ANOMALOUS DISPERSION OF BIREFRINGENCE IN CRYSTALS OF EUROPIUM CHLORIDE HEXAHYDRATE

1962

SovietRxiv

Abstract

Full Text

PHYSICS

N. K. BELSKII

ANOMALOUS DISPERSION OF BIREFRINGENCE IN CRYSTALS OF EUROPIUM CHLORIDE HEXAHYDRATE

(Presented by Academician I. V. Obreimov, November 17, 1961)

By studying the course of birefringence near a strongly polarized absorption line in a crystal, one can obtain the same quantities as in the study of anomalous dispersion in a gas and in a solution.

Among noncubic crystals, it is not uncommon to find a case in which the spectrum contains a strictly linearly polarized absorption band. I. V. Obreimov pointed out to me the possibility of observing in such crystals the anomalous dispersion of birefringence with the aid of a quartz wedge (or Babinet compensator). The idea of the method is as follows (see Fig. 1). As is known ([1,2]), a Babinet compensator consists of two quartz wedges (in our case glued together with Canada balsam), having the same small angle α at the vertex. In one of the wedges the optical axis of the quartz (e in Fig. 1, K) is parallel to the edge of the wedge; in the other wedge it is perpendicular to the edge. The total thickness of the two wedges is equal to h. Thus, both outer faces of the wedges are parallel to one another.

Let us introduce coordinate axes. We direct the Z axis normal to the outer faces of the wedges, the Y axis parallel to the edges of the wedges, and the X axis perpendicular to the Z and Y axes. We place the origin at the point of the wedge for which the thicknesses of the two wedges are equal. If a plane monochromatic light wave is incident on the compensator normally to its surface, and its electric vector makes an angle of 45° with the optical axes of the wedge, then, on entering the wedge, it will split into two coherent waves, one of which will be polarized in the direction of the X axis, and the other in the direction of the Y axis. On emerging from the compensator, the phase difference between the two waves, as is known, will be equal to

$$\delta' = (\mu_e - \mu_o)(2d - h), \tag{1}$$

where d is the variable thickness of the first wedge

$$d = \alpha x \tag{2}$$

Figure 1

Figure 1: Figure 1

in wavelengths

$$\delta' = n\lambda, \tag{3}$$

λ is the wavelength of the light. From (1) and (3) we have

$$n = \frac{\mu_e - \mu_o}{\lambda}(2d - h). \tag{4}$$

If the compensator is placed between crossed Nicols, whose principal sections make an angle of 45° with the axes of the compensator, then the compensator (and the shadow behind it) will be crossed by a series of dark bands parallel to the Y axis. The centers of the dark bands will be where $n = 2k\pi$, and the light maxima where $n = 2(k+1)\pi$. With parallel Nicols, the dark and light bands will exchange places. If polarized white light is incident on the compensator, then the central band at $n = 0$ will be uncolored, while the others will be colored. From (1), (2), (3), and (4) it follows that the width of the bands is equal to

$$\Delta x = \frac{\pi\lambda}{\alpha(\mu_e - \mu_o)} \tag{5}$$

and depends on the wavelength both directly and through the dispersion of the birefringence in quartz.

If the image of the wedge is projected onto the slit of the spectroscope so that the bands cross the slit, the spectrum will be covered by a series of dark and bright bands; of these, the central one (bright or dark, depending on how the nicols are turned) will be strictly horizontal, while the others will broaden toward the red end of the spectrum and narrow toward the violet.

Fig. 1. Optical arrangement for observing dispersion in an $EuCl_3 \cdot 6H_2O$ crystal. L_1, L_2, L_3—lenses; N_1, N_2—nicols; O—specimen; K_v—quartz plate; K—compensator Babinet; $P.Z.$—rotatable mirror; Φ—photographic plate; the KSA-1 spectrograph is outlined by the dashed line.

Placing the plane-parallel crystalline plate under investigation in front of or behind the compensator and setting the direction of the vibrations in it parallel to the vibrations in the wedge, we find that the plate introduces its own path difference, in addition to the path difference introduced by the wedge. If μ_1 and μ_2 are the two refractive indices of the plate, and h' is its thickness, then the path difference introduced by the plate is

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

$$\delta'' = (\mu_1 - \mu_2)h'; \tag{6}$$

together with the path difference introduced by the compensator, we obtain

$$\delta = \delta' + \delta'', \tag{7}$$

and all the interference bands will be displaced by the amount (6). We shall denote this quantity by $\Delta n\lambda$. From (6) we obtain

$$\mu_1 = \mu_2 + \frac{\Delta n\lambda}{h'}.$$

Fig. 2. *A*—unit cell and axes of the optical indicatrix of the $EuCl_3 \cdot 6H_2O$ crystal; *B*—external appearance of the crystal.

In formula (8) the quantities μ_2, Δn, λ, h' are known.

In the case of rare earths, with their narrow absorption bands, all the calculations can be simplified. Namely, near an absorption band the quantities μ_2, μ_e, and μ_o may be taken as constant. Then μ_1 can be represented as the sum of two terms: the first, independent of the wavelength and having the meaning of the refractive index in the transparency region, and the second, varying rapidly near the absorption band.

The scheme of the spectral setup for observing anomalous dispersion is shown in Fig. 1. Here C is the light source, which is focused by lens L_1, through nicol N_1, onto the crystal under investigation. The crystal is oriented so that its principal sections make an angle of 45° with the principal sections of the polarizer and analyzer N_2, i.e., are parallel to the axes of the compensa-

To the article by N. K. Bel' skii, p. 1313

Fig. 3. Photograph of the spectrum of an $EuCl_3 \cdot 6H_2O$ crystal in the region of the ${}^7F_0$—${}^5D_0$ transition; a —the tilt of the bands is compensated by a quartz plate; b —without compensation

To the article by E. F. Gross and Chzhan Guan-in' , p. 1321

Figure 1

Figure 4: Figure 1

Fig. 4. Curve of birefringence as a function of frequency

Figure 5: Fig. 4. Curve of birefringence as a function of frequency

Fig. 1. Reflection spectrum from a Cu_2O single crystal in the ultraviolet region at $T = 77°$ K. a —maxima λ_1, λ_2, and λ_3 in the reflection spectrum of a Cu_2O crystal; b —emission spectrum of a hydrogen lamp in the same region

tor. The interference bands arising on the compensator are projected, by means of lens L_2, mirror $P.Z.$, and lens L_3, onto the slit of the spectrograph, in whose focal plane Φ the anomalous-dispersion pattern is obtained. To reduce the (generally harmful) reflection from the surface of the sample under study and to smooth out small surface defects (for example, dullness), it is useful to place the specimen being tested in a plane-parallel cuvette with an immersion liquid.

Fig. 4. Curve of birefringence as a function of frequency

With the aid of the setup described above, anomalous dispersion was observed in europium hexahydrate chloride. $EuCl_3 \times 6H_2O$ crystallizes in the form of plates elongated somewhat in length (i.e., along the c axis). The system is monoclinic. The unit cell* proved to be as follows: $a = 9.49 \pm 0.03$ Å, $b = 6.42 \pm 0.02$ Å, $c = 8.01 \pm 0.06$ Å, angle $\beta = 84°09' \pm 18'$; $z = 2$ (see Fig. 2). The developed face of the crystal plate is (010). Thus, the monoclinic axis is normal to the developed face of the crystal plate.

Extinction in crossed nicols is oblique. The principal refractive indices measured by me by the immersion method (^{3}) for the sodium D-line proved to be: $\mu_g = 1.5818$; $\mu_p = 1.5700$; $\mu_m = 1.5788$, $\mu_b = \mu_g$; the directions of the other two axes of the indicatrix are given in Fig. 2. The spectrum of hexahydrate europium trichloride has been analyzed in detail by Hellwege (^{4}). All electronic transitions corresponding to the visible spectrum begin from the level $^7F_0$. In the visible region of the spectrum, Hellwege gives the transitions from this level listed in Table 1.

Table 1

Wave numbers and wavelengths in the absorption spectrum of the salt $EuCl_3 \cdot 6H_2O$ at a temperature of 295° K

	$^7F_0 - {}^5D_0$	$^7F_0 - {}^5D_1$	$^7F_0 - {}^5D_2$
λ, cm$^{-1}\lambda$, Å	17 259.65 792.28	19 003.05 260.86	21 455.94 659.47
ν, cm$^{-1}\lambda$, Å	Singlet	19 025.25 254.73	21 487.24 652.63
ν, cm$^{-1}\lambda$, Å		19 027.85 254.01	21 489.04 652.25
ν, cm$^{-1}\lambda$, Å		Triplet	21 514.64 646.70

	$^7F_0 - {}^5D_0$	$^7F_0 - {}^5D_1$	$^7F_0 - {}^5D_2$
ν, cm$^{-1}\lambda$, Å			21 522.44 645.02
			Quintet

Of all the lines of the spectrum, only the line $^7F_0 - {}^5D_0$ is well isolated. It is polarized strictly parallel to the b axis. Therefore observations of anomalous dispersion were made on a plate from a crystal of europium chloride, cut from the crystal as shown by the dotted line in Fig. 2, and ground to a thickness of 3.15 mm. The plate was placed in a cuvette with an immersion liquid and set in the apparatus of Fig. 1. A photograph of the spectrum with anomalous dispersion at the line 17 259.6 cm^{-1} is shown in Fig. 3. In Fig. 3b the interference bands are not horizontal. This is explained by the fact that, in addition to the anomalous dispersion at the absorption band, there is a general variation of the birefringence in the crystal. If the general inclination of the interference band interferes with the measurements, the bands can be made horizontal by placing behind the measured crystal a quartz or mica plate of such thickness that it compensates the dispersion of the birefringence in the europium salt, as is shown in Fig. 3a. The course of the curve of birefringence was measured from the photograph in Fig. 3b. Fig. 4 gives the curve obtained (wave numbers are plotted on the abscissa axis, and on the ordinate axis—the difference of the refractive indices near and far from absorption band). As is known (⌒5), in the case of a gas the relation

$$(\nu_{\max} - \nu_{\min})(\mu_{\max} - \mu_{\min}) = f\,\frac{Ne^2}{2\pi c^2 m \nu_0},$$

must hold, where N is the number of absorbing centers in 1 cm^3 of the crystal; e is the electron charge; m is the electron mass; c is the speed of light; ν_0 is the wave number at the center of the absorption band; f is the so-called oscillator strength; $\mu_{\max}$ and $\mu_{\min}$ are the values of the maximum and minimum on the dispersion curve; $\nu_{\max}$ and $\nu_{\min}$ are the corresponding frequencies. From Fig. 4, $\nu_{\max} - \nu_{\min} = 6$ cm^{-1}, $\mu_{\max} - \mu_{\min} = 6.3 \cdot 10^{-5}$. The error in determining $\nu_{\max} - \nu_{\min}$ and $\mu_{\max} - \mu_{\min}$ does not exceed, respectively, 2 cm^{-1} and $2 \cdot 10^{-5}$.

Measurements of the band shape and of the oscillator strength for a crystal of the hexahydrate salt of europium trichloride were carried out by Hellwege and Kahle (⌒4) by the method of photometry of a photograph of the absorption spectrum of this salt, taken on a 6-meter grating. Their results are substantially different from the result of the present work, namely: the half-width according to Hellwege is 2 cm^{-1}, instead of 6 cm^{-1} in the present work, and the oscillator strength according to Hellwege is $2.2 \cdot 10^{-9}$ instead of $3.5 \cdot 10^{-8}$, i.e., 16 times smaller.

* Determined by Yu. T. Struchkov.

At present I cannot say whether this large discrepancy has instrumental causes (Hellwege' s spectral instrument dispersion was 1–2 Å/mm, mine 18 Å/mm) or whether it is based on deeper reasons–the inapplicability to a crystal of conclusions from the dispersion formula derived for a gas.

The author expresses deep gratitude to I. V. Obreimov for guidance and assistance in the work, and to Yu. T. Struchkov for determining the parameters of the unit cell of the europium hexahydrate chloride crystal.

Institute of Organoelement Compounds
of the Academy of Sciences of the USSR

Received
13 XI 1961

REFERENCES

1. G. S. Landsberg, *Optics*, 2nd ed., Moscow–Leningrad, 1947, p. 258.
2. S. E. Frish, A. V. Timoreva, *Course of General Physics*, 3, 4th ed., 1957, §§ 291, 292, p. 197.
3. I. V. Obreimov, *On the Application of Fresnel' s Formula for Physical and Technical Measurements*, Publishing House of the Academy of Sciences of the USSR, 1945, p. 43.
4. K. H. Hellwege, H. G. Kahle, *Zs. Phys.*, **129**, 62 (1951).
5. G. A. Lorentz, *Theory of Electrons*, 2nd ed., Moscow, 1953.

Note: Figure translations are in progress. See original paper for figures.