Magnetooptics of Pr$^{3+}$ Ions in Trigonal Ca-Gallogermanate Ca$_3$Ga$_2$Ge$_4$O$_{14}$

Mariya M. Malysheva, Uygun V. Valiev, Vasiliy O. Pelenovich and Dejun Fu

ABSTRACT

Experimental investigation of magnetic circular dichroism (MCD) at the temperatures 90K and 300K was carried out in the visible region in disordered trigonal Ca-gallogermanates Ca$_3$Ga$_2$Ge$_4$O$_{14}$ doped with small concentration (~5 at.%) of Pr$^{3+}$ rare-earth (RE) ions. The spectral dependences of MCD (magnetic dichroism) spectra were measured within 400-500 nm. It was found that the squares of MCD bands increased in magnitude with decreasing temperature. The MCD bands belong to the forbidden (in parity) 4f→4f transitions $^3$H$_4$→$^3$P$_2$ ($\lambda = 450$ nm) and $^3$H$_4$→$^3$P$_1$ ($\lambda = 475$ nm) and the results undoubtedly indicated the existence of the so-called "paramagnetic" contribution (C-term of MCD in Ca$_3$Ga$_2$Ge$_4$:Pr$^{3+}$. From the spectral dependence of MCD in the $^3$H$_4$→$^3$P$_2$ transition we conclude that the so-called “diamagnetic” contribution (A-term) to MCD is not so small. We have determined the “paramagnetic” constants C for the transitions to the $^3$P$_2$ and $^3$P$_1$ multiplets in accordance to the formula of the temperature dependence of zero moment<$\theta_0$> (or square) of MCD bands at $\lambda = 450$nm and 475 nm.$^1$

INTRODUCTION

It is well-known that a dominant contribution to the mechanism for “removal” of the parity prohibition for the 4f→4f transitions in rare-earth (RE) compounds

---

$^1$Mariya M. Malysheva and Uygun V. Valiev, Faculty of Physics, National University of Uzbekistan, Tashkent 100174, Uzbekistan
Vasiliy O. Pelenovich and Dejun Fu, School of Physics & Technology, Wuhan University 299 Bayi Rd, Wuchang Distr., 430072 Wuhan, China
can be made by the odd parity crystal field (CF) components, which mixes states
of the excited configurations 4f\(^{n-1}\)5d \((l' = 2)\) and 4f\(^{n-1}\)5g \((l' = 4)\) with the states of
the ground 4f\(^n\) \((l = 3)\) configuration of the RE\(^{3+}\) ion [1,2]. In this case, the \(\Delta S = 0\)
spin prohibition for the 4f \(\rightarrow\) 4f transitions under investigation is removed in the
second order of the perturbation theory by the spin-orbit interaction mixing of
multiplets having \(\Delta S = 1\). In the Judd-Ofelt theory approximation for the 4f \(\rightarrow\) 4f
transition the parameters \(\Omega_\lambda\) (\(\lambda = 2, 4, 6\)) for a given rare earth ion-host
combination [3] can be determined by the fitting of the expression (1) to the
observed oscillator strengths \(f\) for the intermultiplet transition \((LSJ \rightarrow L'S'J')\):

\[
f(LSJ; L'S'J') = \frac{4\pi m}{3h(2J+1)\lambda_{JJ'}e^2n^2} \sum_{\lambda = 2, 4, 6} \Omega_\lambda \cdot |< LSJ // U^{(\lambda)} // L'S'J' |^2\]  (1)

where \(n\) is the mean refractive index and \(\chi_{ed}\) is the Lorentz correction for the
RE-ion at the wavelength \(\lambda_{JJ'}\) of the absorption representing the transitions
between the multiplets; \(L, S, J\) and \(L', S', J'\) are the corresponding angular
moments of the ground and excited multiplets of the RE-ion, respectively,
combining in 4f \(\rightarrow\) 4f transition; the doubly-reduced tensor operators
\(< LSJ // U^{(\lambda)} // L'S'J' >\), which are generally taken to be host invariant [1-3].

Note that the \(\chi_{ed} = \frac{9}{(n^2 + 2)^2}\), for the transitions under consideration. Once the
Judd-Ofelt parameters \(\Omega_\lambda\) are determined, they can be used to calculate the
oscillator strengths and other transition properties between ground and excited
states of the RE-ion in crystal.

A similar mechanism of the forbidden 4f \(\rightarrow\) 4f transitions “permission” seems
to play an essential role in the magnetooptics of RE-compounds, as well. For
instance, in Refs. [4-6], a theoretical scheme similar to that of the Judd-
Ofelt theory [1-2] was used to interpret the magnetooptical spectra caused by the
forbidden 4f \(\rightarrow\) 4f transitions. This scheme contains several phenomenological
parameters \(F_\lambda\) (usually there are three, i.e., \(\lambda = 2, 4, 6\), but in some cases there may
be fewer) depending on the asymmetrical electrostatic field of the RE-ion
environment in the media (crystal, paramagnetic glasses, and solutions).
According to [4-6] the corresponding expression for the MCD "paramagnetic"
contribution (i.e., C-term of MCD) can be written as:

\[
C = \frac{1}{(2J_0 + 1)} \sum_\lambda \left| F_\lambda \right|^2 (-1)^{\lambda} \left[ J_0 \begin{array}{c} L_0 \\ J_0 \end{array} S_0 \right] \left\{ \begin{array}{c} \lambda \\ \lambda \end{array} \right\} \left[ \begin{array}{c} \lambda \\ J_0 \end{array} \right] \cdot g_0 \cdot |< J_0 \| U^{(\lambda)} \| J_0 > | \cdot |< L_0 S_0 \| U^{(\lambda)} \| L S_0 > |
\]  (2)
Here is the 6j-symbol [5,6]; $g_{0}$ is the Lande factor of the ground $L_{0}S_{0}J_{0}$ multiplet RE-ion under consideration. $F_{\lambda}$ parameters can be determined from the magneto-optical experiment and are common for all electronic transitions within the RE-ion 4fn ground configuration. Let us now consider this theoretical scheme in more detail; the interpretation of the magnetic circular dichroism (MCD) spectra [4] are caused by the parity-forbidden intra-configurational 4f→4f transitions in the specific case of disordered RE-compounds (solutions, paramagnetic glasses etc.). Then according to [5,6], the main factor determining the features of an energy spectrum and wave functions of the RE-ions in disordered media are the fluctuations of the local parameters of both the even and odd crystal fields. Indeed, supposing that the CF parameter fluctuations are independent, and performing the statistical averaging of the odd CF coefficient combinations over all possible orientations of RE-centers in disordered media, we can obtain the following useful expression [5,6]:

$$F_{\lambda} = \sqrt{\frac{2}{3}} \sum_{\tau} (2\lambda + 1) \left[ \frac{\lambda}{1} \frac{1}{\lambda} t \right] \Omega_{\lambda}(t)$$  \hspace{1cm} (3)

where $\Omega_{\lambda}(t)$ is the partial contribution to the Judd-Ofelt parameter $\Omega_{\lambda}$ due to a specific value of $t$, i.e., $\Omega_{\lambda} = \sum_{t} \Omega_{\lambda}(t)$. Now apply this scheme to the consideration of the magneto-optical features in the disordered trigonal Ca-gallogermanates Ca$_3$Ga$_2$Ge$_4$O$_{14}$ doped with small concentration (~5%) of Pr$^{3+}$ ions.

Figure 1. MCD spectral dependences at T = 90 K (- • -) and 300 K (- • -) of Ca$_3$Ga$_2$Ge$_4$O$_{14}$ doped by Pr$^{3+}$ (5%) ions (Inset: Optical absorption spectrum at T = 300 K.).
The absorption spectrum of the Ca$_3$Ga$_2$Ge$_4$O$_{14}$:Pr$^{3+}$, recorded at $T = 300$ K in the region of absorption bands due to $4f \to 4f$ transitions in Pr$^{3+}$ ion: $3H_4 \to 3P_2$ ions ($\lambda = 450$ nm), $3H_4 \to 3P_1$ ($\lambda = 475$ nm) and $3H_4 \to 3P_0$ ($\lambda = 485$ nm) gives convincing evidence about of a fairly significant degree of disorder in the crystal environment of the rare earth ion in this compound. In Fig. 1, both the broadening of the considered absorption lines and their strong overlap in the range of 400-500 nm caused by this disorder of CF are clearly visible (see inset in Fig. 1). At the same time the spectral dependences of MCD spectrum measured in this crystal at $T = 90$ K and 300 K are presented in Fig.1. As one can see from this figure the squares of MCD bands are increasing in a magnitude with the decrease of temperature in range of the forbidden (in parity) $4f \to 4f$ transitions $3H_4 \to 3P_2$ ($\lambda = 450$ nm), $3H_4 \to 3P_1$ ($\lambda = 475$ nm) and $3H_4 \to 3P_0$ ($\lambda = 485$ nm), which undoubtedly indicates on an existence of the so-called "paramagnetic" contributions, i.e., C-terms of the magnetooptical activity (MOA) [4-6] for the observed MCD bands in Ca$_3$Ga$_2$Ge$_4$:Pr$^{3+}$. From the type of the spectral dependence of MCD at the $3H_4 \to 3P_2$ transition we conclude that the so-called “diamagnetic” contribution (A-term [4-6]) to the MCD is not so small.

We have determined the “paramagnetic” constants C for the transitions to the 3P$_2$, 3P$_1$ and 3P$_0$ multiplets in accordance to the well-known formula for the temperature dependence of zero moment <$\theta_0$> = \int_{\omega_{onband}}^{o} \theta d\omega \text{ of MCD bands [5,6] at } \lambda=450\text{nm, } 475 \text{ nm and } 485 \text{ nm in the temperature range } 90-300 \text{ K. For example, we have found that the ratio of the “paramagnetic” contributions C for the transitions } 3H_4 \to 3P_1 \text{ and } 3H_4 \to 3P_0 \text{ is equal, } C(3P1):C(3P0)=(-1.14):(-1.0), \text{ that well affirms by the experimental data given in Fig.1. Using further the fact that the ratio of the “paramagnetic” contributions C for the transitions from ground multiplet } 3H_4 \text{ into the multiplets } 3P_2 \text{ and } 3P_1 \text{ of Pr}^3+ \text{ ions one can expressed by the ratio F6:F4 parameters for the } 4f \to 4f \text{ transitions according to the formula [4]}
\[
\frac{C(3P2)}{C(3P1)} = 3.8+ 2.6(F6/F4)
\]

Then we can find the ratio of the Judd's parameters of intensity of transitions $\Omega_6:\Omega_4$ using the MCD experimental data for the crystals Ca$_3$Ga$_2$Ge$_4$O$_{14}$:Pr$^{3+}$ (see Fig.1) and compare the magnitude of experimentally determined the ratio $\Omega_6:\Omega_4$ with analogous ratio obtained from absorption measurements for is ostructural crystal La$_3$Ga$_5$Si$_4$O$_{14}$:Pr$^{3+}$ [7]. In this case for transitions to the multiplet 3P$_0$ and 3P$_1$ one can to confine oneself to only the value of the transition angular moment $\lambda = 4$ (following the “triangle rule” for the 6j-symbols [5,6]), while for transition to 3P$_2$ the $\lambda = 4,6$ (from the “triangle rule” for (J J0 $\lambda$) and (L L0 $\lambda$) [5,6]). An assumption about the admixing" of the mixed excited $4f(n-1)5d$ configuration (l′= 2) states to the states of the ground 4f(n) configuration (l = 3) by the odd CF permits us to keep the terms with $t = 3,5$ of
the crystal potential odd spherical harmonics, following the “triangle rule” for 3j -
symbols in expression for C-term [5,6]. Because the C-term of MCD depends on
contributions with different t (at definite λ) these ones always partly compensate
each other, so one can choose some contribution of odd CF with the definite t
(and λ) which plays the substantial role in mechanism of the permission of the
forbidden 4f→4f transition [5].

In this case one can choose the t = 5 index of the odd CF potential for
experimental estimation of the ratio of Judd-Ofelt parameters equal to Ω6:Ω4 =
2.0 using the results of above-mentioned MCD measurements in
Ca3Ga2Ge4O14:Pr3+, while for an isostructural crystal La3Ga5SiO14:Pr3+ this
ratio is Ω6:Ω4 = 2.5 [7]. Besides using the so-called dipole “transition strength”
D (proportional to the oscillator strength f [5,6]) we have carried out the
estimation of the magnetooptical activity (MOA) factor C/D value for MCD
bands at λ = 450 nm and 475 nm. It appears that for 4f→ 4f transitions to the
multiplet 3P2 and 3P1 the experimental determined values of C/D ratio are equal
to 0.8 $\mu_B$ and -0.7 $\mu_B$, respectively, while the theoretical estimation of C/D factor
at the λ = 4, t = 5 parameters (for multiplet 3P1) and λ = 4,6; t = 5 (multiplet 3P2)
leads to the C/D values equal respectively,-1.5 $\mu_B$ and 1.6 $\mu_B$ for 3H4→3P1 and
3H4→3P2 transitions, respectively, which generally speaking exceed the
experimental data on the module but while coincide with them by sign.

REFERENCES

6. U.V. Valiev, J.B. Gruber, G.W. Burdick. 2012. Magnetooptical Spectroscopy of the Rare -
139.