Optical Study of the Electronic Structure and Magnetic Ordering in a Weak Ferromagnet FeBO₃

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Spectral dependences of the relative permittivity ε = ε₁ - iε₂ of a uniaxial weak ferromagnet FeBO₃ are measured for two principal polarizations in the energy range 0.6–5.6 eV. The positions have been determined for the charge-transfer transitions that make the main contribution to absorption above the bandgap and determine the refractive-index dispersion below the bandgap. The isotropic magnetic contribution to the refractive index has been detected by studying the temperature dependence of the refractive index in the range 100–700 K; its value (≈2 × 10⁻²) is found to be record high for magnetic dielectrics. The energy shift of the effective oscillator, which characterizes the shift of the positions of the charge-transfer transitions due to magnetic ordering, is determined from these data within the framework of a single-oscillator model. The value of the exchange interaction in FeBO₃ is determined from optical measurements.

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INTRODUCTION

Magnetically ordered materials and structures exhibit specific features in the spectra of electronic, magnon, and phonon excitations, because of which their interaction with electromagnetic radiation results in a number of physical phenomena. The same spectral features result in large values of linear and nonlinear magneto-optical phenomena such as Faraday and Kerr effects [1–3], magnetic linear birefringence [4, 5], and the generation of the second and higher optical harmonics [6]. These and other magneto-optical phenomena serve as an alternative and, sometimes, preferable method for studying electronic and magnetic structures.

In very recent years, a new area has been formed in the physics of magnetic materials whose main task is to study the processes of control of the magnetic state of solids using short laser pulses [7, 8]. Magneto-optical effects are the most effective and relatively simple means of monitoring ultrafast demagnetization processes [9], the excitation of spin precession [8], and magnetization reversal [10], when the large value of the former provides the possibility of achieving a high sensitivity and time resolution. This circumstance has put forward the problem of a more detailed spectroscopic investigation of the electronic structure as the microscopic basis of magneto-optical effects.

In this work, we report the results of studying the electronic structure and magnetic ordering in a well-known weak ferromagnet iron borate FeBO₃. A review of its magnetic, optical, and magneto-optical properties can be found in [11]; therefore, we will consider here only its brief characteristics. FeBO₃ is crystallized in the rhombohedral calcite structure with the space group D₃d and, hence, is optically uniaxial. It represents a rare example of a magnetically ordered ferric oxide with a high transparency in the visible spectral region and with a Faraday rotation reaching 5000°/cm [12].

EXPERIMENTAL PROCEDURES AND SAMPLES

Studies of the dispersion of the dielectric functions ε_xx and ε_zz in the optical region 0.6–5.6 eV were carried out using a spectroscopic ellipsometer in reflection geometry. The details of the studies and the corresponding calculations were described previously in [13]. The absorption spectrum α_xx in the region of relative transparency 1–3 eV was obtained by measuring absorption in the transmission geometry.

The temperature dependence of the refractive index was studied using a homodyne interferometer at a helium–neon laser wavelength of 1.078 eV (1.15 μm) [14–16]. A distinctive feature of this method is that the sensitivity of measurements is not reduced both under a strong (by 1–2 orders of magnitude) change in the intensity due to temperature variations of absorption.
and under light depolarization, for example, in the case of a domain structure formation. The relative variations of the optical light path in the crystal $\delta \psi(T)$ (relative to vacuum) normalized to the crystal thickness associated with variations of the refractive index $\delta n(T)$ and the thermal expansion of the sample $\delta l/l$ can be calculated by this method according to the equation

$$\delta \psi_{ij} = \delta n_i + (n_i - 1) \frac{\delta l}{l_j},$$

where the first index ($i$) indicates the light polarization and the second one ($j$) indicates the propagation direction.

Samples were polished plane-parallel single-cristalline plates with thicknesses in the range 20–1000 $\mu$m. Plates with the normal oriented along and perpendicular to the optical $z$ axis were obtained from crystals grown from a solution in a melt and from a gas phase, respectively. This allowed the dielectric function of FeBO$_3$ to be obtained for two main light polarizations.

OPTICAL PROPERTIES OF FeBO$_3$

Spectra of the dielectric functions $\varepsilon_{zz}$ and $\varepsilon_{xx}$ for light polarized along and perpendicular to optical $z$ axis are given in Figs. 1b and 1c. The inset in Fig. 1 shows the absorption spectrum $\alpha_{xx}$ in the energy range 1–3 eV for...
a value of about $3.1 \times 10^3$ cm$^{-1}$, which is almost two times lower than our data. On the other hand, the intensities of the 1.4 and 2.0 eV bands are close. Note that the spectrum of the absorption factor $\alpha_{xx}$ was obtained at $T = 15$ K, while the spectra reported in [17, 20] were measured at a temperature of about 80 K.

The $^6A_{1g} \rightarrow (^4A_{1g}, ^4E_g)$ band is hybridized with charge-transfer transitions and exhibits a significant anisotropy (Figs. 1b and 1c). The local maximum in the $\varepsilon_{2xx}$ spectrum is located higher in energy and has a lower amplitude than that in the $\varepsilon_{2zz}$ spectrum. This is probably associated with the anisotropy of the charge-transfer transitions, which will be discussed below.

The bands in the absorption spectrum $\varepsilon_2$ (Figs. 1b and 1c) located above 3 eV correspond to the charge-transfer transitions. The fundamental absorption band edge is determined by the $p^6d^6 \rightarrow p^5d^6$ charge-transfer transition from the top of the valence band to the unfilled $d$ band of iron. The fundamental absorption edge for FeBO$_3$ is conventionally determined at a level of 2.9 eV [17, 20], and theoretical calculations give a close value [20, 23]. There are no ab initio electronic structure calculations for the above-bandgap absorption available in the literature.

The decomposition of the spectra into Lorentzian oscillators was performed by the equation

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 = \varepsilon_0 + bE + \sum \frac{f_{0j}}{E_j - E^2 - iE\gamma_j},$$  

(2)

where $f_{0j}$ is the oscillator strength for the $j$th transition, $E_j$ is the central frequency of the transition, and $\gamma_j$ is a value characterizing the width of the transition. The term $bE$ takes into account the transitions located at higher energies outside the studied range. The calculation in the cubic-field approximation for an iron ion in an octahedral cluster of oxygen ions [22] allows the observed bands to be qualitatively compared with the charge-transfer transitions from sublevels of the valence band formed by the oxygen $s$ and $p$ states [23] to sublevels of the iron ion. It is seen in Figs. 1b and 1c that the anisotropy of the optical response of FeBO$_3$ is determined by (a) the anisotropy of the transitions lying in the range 4.6–5.5 eV and (b) the anisotropy of the lowest $t_{1g}(\sigma) \rightarrow t_{2g}$ transition. It is the second factor that determines the anisotropy of the 2.8 eV band and the anisotropy of the fundamental absorption edge. It is clearly seen in Fig. 2, where the spectra of absorption factor $k$ and refractive index $n$ for light polarized perpendicular and parallel to the $z$ axis are shown.

The dispersion and anisotropy of the refractive index (Fig. 2) in the range 1–2 eV are also determined by the charge-transfer transitions located above 3 eV and their anisotropy. With accuracy to experimental
Temperature dependences of the variation of the refractive index in the temperature range 100–700 K with an accuracy of about 10%. In the calculations, we used our data for the principal values of the refractive index (Fig. 2) for a photon energy of 1.078 eV $n_x = n_y = 2.101$ and $n_z = 2.022$.

The difference in the values of $\Delta n_{x,z} = \Delta n_{y,z}$ measured upon light passing along and perpendicular to the optical axis allows the determination of the thermal expansion from the measured values of $\Delta n_{x,z}$. The line gives an extrapolation of the regular contribution to the optical axis in the range 80–500 K does not exceed values $\Delta n_{x,z} \leq 5 \times 10^{-4}$ in relative units [24]. From our calculations, it follows that, in the same temperature range, $\Delta n_{x,z} \leq 5 \times 10^{-3}$ (Fig. 4a); therefore, it may be assumed for FeBO$_3$ that $\Delta n_{x,z} \leq 5 \times 10^{-3}$ with an accuracy of the order of 10%. A quantitative comparison shows that the contribution of the thermal expansion to $\Delta n_{x,z}$ and $\Delta n_{y,z}$ is lower than the variations in these values.
by an order of magnitude. Thus, the temperature dependences \( \delta \psi_\omega (T) \) and \( \delta n_{z}(T) \) presented in Fig. 3 correspond to the temperature variations of the principal values of the refractive index \( \delta \psi_\omega (T) = \delta n_{x}(T) = \delta n_{z}(T) \), \( \delta n_{z}(T) \) being the total magnetic contribution to the refractive index. As was shown in [14, 25], the dependences \( \delta n_{x,z}(T) \) can be approximated by the corresponding integral Debye–Einstein function. We used this approach to approximate the temperature variations of the regular part of the light refraction in FeBO\(_3\). Figure 3 demonstrates an extrapolation of the regular part \( \psi_\omega^{0}(T) \) of the temperature variations of the light refraction in FeBO\(_3\) from the region of high temperatures, where one may neglect the effect of magnetic ordering. The difference between the experimental curves \( \psi(T) \) and the dependences \( \psi^{0}(T) \) represents the total magnetic contribution to the light refraction for the ordinary and extraordinary rays, which is shown in Fig. 4b. This contribution equals

\[
\delta n_{x,z}^{m} = \delta n_{z}^{m} = (\delta \psi_\omega^{m}(T)) \approx 2 \times 10^{-2} \text{ at } 80 \text{ K.}
\]

This value of the magnetic contribution to the refractive index is a record for magnetic dielectrics and is inferior only to the analogous value in magnetic semiconductors [5]. The magnetic contribution to the principal values of the refractive index found in this work exceeds the value of the magnetic linear light birefringence by two orders of magnitude; the latter is determined by anisotropic increments in the refraction depending upon the orientation of the magnetic moments with respect to the crystallographic axes. Hence, it follows that the found contribution is isotropic with respect to magnetization.

From our optical data, we can also estimate the exchange striction along the \( z \) axis. The dashed line in Fig. 4a shows an extrapolation of the regular contribution not associated with the magnetic order to the thermal expansion along the \( z \) axis (performed using the same procedure as for the light refraction). The difference between the dashed line and the curve designated by dots represents the contribution of the exchange striction along the \( z \) axis, which reaches a value of \( \approx 2 \times 10^{-3} \text{ at } 100 \text{ K.} \)

From the microscopic point of view, the magnetic contribution to the light refraction is associated with the isotropic magnetic exchange interaction [14, 5]. From our data on the determination of \( \delta n_{x}^{m} \) and \( \delta n_{z}^{m} \) at 100 K, the energy shift of the effective oscillator \( \delta E_{x,z}^{m} \) can be estimated in the framework of the one-oscillator model under the assumption that the effective oscillator strength does not change substantially upon magnetic ordering

\[
\delta E_{x,z}^{m} \approx -6.9 \times 10^{-2} \text{ eV (1.2%)} \text{ and } \delta E_{z}^{m} \approx -7.3 \times 10^{-2} \text{ eV (1.3%)} \text{ at } T = 100 \text{ K.}
\]

Because the effective oscillator energy lies in the region of the charge-transfer transitions, the energy shift of the effective oscillator characterizes the shift of these transitions due to an isotropic exchange.

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