Applications of the Generalized-High Accuracy Universal Polarimeter (G-HAUP) to Solid State Sciences

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The optical study on condensed matters is a powerful tool for investigating spatial symmetry breaking and/or time-reversal symmetry breaking. Optical activity (OA) and circular dichroism (CD) are related to spatial and time-reversal symmetry. Natural OA and CD, which are reciprocal signals, were observed when the spatial symmetry was broken. On the other hand, Faraday rotation and magnetic circular dichroism, which are non-reciprocal signals, were observed when the time-reversal symmetry was broken. [1] Here, we emphasize the consideration of linear birefringence (LB) and linear dichroism (LD) in the measurement of OA and CD in anisotropic crystals. LB and LD are optical anisotropies that denote the difference in refractive indices and absorptions, respectively, between two orthogonally polarized lights in an anisotropic crystal. Schellman *et al.* [2] reported that LB and LD signals are usually 10^3–10^5 times larger in magnitude than OA and CD signals. Therefore, the accurate separation of OA and CD from LB and LD is a challenge. Furthermore, Shindo *et al.* [3] pointed out that optical elements, devices, and detectors installed in polarization modulation spectroscopy cause serious systematic errors and non-negligible artifacts. This critical issue has been widely recognized in the field of chiral science. Many research groups have developed optical measurement theories and polarimeters to overcome this issue. Eventually, OA and CD in the anisotropic condensed matter were successfully measured. In particular, we developed a novel optical apparatus called the generalized-high accuracy universal polarimeter (G-HAUP), which simultaneously measures the wavelength dependences of the OR, CD, LB, and LD in an anisotropic medium. [4–10] Regardless, some researches in the field of magneto-optics neglected optical anisotropies, systematic errors, and artifacts in OA and CD measurements.

This study investigates the wavelength dependences of linear birefringence, linear dichroism, Faraday rotation and magnetic-circular dichroism in a single crystal rare-earth fluoride, namely CeF_3. The subject material selected Faraday rotator in the present study CeF_3 single crystal, is characterized by its wide transparency range (300 nm to 2500 nm) and an outstanding Verdet constant, besides of being uniaxial. Cerium is usually found as a trivalent ion Ce^{3+} in condensed matter. The electronic configuration of Ce^{3+} is $1s^2 2s^2 2p^6 \dots 4d^{10} 4f^1 5s^2 5p^6$. Electronic transitions from $4f$ to $5d$ confer the magneto-optical properties observable in the UV-Vis-IR region1. In a previous report, the refractive indices of the ordinary and extraordinary light rays in single crystal CeF_3 at 633 nm were determined as 1.616 and 1.609, respectively. Therefore the LB is 0.007, comparable to that of the α-quartz crystal along its a axis. Even at this low order of LB magnitude (10^{-3}), the OR of the crystal cannot be accurately measured by conventional optical apparatuses [16]. Previously, When a sample is subjected to a magnetic field applied parallel/anti-parallel to the light propagation direction, the G-HAUP can measure its FR and Magnetic-CD (MCD). In this study, we measured the wavelength dependences of the FR, MCD and optical anisotropy in CeF_3 single crystal along the optic axis (c axis) and perpendicular to the optic axis (a axis) with the G-HAUP. [9] A magnetic field parallel/anti-parallel to the light propagation was generated by Nd-Fe-B (NIB) magnets introduced for that purpose.

We prepared a 307-μm thick (001) plate of single-crystal CeF_3 by polishing. In structure, the CeF_3 crystal belongs to the uniaxial and optically inactive crystal point group D_{3d}. Therefore, when the magnetic field is applied parallel to the light propagation direction, FR occurs only along the c axis. To apply the magnetic field parallel or anti-parallel to the light propagation direction, we mounted the sample on a pinhole plate, and sandwiched it between two ring NIB permanent magnets. The wavelength dependences of the Verdet constant along the *c* axis at 25 °C are plotted as black rhombuses in Fig. 1(c). The Verdet constants along the *c* axis were positive over the observed wavelength region, indicating that the right-handed circularly-polarized light propagates faster than its left-handed counterpart.

We then prepared a 58.0-μm thick (100) plate sample of single-crystal CeF_3 by polishing. Before measuring the magneto-optical properties, we determined the wavelength dependences of the LB, LD, OR and CD along the *a* axis in the absence of the magnetic field at 25 °C (blue rhombuses in Fig. 1). The LB along this axis was of the same order of magnitude as the LB of α-quartz crystal (Fig. 1(a)). However, the LDs were almost zero over the wavelength region (Fig. 1(b)). This result is consistent with the UV-Vis spectrum, which exhibits no significant absorption above 282 nm.

Then, the wavelength dependences of the LB, LD, FR, and MCD along the *a* axis under a magnetic field parallel to the light propagation direction at 25 °C were measured (red rhombuses in Fig. 1). In general, reversing the magnetic field direction inverted the signs of FR and MCD. Therefore, in order to obtain accurate spectra, we applied the magnetic field anti-parallel to the light propagation direction, re-measured the wavelength dependences, and averaged the absolute magnitudes of both sets of measurements. The values of LB and LD hardly changed with and without the magnetic field (Fig. 1(a,b)). The Verdet constants along the *a* axis were positive throughout the wavelength region (Fig. 1(c)).

In conclusion, the wavelength dependences of LB, LD, FR and MCD were investigated along the *a* and *c* axes of single crystal CeF_3 under an applied magnetic field. These measurements were successfully collected by the G-HAUP equipped with NIB magnets. The Verdet constants along the *c* and *a* axes were positive and nearly equal in magnitude in the measured wavelength region.

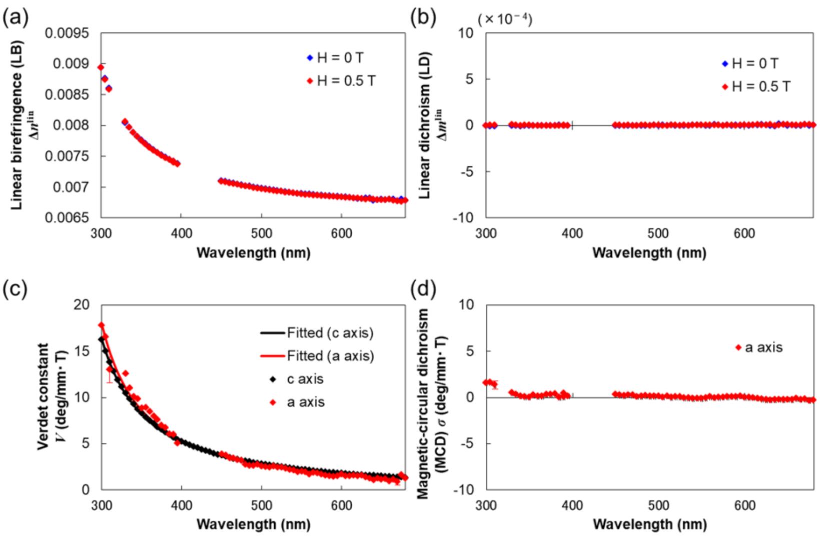

Figure 1. Wavelength dependences of the LB (a), LD (b), Verdet constant (c) and MCD (d) in single-crystal CeF_3 at 25 °C. Reproduced from Ref. [9] with permission from Springer Nature.

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