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Band Structure and Special Features of the Optical Properties of Rare-Earth Molybdates

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The reflectivity of gadolinium and dysprosium molybdates has been measured between 0.1 ~ 35 eV using synchrotron radiation. The data have been Kramers-Kronig analyzed. From the measurements carried out, we determined the characteristic constants for gadolinium molybdate.

§1. Introduction

Molybdate of rare-earth elements, improper ferroelectrics are interesting objects of investigation,[1~3] as most of them show anomalies of physical properties closely associated with the machanisms involved in the origination of ferroelectricity. On the other hand, a number of special physical properties of the rare-earth molybdates make them promising materials for use in optoelectronics.[3]

Gadolinium molybdate (GMO)-$Gd_2(MoO_4)_3$ is a representative of this family of improper ferroelectrics that has received the most of the study.[1~3] A certain amount of data has been accumulated, especially on the dielectric and electro-, piezo- and acoustooptical properties, and on the domain structure of GMO; a smaller body of data is available on their optical properties,[4~5] though the optical constants are likely to be very sensitive to the typical mechanisms involved in the origination of improper ferroelectricity.[6] In this connection the investigations of the optical properties of the GMO in the fundamental absorption region, the effect of the phase transition (PT) on the optical properties, and the structural variations associated with reduction in the symmetry in the transition from nonpolar to polar phase are of some interest. The investigation of the optical properties gives also a wealth of information on the band structure, the electronic states in the crystal and their variations at PT. All of these properties are determined and a set of questions are dealt with in the present paper.

This paper gives the data resulting from a study of the optical properties of GMO and $Dy_2(MoO_4)_3$-DMO in the energy region from 0.1 to 35 eV and in the temperature range from 15 to 600 K covering the PT region, with polarized light.

§2. Experimental Procedure and Treatment of Crystals

The light source was the electron storage ring at the SSRL of the Stanford University.

The monochomator was an ion-pumped McPherson 225 (I-m, normal incidence) used primarily with a 1200 line/mm ($Al+MgF_2$)-coated grating.

The detector was a Bendix channeltron. Data acquisition was based on SSR model Digital Synchronous Computer. It was most commonly used in the chopper mode with the monitor signal as an external clock.

Separate wavelength scans were made for the incident beam (I_0) and reflected beam. Because of the stability of the source and the use of the beam splitter, several different reflectivity runs were made for each I_0, resulting in a great improvement in efficiency. Also, use of a monitor made it possible to normalize the runs for the beam decay, and reduced the effect of change in intensity as a function of wavelength. The normalization for the wavelength dependence of I_0 was not perfect, because the portion of the beam transmitted by the beam splitter is weighted to short wavelengths. Nevertheless, the I_0 spectrum is flat enough so that the approximate reflectivity can be determined from the strip chart. Accurate determination of R requires dividing by I_0. For a few runs this was carried out with printed teletype output. The major data reduction was done in off-line using the paper tape from the teletype and IBM 360/75 computor.

A conventional modulation technique was used to conduct the measurements in the low-energy region of the spectrum. A VSU-2P spectrometer and a Xe-lamp were used to provide the monochromatic light.

§3. Experimental Results

The reflection spectra of GMO crystals were studied in the temperature range from 15 to 600 K and in the energy region $h\nu = 0.1 \sim 35$ eV. Figure 1 depicts the near-normal reflection spectrum ($\sim 10°$) of a Z-cut GMO single crystal at 300 K (curve 2). As seen in the figure, the reflection spectrum (R) is characterized by a structure consisting of 8 peaks and concentrated in two wide bands (3.67 eV, 3.91 eV, 4.42 eV, 4.93 eV, 5.35 eV; 8.25 eV, 10.11 eV, 15.40 eV) in the energy region $h\nu = 1.0$ to 16 eV with reflectivities less than 30%. As the energy from the incident photons increases, a step of decay reflectivity is observed, which is associated with the collective oscillations of valence electrons-plasmons. After this takes place, no structure is observed at energies above 16 eV. Lowering of the temperature causes the R spectrum to become complicated and brings about the splitting of some peaks, the appearance of new peaks and the disappearance of the peaks observed at room temperature and above. All these changes are accompanied by decrease in the reflectivity below 20%, and in this case the temperature shift of the energy position of the peaks is insignificant. Measurements of GMO reflection spectra, conducted with samples of different shearing cuts, have shown that the R-spectra of X- and Y-cuts are similar to each other, but differ greatly between those of Z- and XY-cuts. Such spectra are also observed in DMO.

Besides, we have calculated the transmission and reflection spectra in the low-energy spectral region ($h\nu = 0.1$ to 4 eV) in more detail. The

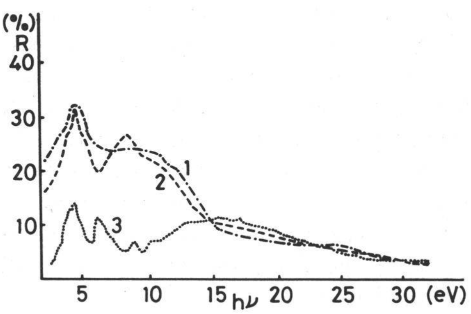

Fig. 1. The spectral dependence of reflectivity for GMO, Z-cut: 1–450 K, 2–300 K, 3–15 K.

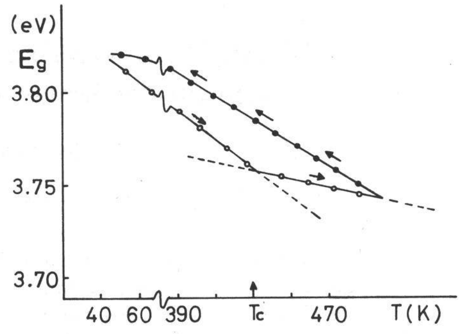

Fig. 2. The temperature dependence of E_g for GMO, XY-cut.

results of measurements carried out showed that the absorption edge up to 700 cm^{-1} is badly smeared-out and is of an exponential nature. Based on these measurements, the forbidden gap E_g (Fig. 2) and its temperature behaviour in the PT region have been determined in the ferroelectric and paraelectric phases. Measurements have shown the presence of a hysteresis in the temperature dependence of E_g (determined at the level ~ 800 cm^{-1}). This hysteresis is observed only in the measurements conducted with the XY-th cut crystals and is not observed with those of other directions. Such a typical feature of E_g in the PT region was observed for all the different crystals measured.

§4. Discussion

The Kramers-Kronig analysis was applied to calculate the spectral dependences of the optical constants, the real (ε_1) and imaginary (ε_2) parts of the dielectric constant, as well as the value Im ε^{-1}, characterizing the energy losses of electrons (Fig. 3) from the measured reflection spectra of GMO crystals. As seen in the figure, ε_2 has a structure above 4 eV. Lack of calculation of the band structure makes it difficult to interpret the experimental results and to identify the observed peaks to some interband transitions. In this connection one can only note the presence of a certain interrelation between the reflection spectra and the structural variations taking place in GMO at PT. And the presence of anisotropy in the reflection spectra points out the different nature of interband transitions and the proper rules of selection along various high-symmetry directions. All these differences are indicative of the difference of the spontaneous deformation in GMO because of the selection rules and the

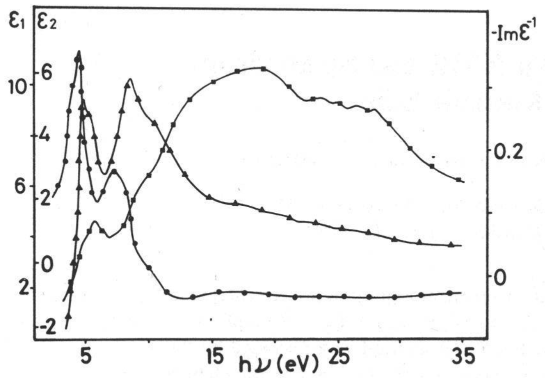

Fig. 3. The energy dependence of real (ε_1, ●-●-●) and imaginary (ε_2 ▲-▲) parts of the dielectric constant and Im ε^{-1}, characterizing the losses of electrons (■-■-■) for GMO, *Z*-cut; $T=300$ K.

formation of the band structure in GMO. In the Im ε^{-1} spectrum, a few maxima are observed, which characterizes the frequencies corresponding to the plasma oscillations. The sum of oscillators for the valence band is known to deplete with increasing energy of incident photons, and the steep drop of the reflectivity and nullification of the imaginary part of the dielectric constant are observed. One may think that in this region the valence electrons are unbounded and can take part in collective oscillations. The frequency of plasma oscillations can be determined from the Im ε^{-1} maximum. In a higher-energy region of the spectrum a drop of the Im ε^{-1} value is observed. This confirms indirectly that in GMO the d-zones are very far removed from the valence bands. It may be thought that the conduction band and valence band are very far from the other zones in energy (at least by 20 eV to 25 eV). The other peaks may be interpreted as interband transitions (in the Im ε^{-1} spectrum). However, at present it is somewhat difficult to reveal the conformity of these peaks to one or another of the transitions. Calculating and plotting the spectral dependence of Im ε^{-1} we observed a special feature that consisted of the following. Above the Curie point the first two peaks disappear, whereas the peak at $E=18.7$ eV shifts towards the long waves. As this takes place, the amplitude of the Im ε^{-1} value decreases steeply and shows a maximum of "smearing-out." Similar variations are observed also in the behaviour of ε_2, but in Im ε^{-1} these variations manifest themselves more distinctly. All these calculations brought us to revise our views concerning the behaviour of the plasma oscillations of valence electrons in ferroelectrics. For sure, the behaviour of the plasmons in conventional semiconductors, but how? More thorough experiments in the PT region and above the PT point will provide answers to all of these questions.

We also calculated $N_{\text{eff}} \sim \int_0^{\omega_0} E \cdot \varepsilon_2\,(E)\mathrm{d}E$,

$$\varepsilon_{\text{eff}} \sim \frac{2}{f}\int_0^{\omega_0} E^{-1} \cdot \varepsilon_2(E)\mathrm{d}E, \quad \omega_p^2 \sim N_{\text{eff}}$$

for GMO.

Investigations of the optical absorption edge in GMO have shown that the optical absorption edge obeys the modified Urbach rule. As this takes place, a dichroism of the optical absorption edge is observed ($\Delta E_g = 0.04$ eV at $T = 300$ K). In the higher-energy region ($\geqslant 4$ eV), mixed and crossover optical interband transitions are observed. From the measurements carried out, we determined the characteristic constants, the absorption edge steepness, the E_g temperature coefficients and other values characterizing the GMO absorption edge and the interband transitions at the absorption edge.

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