Magneto-optical spectroscopy of Yb^{3+} ions in huntite structure

A.L. Sukhachev, A.V. Malakhovskii *, I.S. Edelman, V.N. Zabluda, V.L. Temerov, I.Ya. Makievskii

L.V. Kirensky Institute of Physics, Siberian Branch Russian Academy of Sciences, 660036 Krasnoyarsk, Russian Federation

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ABSTRACT

We report the first measurements of magnetic circular dichroism (MCD) and magneto-optical activity (ratio of zero moments of MCD and absorption bands) of Yb^{3+} ion in the trigonal single crystals $Yb_xTm_{1-x}Al_3(BO_3)_4$ as a function of temperature in the range of 100–293 K. Magneto-optical activity follows the Curie–Weiss law with the Weiss constant $\theta = -55$ K for $Yb_{0.1}Tm_{0.9}Al_3(BO_3)_4$ crystal. The value and origin of the magneto-optical activity is theoretically analyzed.

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1. Introduction

Magnetic circular dichroism (MCD) spectroscopy is a valuable tool for the detection of degenerate crystal field levels of the rare-earth (RE) ions in compounds and for observation of electron transitions not resolved in absorption spectra, as well as for the study of the site symmetry [1]. However, in contrast to the optical spectroscopy, only a few studies of MCD in RE ions, predominantly, diluted in glass matrices have been reported up to now [2–8]. There are also not so many papers devoted to MCD spectra of RE ions in crystals (see, e.g., [9–14]). A variety of features in MCD of f–f transitions behavior in different RE ions and compounds and further progress in the development of MCD technical applications require more profound study of microscopic mechanisms of the magneto-optical activity of f–f transitions in RE ions in different matrices. Yb^{3+} ion in trigonal crystal field (CF) of $Yb_xTm_{1-x}Al_3(BO_3)_4$ is one of the proper objects for such kind of investigations. Crystals, containing both Yb^{3+} and Tm^{3+} ions are interesting from the view point of the excitation transfer between RE ions. Here we present first investigation of spectral and temperature dependences of the f–f transition MCD in Yb^{3+} ion in trigonal crystals $Yb_xTm_{1-x}Al_3(BO_3)_4$ ($x = 0.1$, 0.2, and 1.0) in combination with the similar study of the optical spectra. Paramagnetic magneto-optical activity (MOA), determined as the ratio of the first moments of MCD and optical absorption bands, is obtained, and the origin of the observed MOA is analyzed.

2. Samples preparation and experimental technique

The crystals have been grown from the solution–melt [15]: 86% mass $[Bi_2Mo_3O_{12}+p\ Li_2MoO_4+q\ B_2O_3]+14\%$ mass $Tm_{1-x}Yb_xAl_3(BO_3)_4$. For $x = 1$ the coefficient values were $p = 0.5$ and $q = 2$, and for $x = 0.1$, 0.2 they were $p = 0.75$ and $q = 2.5$. Crystallization parameters, the saturation temperature $T_{sat} \approx 985\ °C$ including, were practically the same in all cases.

When growing crystals $Yb_xTm_{1-x}Al_3(BO_3)_4$ with $x = 0.1$, 0.2, the initial solution–melt remaining after synthesis of the crystal with $x = 0$ was used. New portions of the crystal-forming oxides were added in it in quantities corresponding to the mass of the crystal synthesized. Ytterbium oxide was added in the proportions Yb_2O_3:$Tm_2O_3 = 1$:10 and Yb_2O_3:$Tm_2O_3 = 1$:5. Dimension of the crystals grown was $\sim 1\ cm^3$. The crystal lattice parameters were $a = 9.274(3)$ Å, $c = 7.212(3)$ Å for $YbAl_3(BO_3)_4$. The samples of crystals prepared for measurements were plane-parallel polished plates, oriented parallel and perpendicular to the threefold crystallographic axis. Thickness of $Tm_{1-x}Yb_xAl_3(BO_3)_4$ ($x = 0.1$, 0.2) samples was 0.3 mm and thickness of $YbAl_3(BO_3)_4$ samples was 0.168 mm.

Magnetic circular dichroism (MCD) and polarized absorption spectra of the crystals were measured in the region of the only f–f transition $^2F_{7/2}$–$^2F_{5/2}$ of Yb^{3+} ion in the temperature range of

* Corresponding author. Tel.: +7 391 2494556; fax: +7 391 2438923.
E-mail address: malakha@iph.krasn.ru (A.V. Malakhovskii).

100–293 K. Three light polarizations were used: α—light wave vector $\vec{k}$ was parallel to C_3 axis of the crystal and electric vector $\vec{E}$ of light was perpendicular to C_3 axis; $\pi - \vec{k} \perp C_3$, $\vec{E} \| C_3$; $\sigma - \vec{k} \perp C_3$, $\vec{E} \perp C_3$. The light was polarized by the Glan prism. Precise positions of polarization parallel to the main crystal axes were found according to minimum transparency of the sample in crossed polarizers. The absorption spectra were measured with the optical slit-width 0.4 nm by the two-beam technique using an automated spectrophotometer, designed on the bases of MDR-2 monochromator. MCD was measured using the modulation of the light wave polarization with piezoelectric modulator. This modulator consists of the plate of fused silica and pasted to it piezoelectric ceramic element. The modulator is a part of the self-contained generator and oscillates with its resonance frequency of about 25 kHz. Linearly polarized light passed through the plate of the fused silica changes its polarization from right to left circular one with the resonance frequency of the modulator. These circularly polarized light passed through the sample acquires a modulation of its intensity due to circular dichroism of the sample. The photomultiplier direct current level is maintained constant at the light wavelength change due to the feedback controlled high voltage power supply of the photoelectron multiplier. Thus, circular dichroism is proportional to alternating current of the photoelectron multiplier. Calibration of the circular dichroism measurements was fulfilled by the method described in Ref. [16]. MCD was measured as a difference of circular dichroism in plus and minus magnetic field. So natural circular dichroism, existing in the non-centrosymmetrical crystal, was excluded. The MCD spectra were measured automatically with the help of the computer controlled program. The MCD measurements accuracy was 10^{-4} and the optical slit-width was ~2 nm. Magneto-optical measurements were carried out in a magnetic field of 5 kOe, created by electromagnet. The samples were put in a nitrogen gas flow cryostat. Accuracy of the temperature measuring was ~1 K.

3. Results and discussion

At room temperature, absorption spectra of Yb^{3+} ion, measured in molar extinction, are practically identical in all studied crystals. Spectra of Yb^{3+} ion in $Yb_{0.1}Tm_{0.9}Al_3(BO_3)_4$ and $Yb_{0.2}Tm_{0.8}Al_3(BO_3)_4$ crystals are identical down to, at least, 100 K. This is rather natural, since ion radii of Tm^{3+} and Yb^{3+} are close to each other. At low temperatures, absorption of the ytterbium crystal ($x = 1$) at the energy of the maximum absorption is too high to be measured even on the sample of 0.168 mm thickness. Therefore we studied
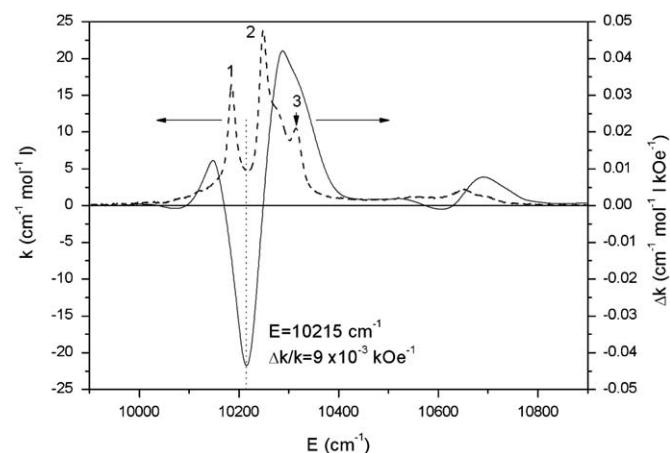

Fig. 1. MCD (solid line) and absorption (dash line) spectra of $Yb_{0.1}Tm_{0.9}Al_3(BO_3)_4$ crystal at α-polarization and temperature $T = 100$ K.
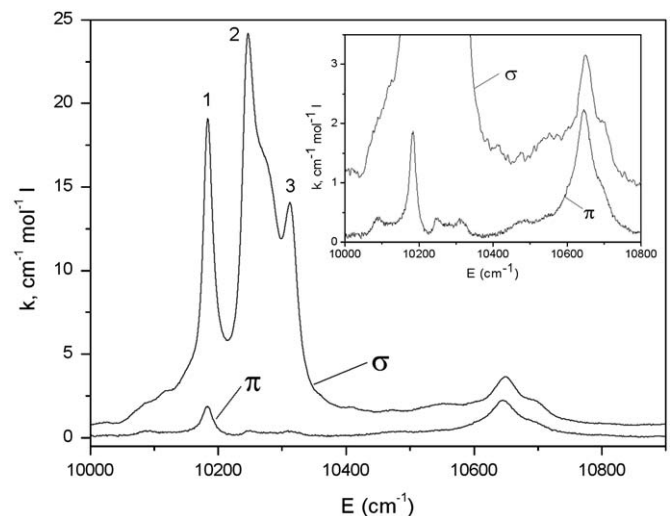

Fig. 2. π and σ-polarized absorption spectra of $Yb_{0.2}Tm_{0.8}Al_3(BO_3)_4$ crystal at temperature $T = 100$ K. Inset: the same spectra at a larger scale.

temperature variation of the absorption and MCD spectra of $Yb_{0.1}Tm_{0.9}Al_3(BO_3)_4$ crystal. MCD measurements were made in α-polarization. An example of the MCD spectrum together with the corresponding absorption spectrum is shown in Fig. 1. The α and σ absorption spectra of the crystals coincide (see Figs. 1 and 2), that testifies to the electric–dipole character of the transition. Fine structure of $YbAl_3(BO_3)_4$ absorption spectra at low temperatures was earlier analyzed in detail in Ref. [17].

Ytterbium ions, like other RE ions in the huntite structure, are surrounded by six crystallographic equivalent oxygen ions, forming trigonal prisms [18]. The local symmetry of Yb^{3+} ion in the mentioned crystals, by analogy with the same crystals with Tb, Pr and Nd [19–21], is supposed to be D_3 at room temperature. At the same time, absorption spectrum of Yb^{3+} ion in the studied crystals (Fig. 2) noticeably differs from that in diluted crystals $Yb^{3+}:YAl_3(BO_3)_4$ [22] and $Yb_xGd_{1-x}Al_3(BO_3)_4$ [23]. In particular, in our crystals very high natural linear dichroism takes place (Fig. 2), while in $Yb^{3+}:YAl_3(BO_3)_4$ [22] it is small. All this means, that, in spite of generally the same structure of the considered crystals, parameters of the local environment of Yb^{3+} ions are different.

There are three contributions to the MCD: (1) the diamagnetic effect independent of temperature, (2) the temperature-dependent paramagnetic effect, and (3) the temperature-independent paramagnetic effect or the "mixing effect" due to mixing of states by magnetic field. This effect exists only in condensed substances, in which the atomic states are split by the crystal field, and states with zero magnetic moments appear [24].

The zero moment of an MCD band characterizes the total paramagnetic contribution into the dichroism (the contribution of the diamagnetic effect to the zero moment is identically zero). Yb^{3+} ion has an odd number of $4f$ electrons and shows therefore Kramers' degeneracy in any crystal field (CF). Magnetic field lifts all CF degeneracy. Consequently, temperature-dependent paramagnetic MCD will take place. This effect, if it exists, is usually much larger than the mixing effect, and we shall consider only the former one. Thus we can write:

$$\langle \Delta k(\omega) \rangle_0 = C\mu_B H / kT, \qquad (1)$$

where $\langle \Delta k(\omega) \rangle_0$ is the zero moment of the MCD spectrum, corresponding to the absorption band; H the magnetic field; T the temperature; and C is a constant which is dependent on the electronic transition parameters. Therefore, in the first approx-