{2d} symmetry. An inhomogeneous distribution of rare-earth ions leads to a significant distortion of the local point symmetry (C_1). It seems that strong dipole–dipole interactions between Yb^{3+} ions are responsible for the distortion. As a result, two types of ytterbium magnetic centers appear. They correspond to paired magnetic centers and distorted isolated paramagnetic centers that are strongly sensitive to the magnetic field directions and some imperfections of the crystal. Pair centers can be recorded through the rotation around the c -crystal axis, whereas isolated centers can be measured when the crystal is rotated around the a -crystal axis. With the increasing temperature, the ytterbium signal disappeared at about 23 K and a group of narrow lines became visible. These lines, observed in the range of 240–550 mT, correspond to the Gd^{3+} ($S = 7/2$) ions, doped to the structure unintentionally from the basic materials.

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1. Introduction

Yttrium, ytterbium and thulium vanadates are iso-structural and crystallize in the tetragonal space group D_{4h}^{19} ($I4_1/amd$). A quite simple crystal structure allows for only one substitution site for rare earth (RE) ions at the Y^{3+} of D_{2d} point symmetry. Since the first preparation of YVO_4 [1,2], extensive studies have been devoted to the growth of single crystals and variation of the optical properties in correlation with various crystal synthesis processes, dopants and co-dopants. Crystal field calculations and electron paramagnetic resonance (EPR) studies have been performed on zircon-type materials Nd:YMO ($M = \text{V, As, P}$) by Guillot-Noel et al. [3,4]. It has been found that Nd^{3+} ions in these three hosts exhibit a multisite character, as evidenced in the absorption and emission spectra. Both optical and EPR spectroscopy measurements have revealed that Nd–Nd exchange and dipolar interactions occur in the zircon family, even at a very low doping content. Nd–Nd pairs at the distances of 3.9, 5.9 and 6.3 Å have been identified. Nd^{3+} ions have been found to be inhomogeneously distributed in the tetragonal D_{2d} symmetry sites as isolated ions, “shallow clusters” and pairs. These authors have also identified a third type of Nd^{3+} ions that correspond to the sites of the D_2 or C_{2v} point symmetry [4,5].

The proportions of different local environments have proved to be dependent on the total neodymium concentration.

Jabłoński et al. [6] have revealed that Gd^{3+} and V^{4+} ions are present in YVO_4 crystals. The existence of Gd^{3+} is due to unintentional doping while V^{4+} can be connected with oxygen vacancies which are formed during growth in the nitrogen atmosphere. The concentration of V^{4+} ions is very low, even lower than that of Gd^{3+} .

The purpose of the present work was to observe and analyze the multisite and multi-ion character in the YVO_4 doped with Yb^{3+} and co-doped with Tm^{3+} by an EPR analysis in correlation with the optical studies. EPR measurements were performed in order to obtain structural information on the inhomogeneous behavior of the YVO_4 matrix. This inhomogeneous multisite character could refer to a site distortion by neighboring defects and to an inhomogeneous distribution of ytterbium, leading to the existence of pairs and a low symmetry isolated Yb^{3+} ions.

2. Experimental

A $\text{YVO}_4:\text{Yb}^{3+},\text{Tm}^{3+}$ (5 mol.%, 2 mol.%) single crystal was grown by the Czochralski method, oriented using the X-ray technique, cut and polished.

The polarized Raman spectra were measured at room temperature with a Bruker FT 100/S spectrometer and the YAG:Nd laser excitation. The $x(\text{zz})-x$, $x(\text{yy})-x$, $z(\text{xy})-z$ and $x(\text{yz})-x$ spectra were measured with a resolution of 2 cm^{-1} .

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The EPR spectra were recorded using a Bruker E 500 X-band spectrometer (~ 9.4 GHz) with a 100 kHz field modulation equipped with an Oxford flow cryostat for measurements at temperatures of 3–300 K and a goniometer to measure the angular dependence of the EPR spectra. The experiment was performed at a magnetic field of 10–1400 mT. A well oriented rectangular sample was rotated around perpendicular axes coincident with the *a*-, and *c*-crystallographic directions.

3. Raman spectra

The polarized Raman spectra of the $\text{YVO}_4:\text{Yb}^{3+},\text{TM}^{3+}$ crystal are shown in Fig. 1. This sample was measured instead of $\text{YVO}_4:\text{Yb}^{3+},\text{TM}^{3+}$ due to strong luminescence of Yb^{3+} ion in the double-doped crystal which completely obscured the Raman signal.

The Raman active phonons for the crystal studied form the representation $2A_{1g} + A_{2g} + 4B_{1g} + B_{2g} + 5E_g$ and the IR active phonons belong to the representation $A_{1u} + 4A_{2u} + B_{1u} + 2B_{2u} + 5E_u$ ($A_{2u} + E_u$ are acoustic phonons). The A_{1g} lines are observed at 891 (ν_1) and 379 (ν_2) cm^{-1} , the B_{1g} modes at 817 (ν_3), 489 (ν_4) and 261 (T) cm^{-1} , the B_{2g} modes at 490 cm^{-1} (ν_4) and the E_g modes at 839 (ν_3), 263 (T), 163 and 157 (L) cm^{-1} . These data fill well to the phonon distribution in other rare earth vanadates [7,8]. The temperature dependence of Raman spectra show no anomalies in the 10–300 K range indicating that no structural phase transition is observed in this range.

4. EPR results

A low temperature EPR spectrum consists of a group of very intense asymmetric lines centered roughly at 400 mT (Fig. 2, upper spectrum). With the increasing temperature this signal becomes lower and disappears completely at about 50 K, where an addi-

tional group of narrow lines become visible in the field range of 200–500 mT (Fig. 2, lower spectrum).

Angular dependence of the resonance position at a constant temperature of 7 K was analyzed, when the magnetic field operated in the *bc*-plane (Fig. 3a) and *ab*-plane (Fig. 3b). Complete roadmaps representing both directions of rotation are shown in Figs. 4 and 5. In the *bc*-plane, the pattern reveals the existence of three very intense lines: one central and two satellites attributed to the existence of Yb^{3+} ions at the C_1 point symmetry, whereas the satellite lines represent hyperfine interactions of the odd $\text{Yb}^{171,173}$ isotopes.

In the ytterbium ions, being Kramers type ions, the crystal field splits energy levels giving only the lowest doublet populated. In this case the spin Hamiltonian has the form:

$$H_s = \mu_B \mathbf{BgS} + \mathbf{SAI}, \quad (1)$$

where: the first term represents Zeeman interactions with an effective spin of $S' = 1/2$ and the second term describes the hyperfine interactions. The result of a simulation using the EPR–NMR program is shown in Fig. 4. The calculated parameters are:

$$g = \begin{pmatrix} 2.9 & 0.75 & \\ & 2.8 & 3.0 \\ & & 2.9 \end{pmatrix}_{abc} \quad (2)$$

For the *g* matrix $A = 150$ mT for hyperfine interactions. Nondiagonal terms of the *g* matrix indicate that the principal magnetic directions do not coincide with the crystallographic ones. The polar coordinates (θ , φ) of the magnetic axes as compared to the crystallographic *a*, *b*, *c* directions are (104.0, 0), (132.9, 103.4) and (46.3, 76.2) degrees, respectively.

The resonance positions during the crystal rotation around the *c*-axis (in the *ab*-plane) are shown in Fig. 5. Instead of the Yb^{3+} of C_1 symmetry some intense lines of a higher symmetry are de-

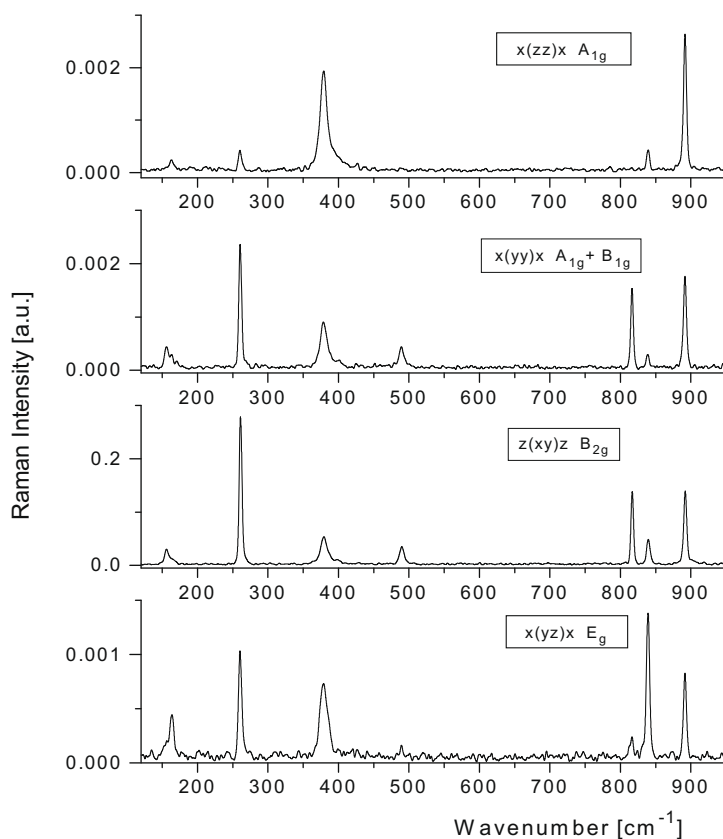


Fig. 1. Polarized Raman spectra of an oriented $\text{YVO}_4:\text{Tm}$ single crystal.

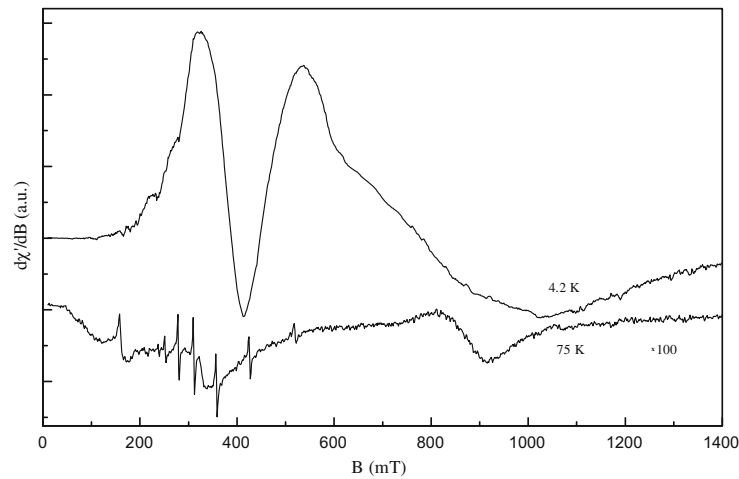


Fig. 2. Examples of the EPR spectra of a YVO₄:Yb, Tm crystal at two fixed temperatures 4.2 and 75 K (the signal centered at about 900 mT has an external meaning).

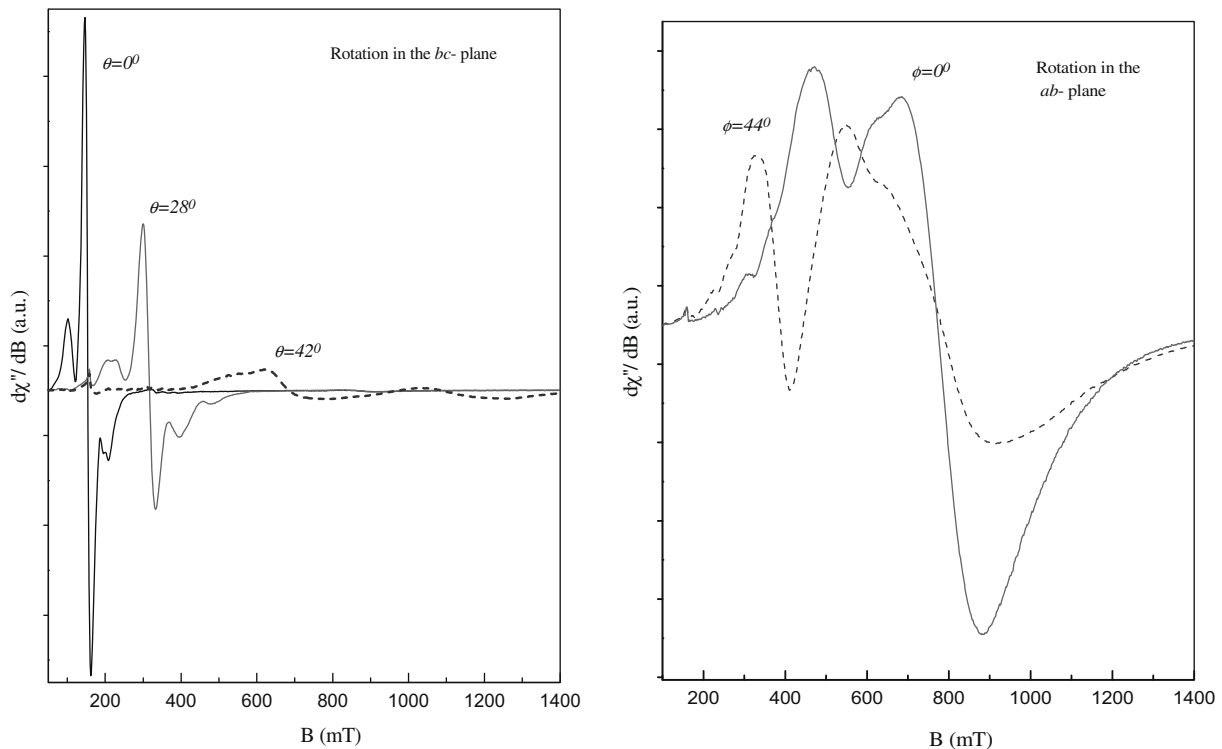


Fig. 3. Examples of the EPR spectra registered when YVO₄:Yb, Tm crystal was rotated: (a) in the *bc*-plane, (b) in the *ab*-plane.

tected. Due to a large linewidth (see upper spectrum in Figs. 2 and 3b) these lines are not well resolved and the establishing of their resonance position is difficult, especially at a high magnetic field. However, the EPR–NMR simulation allowed this signal to be ascribed to the $S = 1$ paramagnetic centers. The spin Hamiltonian employed here had the form:

$$H_s = \mu_B \mathbf{BgS} + D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2), \quad (3)$$

where the first term describes the Zeeman interactions, the second and third terms represent the zero field splitting of axial and rhombic crystal fields, respectively. The g matrix components are:

$$g = \begin{pmatrix} 0.88 & 0.48 & \\ & 0.88 & \\ & & 1.36 \end{pmatrix}_{abc} \quad (4)$$

and the zero field splitting parameters are: $D = 144$ mT and $E = 0$. The nondiagonal term g_{xy} indicates that the magnetic principal axis system in this case is just tilted (about 45°) in the *ab*-plane with respect to the crystallographic a , b directions.

In the YVO₄:Yb,Tm crystal, the signal with $S = 1$ could be attributed to the Tm³⁺ paramagnetic centers, to the V³⁺ paramagnetic centers or to the pair system of Yb³⁺–Yb³⁺. Thulium ions are usually known to be EPR silent due to the mixing of the spin–orbit coupling with the nonmagnetic lowest term $m_J = 0$. Ascribing the observed signal to the vanadium ions is doubtful too, because V³⁺ ions should reveal eight narrow lines split due to hyperfine interaction in the EPR experiment. Therefore we attributed this signal to the ytterbium pairs. This conclusion is additionally confirmed by the analysis of some spectroscopic parameters described below.

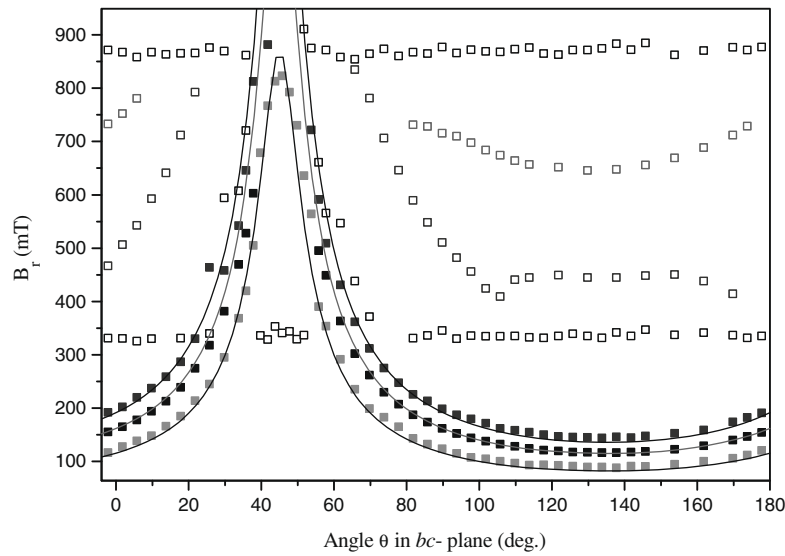


Fig. 4. Angular dependence of the EPR lines when the crystal was rotated in the bc -plane ($B \perp a$). The solid points represent the Yb^{3+} resonance signal. The lines result from a simulation using the EPR/NMR program, performed for Yb^{3+} ions: ($S = 1/2, l = 0$) – central line and ($S = 1/2, l = 1/2$) – two satellite lines.

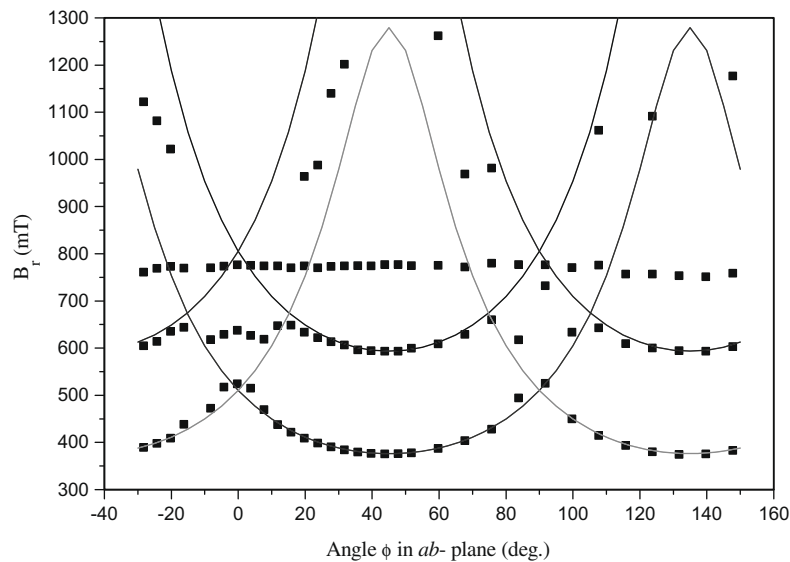


Fig. 5. Angular dependence of the EPR lines when the crystal was rotated in the ab -plane ($B \perp c$). The lines result from a simulation using the EPR–NMR program for the paramagnetic centers with $S = 1$ at C_4 point symmetry.

The integral intensity I as a function of reciprocal temperature for isolated paramagnetic centers should be a straight line, according to the Curie-Weiss relation. In our case, for a selected component of $S = 1$ signal, a significant deviation from this scheme was observed. Also the linewidth as a function of temperature revealed a characteristic increase at higher temperatures, typical for collective paramagnetic centers. Additionally, a visible shape of resonance lines is rather of a Gaussian than Lorentzian type, which suggests a significant dipole–dipole interaction in the pairs of ytterbium ions.

Another characteristic $IT = f(T)$ dependence could indicate the nature of the interactions between Yb^{3+} – Yb^{3+} pairs. Observing the inclination of the calculated $IT = f(T)$ relation, it can be said that antiferromagnetic interactions dominate at temperatures below 8 K, whereas ferromagnetic interactions prevail above 8 K. The temperature of 8 K is also characteristic for the spectroscopic parameter g , i.e. the effective value of g_{eff} decreases significantly

with the temperature increasing up to 8 K, whereas above this temperature g_{eff} strongly increases. Both variations can be attributed to a specific contribution of the internal magnetic field changing the resonance conditions.

As has been mentioned above, the ytterbium signal disappears with the increasing temperature, at about 23 K, and a group of narrow lines becomes visible (Fig. 2). These lines, observed in the range of 240–550 mT could be ascribed to the Gd^{3+} ions, doped to the structure unintentionally from basic materials.

A detailed analysis of the EPR gadolinium lines was made at liquid nitrogen temperature. The observed lines were attributed to the allowed transitions between $m_j = 7/2; 5/2; \dots -5/2; -7/2$ terms.

The simulation results are good enough, confirming the axial nature of a crystal field around gadolinium sites. The calculated parameters are as follows:

$g_{\parallel} = 1.982$, $g_{\perp} = 1.989$, $D = 51$ mT, $B_4^0 \sim 0$, $B_4^4 = 0.08$ mT, $B_6^0 \sim 0$, $B_6^4 \sim 0$, similar to those reported previously by Jabłoński et al. [6].

5. Conclusions

The EPR method revealed that Yb^{3+} dopants occupied eight-coordinated bisdisphenoidal Y^{3+} crystal positions, leading to a significant distortion of the local point symmetry. A plausible explanation is that strong dipole–dipole interactions between Yb^{3+} ions are responsible for the observed distortion. The nature of the interactions is rather complex, leading to a domination of antiferromagnetic interactions at low temperatures, and ferromagnetic interactions at temperatures above 8 K.

According to the crystal structure we are dealing with different Y–Y distances in the YVO_4 single crystal. Therefore, depending on the mutual distance and local distribution of the ytterbium ions, interactions between them are able to create pairs of $\text{Yb}^{3+}\text{--}\text{Yb}^{3+}$. These ions remain isolated if the distance is larger. As a result, we observed two types of ytterbium magnetic centers: paired mag-

netic centers and distorted isolated paramagnetic centers. Both types of centers were strongly sensitive to the magnetic field directions and some imperfections of the crystal. Therefore, we observed pair centers and isolated centers during a crystal rotation around the c - and a -crystal directions, respectively.

Contrary to Yb^{3+} , the Gd^{3+} ions did not change significantly the local crystal symmetry due to their extremely low concentration.

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