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Abstract

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CRYSTALLOGRAPHY

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POLARIZATION DIAGRAMS OF THE LUMINESCENCE OF STILBENE SINGLE CRYSTALS

(Presented by Academician A. V. Shubnikov, 5 IV 1957)

Polarization diagrams of the luminescence of crystals, showing the dependence of the degree of polarization on the direction of observation, make it possible to solve an important problem—determining the orientation of molecules in the crystal lattice.

In a previous work by one of the authors ⁽¹⁾, the polarization diagrams of single-crystal plates of anthracene were investigated, and it was shown that, if corrections for birefringence are taken into account, the experimental diagrams agree qualitatively with diagrams calculated on the basis of X-ray structural data. Introducing corrections substantially complicates the matter, since, first, it is associated with rather cumbersome calculations and, second, it requires knowledge of the optical anisotropy of the crystal (indicatrix), which is a rather laborious experimental task.

However, for directions close to the normal to the crystal surface ($\pm 20^\circ$), the corrections are very small; they become significant only at large angles between the normal and the direction of observation. This suggests modifying the experimental conditions so that, in all directions, the luminescence light falls normally on the crystal surface. Such conditions can be obtained if crystals of spherical shape are used and the luminescence is excited at their center.

In the present work, such investigations were carried out on spherical stilbene crystals. To excite luminescence at the center, the spheres were cut along diametral planes of definite orientation. The polarization diagrams were measured on the polarization-goniometric setup described in ⁽¹⁾, with excitation by radiation from a mercury lamp of wavelength $365\text{ m}\mu$.

Preliminarily, for each hemisphere, the dependence of polarization on the angle of rotation of the crystal about a horizontal axis coinciding with the axis of the setup (the azimuthal dependence) was measured, and crystal positions were determined with such an orientation at which the polarization has a maximum positive or maximum negative value. In these positions the polarization diagrams, respectively “positive” and “negative,” were measured.

The specimens were prepared from stilbene single crystals grown in a sealed test tube by the Obreimov-Shubnikov method. A large single crystal was sawn into smaller pieces of the required size, which were then given a spherical shape with the aid of a rotating tube and emery; the resulting sphere was polished with a soft cloth moistened with kerosene by rotation in the same tube. After such treatment, perfectly transparent balls with an even polished surface were obtained. The diameter of the balls was from 10 to 25 mm.

Stilbene is a biaxial crystal. The spherical shape of the specimen makes it possible, from the conoscopic figure, to see and mark on the surf-

ness of the sphere and the exits of the optical axes by the method proposed by A. V. Shubnikov ⁽²⁾.

The angle between the optical axes of stilbene is large; therefore it is not possible to see the exits of both axes at once. This can be done by rotating the sphere and noting the exit first of one axis and then of the other. The specimens were oriented by the exits of the axes. The sphere was ground down to a hemisphere. The section was polished with cloth moistened with kerosene.

Hemispheres were made, cut along the following planes: I—along the plane of the optical axes; II—perpendicular to the bisector of the acute angle between the optical axes; III—perpendicular to the bisector of the obtuse angle between the optical axes.

In orienting the specimens, substantial help may also be provided by determining the cleavage planes from the appearance of a series of cracks when the specimen is cooled with abundant wetting by a rapidly evaporating substance (for example, dichloroethane). In the case of stilbene, the series of cracks is parallel to the plane of the optical axes.

Taking into account the X-ray structural data on the unit cell of a stilbene crystal ⁽³⁾, one may suppose that the cleavage plane is the plane of the crystallographic axes a, b , since the c axis corresponds to the largest lattice constant and it is natural to suppose the weakest bonding here. The correctness of this assumption can be confirmed or refuted only by experiment. If we accept this assumption, then the axes a and b must lie in the plane of the optical axes corresponding to the given wavelength. The fluorescence spectrum is continuous; it corresponds to some mean plane.

The crystal lattice of stilbene belongs to the monoclinic system; consequently, the b axis must coincide with one of the principal axes of the indicatrix, i.e., either with the obtuse or with the acute bisector of the optical axes. It remains to decide which one. This choice can be made with the aid of the azimuthal dependence of the degree of polarization for a hemisphere cut along the plane of the optical axes.

Starting from X-ray structural data on the orientation of the molecules in the lattice, and making a definite assumption about the orientation of the emis-

sion oscillator in the molecule, one can theoretically calculate the azimuthal dependences and polarization diagrams of luminescence.

Calculation of the azimuthal dependence for a section along the plane of the optical axes leads to the result that the positive maximum of polarization approximately corresponds to such a position of the crystal when the a axis is vertical, and the negative maximum to such a position when the b axis is vertical. On the other hand, experimental measurement of the azimuthal dependence shows that the negative maximum corresponds to the vertical position of the obtuse bisector, and the positive one to the acute bisector. Hence it follows that the b axis coincides with the obtuse bisector, and the a axis with the acute one. Thus knowing the orientation of the crystallographic axes in all three sections of the hemispheres, we can use the angles, known from X-ray structural data ⁽³⁾, between the molecular axes and the crystallographic axes, and calculate the degree of polarization of luminescence for any crystal orientation of interest to us and any observation direction, i.e., all the polarization diagrams of interest to us. In a stilbene crystal there are molecules oriented in two different ways. We must assign a definite position to the emission oscillator in the molecule. Calculations were made under two assumptions: the emission oscillator is directed along the long axis L and along the transverse axis M of the molecule. Agreement with experiment was obtained under the first assumption, on the basis of which it may be considered that the emission oscillator is directed along the long axis L of the molecule. This agrees with the results of Pesteil ⁽⁴⁾. Calculations of polarization diagrams are not complicated in principle, but are laborious.

Figure 1 gives the calculated positive and negative

polarization diagrams for all three indicated sections. In Fig. 2 are shown the experimentally measured positive and negative polarization diagrams for the same orientations of the hemisphere sections.

It may be said that qualitatively the behavior of the corresponding calculated polarization diagrams in all cases agrees quite well with the behavior of the experimental polarization diagrams without introducing any corrections for birefringence. This thereby justifies the choice of a spherical form of the crystals for these measurements. The agreement between the calculated and measured diagrams makes it possible to raise the question of determining the orientation of molecules in crystal lattices from the polarization of luminescence, since even the qualitative character of the diagrams makes it possible to judge the nature of the orientation of molecules in the lattice; in other words, the possibility opens up of using a new method for studying the struc-

Fig. 1. Calculated polarization diagrams of a stilbene crystal:
 a –positive; b –negative. I –section in the plane ab ;
 II –section in the plane bc^1 ; III –section in the plane ac^1

Fig. 2. Experimental polarization diagrams of a stilbene crystal. For notation see Fig. 1

Fig. 1. Calculated polarization diagrams of a stilbene crystal: a – positive; b – negative. I – section in the plane ab; II – section in the plane bc¹; III – section in the plane ac¹

Figure 1: Fig. 1. Calculated polarization diagrams of a stilbene crystal: a – positive; b – negative. I – section in the plane ab; II – section in the plane bc¹; III – section in the plane ac¹

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Figure 2: Fig. 2. Experimental polarization diagrams of a stilbene crystal. For notation see Fig. 1

...structure of crystals, which may be auxiliary to the method of X-ray structural analysis.

However, there is no quantitative agreement between the calculated and experimental diagrams—despite the fact that the course of the curves is the same, the experimental values of the degree of polarization are smaller than the theoretical ones, as in the case of anthracene. It is possible that this is the result of the influence of temperature and of thermal vibrations of the molecules. To verify this, it will be necessary in the future to study the influence of temperature on the polarization of crystal luminescence.

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