

OPTICS
AND LASER PHYSICS

Giant Natural Circular Dichroism of Vibronic Transitions in $\text{HoAl}_3(\text{BO}_3)_4$

A. V. Malakhovskii^{a,*}, A. L. Sukhachev^a, V. V. Sokolov^b, and I. A. Gudim^a

^a Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk, 660036 Russia

^b Siberian Federal University, Krasnoyarsk, 660041 Russia

*e-mail: malakha@iph.krasn.ru

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The giant natural optical activity of vibronic replicas of the $f-f$ $^5I_8 \rightarrow ^5F_2$ transition in $\text{HoAl}_3(\text{BO}_3)_4$ is observed. It exceeds the optical activity related to purely electronic transitions by two orders of magnitude and corresponds to the almost complete circular polarization of the transitions. This effect is explained by the local distortions of the crystal in the excited electronic state, which lead to the mixing of electron and vibrational wavefunctions and, as a consequence, to the delocalization of the vibronic wavefunction and the enhancement of spatial dispersion, which is responsible for the optical activity.

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INTRODUCTION

Natural circular dichroism (CD) has long enjoyed wide use in the studies of organic compounds. In contrast, natural CD in ionic crystals, in particular, in $4f$ compounds, has been investigated much less extensively, for example, in the optical range in [1–5] and at gigahertz frequencies in [6]. Still, along with magnetic circular dichroism (MCD), this effect attracts considerable interest, because it provides additional insight into atomic states in crystals.

The $\text{HoAl}_3(\text{BO}_3)_4$ crystal has the $R32$ space symmetry, with each Ho^{3+} ion located at the center of a trigonal prism formed by oxygen ions with D_3 symmetry. As far as this point group does not include inversion symmetry, the parity selection rule, forbidding $f-f$ transitions, is lifted, and natural CD becomes possible. The Judd–Ofelt parameters and other spectroscopic characteristics of the $f-f$ transitions in the crystal were determined in [7]. We note that $\text{HoAl}_3(\text{BO}_3)_4$ is particularly interesting owing to the observation of the giant magnetoelectric effect in this material [8, 9].

RESULTS AND DISCUSSION

$\text{HoAl}_3(\text{BO}_3)_4$ crystals were grown from melt solution based on bismuth trimolybdate and lithium molybdate using the technique described in [10]. The spectra of polarized absorption, MCD, and natural CD were measured in the region of the $^5I_8 \rightarrow ^5I_5$, 5F_5 , $^5(S_2 + F_4)$, 5F_3 , 5F_2 , 3K_8 , $^5(G_6 + F_1)$, and 5G_5 transitions at energies of 11000, 15300, 18500, 20500, 21000, 21300, 22000, and 23800 cm^{-1} , respectively. Identify-

ing the transitions, we drew upon [11]. Similar measurements were performed for a $\text{HoFe}_3(\text{BO}_3)_4$ crystal. Below, we present only the results pertaining to the $^5I_8 \rightarrow ^5F_2$ transition (G band), because the effect under discussion was observed only for this transition. In the measurements of natural CD and MCD, the polarization of light incident on the sample was modulated by a piezoelectric modulator [12]. The magnitudes of MCD and natural CD were determined as the half-difference and half-sum, respectively, of the CD signals recorded for two opposite orientations of the applied magnetic field. The CD signal was measured with light propagating along the C_3 axis.

Figure 1 shows the spectra of polarized absorption, natural CD, and MCD for a holmium aluminum borate crystal and the 10-fold magnified natural CD spectrum of holmium ferrobaborate in the region of the $^5I_8 \rightarrow ^5F_2$ transition. Figure 2 shows the spectral curves in the region of weak absorption. Here, the absorption spectra were recorded in a separate run with a long signal accumulation time to reduce noise; we note that the absorption and natural CD spectra of the $\text{HoAl}_3(\text{BO}_3)_4$ crystal are plotted in Fig. 2 on the same scale. It can be suggested that lines V1–V6 in the σ -polarized absorption spectrum and V7–V9 in the π -polarized absorption spectrum are vibronic replicas of the G_1 electronic line (Fig. 1) that originate from vibrations with frequencies of 75, 95, 110, 120, 135, 154, 82, 90, and 116 cm^{-1} , respectively. There is no clear correspondence between the frequencies of these replicas and frequencies of lines observed in the Raman and infrared absorption spectra of the

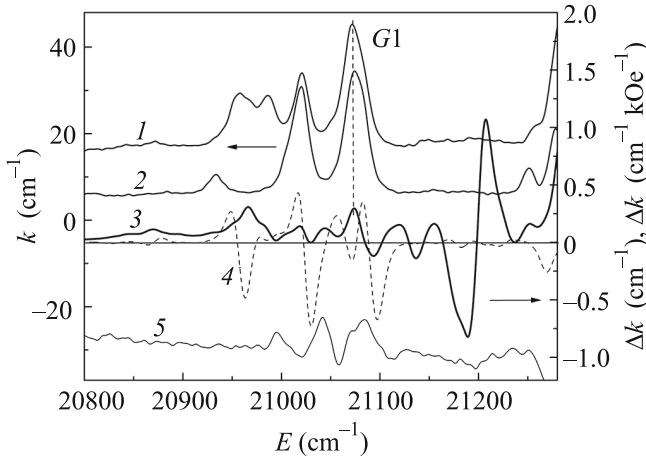


Fig. 1. Absorption spectrum of $\text{HoAl}_3(\text{BO}_3)_4$ in (1) σ and (2) π polarizations; the spectra of (3) natural CD and (4) MCD of $\text{HoAl}_3(\text{BO}_3)_4$; and (5) the spectrum of natural CD of $\text{HoFe}_3(\text{BO}_3)_4$ magnified by a factor of 10. All spectra were recorded at a temperature of 90 K.

$\text{YbAl}_3(\text{BO}_3)_4$ crystal [13]. This is explained by the fact that infrared and Raman spectra characterize the ground state of the translationally invariant crystal, while the vibrations giving rise to replicas in the f - f absorption spectra are local vibrations in the vicinity of an optically excited atom, which, actually, behaves as an impurity.

The natural optical activity of a transition is defined as

$$A = \frac{R_{if}}{D_{if}} \approx \frac{\langle \Delta k \rangle_0}{\langle k \rangle_0}. \quad (1)$$

Here, k is the absorption coefficient; Δk is the natural CD; $D_{if} = |\langle i | \mathbf{d} | f \rangle|^2$; and, according to [14],

$$R_{if} = \text{Im} \left[\langle i | \mathbf{d} | f \rangle \langle f | \mathbf{m} | i \rangle \right], \quad (2)$$

where \mathbf{d} and \mathbf{m} are the electric and magnetic dipole moments, respectively. Only the electric dipole moment is taken into account in the transition strength D_{if} , because the transition has electric-dipole nature (α and σ polarized spectra coincide). Following Eq. (1), we find from Fig. 2 that the optical activity of the V3, V4, and V5 transitions is about 0.7; i.e., these transitions are almost completely circularly polarized. This is possible, first of all, if the crystal consists primarily of twins of one type. Previously, we observed a large natural optical activity for a vibronic absorption line in a $\text{ErAl}_3(\text{BO}_3)_4$ crystal [15]. A comparison of the absolute values of A in different crystals would be incorrect, since we do not know the relation between the opposite twins featuring optical activity of opposite signs. It is more appropriate to compare the ratios of the optical activities for the vibronic and electronic absorption lines. For $\text{HoAl}_3(\text{BO}_3)_4$, this ratio is 70; for $\text{ErAl}_3(\text{BO}_3)_4$, it is a factor of 2 smaller.

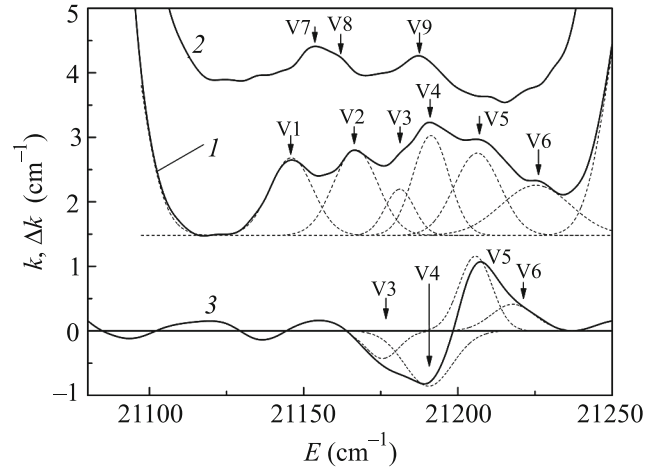


Fig. 2. Absorption spectrum in (1) σ and (2) π polarizations and (3) the spectrum of natural CD of $\text{HoAl}_3(\text{BO}_3)_4$ at a temperature of 90 K.

According to Eq. (2), no transition can be completely polarized, because complete polarization would require the equality of the matrix elements of the electric and magnetic dipole moments. Phenomenologically, the optical activity for an electronic transition in a medium can be possible only in the presence of spatial dispersion: $A \sim s/\lambda$, where s is the size of the object interacting with light and λ is the wavelength of light. Furthermore, natural optical activity can exist only in noncentrosymmetric crystals; i.e., its value should be proportional to the displacement of this active cluster from a centrosymmetric position: $A \sim \delta$, where parameter δ characterizes this displacement. In summary,

$$A \sim s\delta/\lambda. \quad (3)$$

Thus, a large natural optical activity for a vibronic transition can be caused by the high degree of delocalization of the vibronic wavefunction. This suggestion implies that vibronic coupling in this case cannot be described in the adiabatic approximation. Indeed, in this approximation, the vibronic wavefunction represents simply the product of an electronic and a vibrational wavefunction. When the adiabatic approximation becomes invalid, mixing of electronic and vibrational functions takes place with the formation of unified delocalized vibronic wavefunctions.

The MCD spectrum (Fig. 1) shows that the magneto-optical activity of the vibronic transitions is low. Indeed, the transition magneto-optical activity is independent of both the delocalization of the wavefunctions and the displacement of the cluster from the centrosymmetric position. These parameters affect only the intensity of f - f transitions and, thus, the magnitude of the MCD. Figure 1 also shows the spectrum of the natural CD of a $\text{HoFe}_3(\text{BO}_3)_4$ crystal magnified by a factor of 10. Apparently, the small absolute value of the natural CD is explained by the fact that

opposite twins are present here in comparable amounts. In the present context, it is important that the natural optical activity of the vibronic transitions is also low. Thus, the giant optical activity of the vibronic transitions is observed only for one of the $f-f$ transitions investigated and only for $\text{HoAl}_3(\text{BO}_3)_4$. It may be concluded that this effect is caused by the local distortions of the crystal in the given excited electronic state and is sensitive to the details of the crystal structure (the local symmetry of Ho in $\text{HoFe}_3(\text{BO}_3)_4$ is lower than that in $\text{HoAl}_3(\text{BO}_3)_4$).

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