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Magnetooptical activity of spinel type crystals with complex mixed-valence lattice irregularities

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ABSTRACT

In this Letter we analyze the peculiarities of the Faraday rotation in the imperfect spinel type crystals for which the lattice irregularities are represented by the mixed valence clusters of transition metal ions. A such kind of complex system with the electronic configuration $d^5(t_{2g}^3 e_g^2) - d^5(t_{2g}^3 e_g^2) - d^4(t_{2g}^2 e_g^2)$ (for example, Mn^{2+}–Mn^{2+}–Mn^{3+}) is considered in detail. The model takes into account the cubic and low symmetry crystal fields acting on the metal ions, migration of the "extra" hole as well as the orientational degeneracy (hidden optical anisotropy). The electric dipole transitions in these types of clusters with migrating hole coupled to the spin core through the double exchange mechanism are shown to lead to a significant magnetooptical activity in the visible range of spectrum. The intensity of these transitions can be comparable or higher than those for the magnetic dipole ones in the same range of frequencies. The electric dipole mechanism of the magnetooptical effects manifests itself in a highly anisotropic character of the spectra.

1. Introduction

The optical and magnetooptical spectroscopy and especially their combined application are known as efficient tools for the investigation of the electronic structure, magnetic properties and lattice irregularities in the crystalline materials. The present work is devoted to the study of the peculiarities of the Faraday rotation (FR) in the imperfect crystals with complex lattice irregularities comprising several transition metal ions with different oxidation degrees. In general, an excessive charge (electron or hole) is delocalized over spin sites through the double exchange mechanism proposed by Zener [1] and Anderson and Hasegawa [2] that gives rise to a ferromagnetic spin alignment. Such type of mixed valence (MV) clusters including two, three or more $3d$-ions have several equivalent dispositions in the cubic lattice, which are linked by the symmetry operation. The degenerate MV cluster type imperfections are expected to give a significant contribution to the Faraday effect in crystals with spinel, garnet or perovskite type structures. An appreciable dipole moment in combination with the unquenched orbital angular momentum in the orientationally degenerate MV clusters was shown [3–5] to lead to an essential renormalization of the symmetric $\varepsilon(\omega)$ and anomalous increase of the antisymmetric $\varepsilon_a(\omega)$ components of the dynamic dielectric permeability tensor.

These effects become appreciable enough even at relatively small concentrations of MV imperfections ($\geqslant 10^{19}$ cm^{-3}). As a result the FR and magnetic circular dichroism (MCD) can be significantly enhanced. At the same time the new lines appear in the absorption spectrum in unusual for the "dielectric" contribution range of frequencies, namely, in the infrared and far infrared regions. In contrast to the earlier studies [3–5] dealing with the electric dipole transitions between the levels of the ground cluster configuration in this Letter we study the visible range of spectrum arising from the transitions between the ground and the excited cluster states. The considered transitions are related to the electron jumps between the t_{2g}- and e_g-orbitals in the cubic crystal field.

One of the most typical irregularity in crystals with spinel structure is represented by the trigonal clusters involving three $3d$-ions with the electronic configurations $3d^n - 3d^n - 3d^{n-1}$ ($n = 2, \ldots, 9$). Since the sites occupied by the $3d$-ions are equivalent the excessive charge of the $3d^{n-1}$ ion (hole) can be delocalized among the cations. This trigonal irregularity has four equivalent dispositions related to the four C_3 axes in a cubic lattice. Although each cluster has trigonal symmetry and therefore is optically anisotropic, this anisotropy remains

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hidden and the crystal is expected to possess cubic symmetry. In such orientationally degenerate clusters exhibiting delocalization of the excess charge between $3d$-cations at least one of the metal ions turns out to be orbitally degenerate in the ground or excited configuration and therefore possesses an unquenched orbital angular momentum. In this Letter we propose a theoretical background for the study of the magnetooptical activity of the cubic crystals with spinel type lattices containing orientationally degenerate mixed-valence lattice irregularities.

2. Hamiltonian, wave functions and energies of mixed valence cluster type irregularity

Let us consider a trigonal cluster in the spinel structure (Fig. 1) consisting of two magnetic ions with $3d^n$ configuration that are supposed to have an orbitally non-degenerate ground state and one $3d^{n-1}$ ion with orbitally degenerate ground term. Such a cluster type irregularity in a cubic lattice can appear due to the presence of the cation vacancy or non-isovalent cation substitution in the octahedral positions. For sake of definiteness hereunder the case of a trigonal cluster with the typical electronic configuration $3d^5 - 3d^5 - 3d^4$ (for example, Mn^{2+}–Mn^{2+}–Mn^{3+}) will be considered. The ground state of the ions with the configuration $3d^5(t_{2g}^3e_g^2)$ in a cubic crystal field (Mn^{2+}) is the orbital singlet ${}^6A_1$, while the ground state of the high spin $3d^4(t_{2g}^3e_g)$ ions is the orbital doublet (${}^5E$-term). The model of the system includes two main physical factors, namely, the influence of the low symmetry crystal field on the orbitally degenerate ions and the double exchange that appears due to the delocalization of the extra hole within the cluster. Consequently, we shall represent the Hamiltonian of this kind of cluster irregularity by:

$$H = H_0 + \sum_i H_i + H_{res}. \tag{1}$$

In Eq. (1) H_0 is the zeroth order Hamiltonian that includes cubic crystal fields acting on the isolated centers, H_i is the Hamiltonian of low-symmetry crystal fields that act on the constituent Mn ion residing in the site i ($i = 1, 2, 3$), H_{res} is the Hamiltonian describing the resonant interaction (double exchange) in the three center irregularity. This interaction is responsible for the hopping of the “extra” hole between the Mn ions. The orbital doublets are affected by the rhombic component of the crystal field while the excited orbital triplets are split by the joint action of the trigonal and rhombic crystal fields. Therefore the Hamiltonians H_i involving both contributions can be represented as:

$$\begin{aligned}
H_1 &= \alpha\big(l_x^{(1)}l_y^{(1)}xy + l_x^{(1)}l_z^{(1)}xz + l_y^{(1)}l_z^{(1)}yz\big) + h_0\left(-\frac{1}{2}\chi_{E\vartheta} + \sqrt{\frac{3}{2}}\chi_{E\varepsilon}\right),\\
H_2 &= \alpha\big(l_x^{(2)}l_y^{(2)}xy + l_x^{(2)}l_z^{(2)}xz + l_y^{(2)}l_z^{(2)}yz\big) + h_0\left(-\frac{1}{2}\chi_{E\vartheta} - \sqrt{\frac{3}{2}}\chi_{E\varepsilon}\right),\\
H_3 &= \alpha\big(l_x^{(3)}l_y^{(3)}xy + l_x^{(3)}l_z^{(3)}xz + l_y^{(3)}l_z^{(3)}yz\big) + h_0\chi_{E\vartheta}.
\end{aligned} \tag{2}$$

Here α is the parameter of the trigonal field that is represented in the Cartesian frames, $l_x^{(i)}, l_y^{(i)}, l_z^{(i)}$ are the direction cosines of the local trigonal axis directed from ion with number i towards the opposite oxygen ion ($\vec{l}_1 = [\bar{1}\bar{1}\bar{1}], \vec{l}_2 = [\bar{1}1\bar{1}], \vec{l}_3 = [\bar{1}\bar{1}1]$), h_0 is the parameter describing the low-symmetry (rhombic) component of the crystal field produced by the cation vacancy. The explicit form of the orbital operators $\chi_{E\mu}$ depends upon the state of ion with configuration $3d^4$. For the orbital doublet ($3d^4(t_{2g}^3e_g)$ configuration) they are given by Pauli matrices:

$$\chi_{E\vartheta} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad \chi_{E\varepsilon} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{3}$$

The standard basis of the cubic E doublet $E\vartheta$ and $E\varepsilon$ ($\vartheta = 3z^2 - r^2, \varepsilon = \sqrt{3}(x^2 - y^2)$) is used.

For ion with configuration $d^4(t_{2g}^2e_g^2)$ the orbital operators are determined on the trigonal basis functions E_+ and E_- in the following way:

$$\chi_{E\vartheta} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \chi_{E\varepsilon} = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}. \tag{4}$$

The resonant interaction in an impurity cluster resulting in the hole delocalization can be described by the following Hubbard type Hamiltonian:

$$H_{res} = \sum_{m \neq m_1} \sum_{\beta,\gamma} \big(t_{\beta\gamma}^{mm_1} c_{m\beta\sigma}^{+} c_{m_1\gamma\sigma} + \text{h.c.}\big), \tag{5}$$

where $c_{m\beta\sigma}^{+}$ and $c_{m\beta\sigma}$ are the creation and annihilation operators of e_g- or t_{2g}-hole on the center m in an orbital state β and spin projection is σ. For the sake of simplicity we assume that the Hund coupling (ferromagnetic intraatomic exchange interaction) is much larger than the hopping integrals $t_{\beta\gamma}^{mm_1}$ that seems to be a realistic assumption. The following hopping integrals are non-vanishing in the case of 90° metal–ligand–metal angle and trigonal symmetry of the cluster where the local coordinate systems linked to the ions coincide with the cubic axes X, Y, Z:

$$\begin{aligned}
&t_{3z^2-r^2,3z^2-r^2}^{12} = t_{3y^2-r^2,3y^2-r^2}^{13} = t_{3x^2-r^2,3x^2-r^2}^{23} = t_1, \qquad t_{x^2-y^2,x^2-y^2}^{12} = t_{z^2-x^2,z^2-x^2}^{13} = t_{z^2-y^2,z^2-y^2}^{23} = t_2,\\
&t_{xy,xy}^{12} = t_{xz,xz}^{13} = t_{yz,yz}^{23} = t_3, \qquad t_{xz,xz}^{12} = t_{yz,yz}^{13} = t_{xy,xy}^{23} = t_4, \qquad t_{yz,yz}^{12} = t_{xy,xy}^{13} = t_{xz,xz}^{23} = t_5,\\
&t_{yz,xz}^{12} = t_{xy,yz}^{13} = t_{xz,xy}^{23} = t_6, \qquad t_{3z^2-r^2,xy}^{12} = t_{3x^2-r^2,yz}^{13} = t_{3y^2-r^2,xz}^{23} = t_7.
\end{aligned} \tag{6}$$