

résultat de l'application de la théorie mathématique générale de la diffraction des ondes électromagnétiques aux champs d'ondes de rayons X se propageant dans un cristal parfait. Cette théorie générale nous impose d'introduire, dans le calcul de l'amplitude des champs d'ondes diffractés, la fonction de Green du problème; et c'est la forme même de cette fonction, elle même imposée par les équations de propagation des rayons X dans les cristaux qui conduit au résultat de la création des nouveaux champs d'ondes. Le fait que nous ayons établi ce résultat pour le cas d'une fente diffractante n'enlève rien à la généralité du calcul, cette hypothèse ayant pour but uniquement de permettre un calcul plus aisé de la fonction de Green. Des calculs plus compliqués, mais semblables du point de vue théorique, doivent permettre de résoudre des problèmes de diffraction à géométrie plus compliquée.

C'est ainsi, que pour expliquer le contraste des images de dislocation, il faudra adapter ce calcul aux conditions physiques imposées par la dislocation. Le modèle de la fente ne convient certainement pas ici, et il faudra le remplacer plutôt par celui d'un fil plongé dans un milieu transparent aux rayons X. Comme le théorème de Babinet ne peut être appliqué ici sans précautions, il faudra donc reprendre le calcul. De plus, pour être dans les conditions physiques des expériences de topographie aux rayons X, il faudra supposer, comme le fait Kato (1968), que la source de rayons X émet non pas une onde plane, mais une onde sphérique.

Acta Cryst. (1968). A **24**, 676

Optical Activity in a Non-enantiomorphous Crystal: AgGaS_2

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(Received 19 April 1968)

There are no symmetry properties in the theory of optical activity that forbid optical activity in the four non-enantiomorphous crystal classes m , $mm2$, $\bar{4}$ and $\bar{4}2m$, but the existence of such a phenomenon has not, until now, been experimentally verified. This work describes the first positive observation of optical activity in a non-enantiomorphous crystal, silver thiogallate (AgGaS_2). Measurements of the refractive indices of this crystal show that it is accidentally optically isotropic at 4974 Å, although it is of class $\bar{4}2m$. At this wavelength the rotation of the plane of polarization has been measured for propagation along both diad axes. The optical rotatory power is 522 deg.mm⁻¹, the sense of rotation being opposite for the two diad axes. There was no rotation along the c axis. These observations substantiate the theory of optical activity and show that there are no unsuspected conditions forbidding optical activity in these classes; the previous absence of experimental verification of this phenomenon has been due to the lack of crystals with suitable optical properties.

Introduction

Optical activity has been observed for the first time in a non-enantiomorphous crystal, silver thiogallate (AgGaS_2) (Hobden, 1967). The experimental details of this observation are described and considered from

Je remercie Monsieur Authier qui a suscité et dirigé ce travail. Ses suggestions, son aide constante et ses nombreux conseils m'ont permis de la mener à bien.

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a historical and theoretical viewpoint. It is shown that the observation verifies the theory of optical activity based on the gyration tensor.

Optical activity was first observed in quartz as a rotation of the plane of polarization of light propagating along the optic axis. This was explained by

Fresnel on the basis of propagation by two contra-rotating circularly polarized modes of vibration with slightly differing refractive indices. It was observed that the sense of rotation was the same for propagation along both axial directions but that the sense of rotation was opposite in the enantiomorphic form. It was at first assumed that there was a direct and exclusive connection between optical activity and enantiomorphism due to spiral arrangements of atoms along the axis. This idea was supported by the fact that only crystals of the enantiomorphous classes showed the effect. The possibility of spiral structures in crystals with symmetry planes or rotation-inversion axes was overlooked.

However, Gibbs (1882) showed, on the basis of an electromagnetic theory, that optical activity could be present in certain tetragonal crystals ($\bar{4}$ and $\bar{4}2m$) in some directions away from the optic axis. Such crystals are usually birefringent and for this reason the comparatively weak effects due to optical activity cannot be observed. Gibbs remarked, prophetically, 'that it would be difficult to distinguish a case of this kind from an ordinary uniaxial crystal, unless the [index] ellipsoid should approach very closely to a sphere'. It is precisely this situation that forms the subject of this communication.

It was later shown, by Pockels (1906), that optical activity is not forbidden in the uniaxial classes $\bar{4}$ and $\bar{4}2m$ or in the biaxial classes m and $mm2$. Optical activity should be quite easy to observe in crystals of class m or $mm2$ if the optic axes are not in a symmetry plane, for the effect would be seen as a rotation of the plane of polarization along the optic axes when observed under the polarizing microscope. [It was formerly thought that such an effect had been observed in the dimer of methyl mesityl oxide oxalate ($C_9H_{12}O_4$)₂ but this has since been shown to be an error (Rogers, 1953)]. It is surprising that in spite of the immense number of natural and synthetic crystals that have been studied, not one example is known in either class m or $mm2$ where the possibility of optical activity can be experimentally tested. The absence of examples of optically active crystals of these four non-enantiomorphous classes has given rise to occasional doubts about the validity of the theory of optical activity in the present form. Such doubts are quite without foundation; until now the presence or absence of optical activity in these classes has never been established, owing to the absence of crystals with suitable optical properties.

Optical activity in crystals

Optical activity in crystals is the result of a small contribution to the overall permittivity, due to the spatial derivatives of the polarization, that must be taken into account when the dimensions of the unit cell are not negligible in comparison with the wavelength of the electromagnetic wave (Landau & Lifshitz, 1960). This extra contribution to the permittivity

can be described in terms of a gyration tensor. The optical properties of crystals exhibiting birefringence and optical activity can be obtained by combining the two effects using a principle of superposition; in general the modes of propagation are elliptically polarized with slightly modified refractive indices. A concise exposition of the theory of optical activity in crystals, based upon the symmetry properties of the gyration tensor and the principle of superposition, has been given by Nye (1964), whose notation is used here.

In the absence of birefringence, optical activity gives two contra-rotating circularly polarized modes of propagation with a small difference of refractive index, causing a rotation of the plane of polarization when the crystal is examined with linearly polarized light. The directional properties of this rotation can be described in terms of the gyration tensor. The gyration for a particular direction is:

$$G = \pm (g_{11}l_1^2 + g_{22}l_2^2 + g_{33}l_3^2 + 2g_{12}l_1l_2 + 2g_{23}l_2l_3 + 2g_{31}l_1l_3) \quad (1)$$

where the g_{ij} are the tensor elements and the l_i are the direction cosines relative to the chosen axes. The \pm refers to the change of sign in left and right-handed systems of axes, *i.e.* the change of sign of rotation in the enantiomorphic form. The tensor is an axial second rank tensor, having the correct symmetry properties to explain the invariance of rotation upon reversal of the direction of propagation, and the change in sign for the same direction of propagation in the enantiomorphic form of the crystal. The rotatory power, the rotation of the plane of polarization in radians per unit length, is:

$$\rho = \pi G / \lambda_0 \bar{n}, \quad (2)$$

where λ_0 is the free space wavelength and \bar{n} is the mean refractive index for the two modes.

When the symmetry of this tensor is considered in relation to the point symmetry of the 32 crystal classes it is found that only 15 have tensors with non-zero elements. For instance, all classes with a centre of symmetry have zero elements. Those with non-zero elements are the enantiomorphous classes 1, 2, 222, 4, 422, 3, 32, 6, 622, 432 and 23 and the non-enantiomorphous classes m , $mm2$, $\bar{4}$ and $\bar{4}2m$. The forms of the gyration tensor for these classes are given by Nye (1964). They are also given pictorially in the form of gyration surfaces by Shubnikov (1960).

The gyration for crystals of class $\bar{4}2m$ is given by:

$$G = \pm g_{11}(l_1^2 - l_2^2), \quad (3)$$

where g_{11} is the only independent non-zero element of the gyration tensor. The \pm sign has a different meaning in this context, for crystals of this class are identical with their own mirror image. In this case the \pm sign refers to the ambiguity in deciding which diad axis shall be

the reference axis for l_1 . From this it can be seen that the optical rotatory power for this class is:

$$\rho = \pm \pi g_{11}(l_1^2 - l_2^2)/\lambda_0 \bar{n}, \quad (4)$$

showing that it is zero for all directions in the symmetry planes and has a maximum value $\pm \pi g_{11}/\lambda_0 \bar{n}$ along the two diad axes. The sense of the rotation depends upon the absolute configuration of the atomic spirals along the diad axes.

In the presence of birefringence the effects of optical activity are difficult to observe, for optical activity is a weak effect easily overwhelmed by birefringence. The theory of superposition of birefringence and optical activity shows that there are two elliptically polarized modes of propagation with a phase retardation per unit length of

$$\Delta = 2\pi[(n_e - n_o)^2 + (G/\bar{n})^2]^{1/2}/\lambda_0. \quad (5)$$

The ellipticity k , the ratio of the minor to major axis, is given by

$$k = \tan(\beta/2) \quad (6)$$

where

$$\tan \beta = G/\bar{n}(n_e - n_o). \quad (7)$$

This theory has been used to explain successfully the appearance of the axial conoscopic figure in crystals such as quartz (Partington, 1953).

The optical properties of silver thiogallate

Silver thiogallate, AgGaS₂, is reported (Hahn, Franck, Klingler, Meyer & Storger, 1953) to have the structure of chalcopyrite with spatial symmetry $I\bar{4}2d$. It is, therefore, a member of the uniaxial, acentric, non-enantiomorphous class $\bar{4}2m$. The compound was prepared by fusion of Ag₂S and Ga₂S₃, each of which was prepared from high purity elements. Crystallization from the melt produced a polycrystalline matrix from which irregular single crystals, up to 4 mm in diameter and yellow in colour, were obtained. Crystals in the form of polished plates were examined under the polarizing microscope, where it could be seen that they were uniaxial and of good optical quality. There was a strong positive response to the Giebe-Scheibe test for piezoelectricity, thereby confirming acentricity. The X-ray powder pattern was consistent with the reported space group and unit cell dimensions $a = 5.74 \text{ \AA}$ and $c = 10.26 \text{ \AA}$.

From a single crystal a $9^\circ 57'$ prism was prepared with faces $3 \text{ mm} \times 3 \text{ mm}$, the c axis being parallel to the roof edge. The refractive indices were measured at 20°C with this prism using a spectrometer and various He and Hg emission lines. The data are given in Table 1 and Fig. 1. It can be seen that AgGaS₂ has the unusual property that the birefringence changes sign at 4974 \AA . This is probably due to an unusually large difference in the intensity and frequency of the blue and ultraviolet absorption bands for the ordinary and

extraordinary waves, causing an accidental equality of the refractive indices at this wavelength.

At 4974 \AA , silver thiogallate is optically isotropic yet structurally it is tetragonal (class $\bar{4}2m$). This accidental optical isotropy allows the observation of optical activity in all directions as pure optical rotation without the complications of birefringence.

A single crystal of AgGaS₂ was oriented by the Laue method and plates were cut perpendicular to both diad axes which can be arbitrarily labelled x and y .

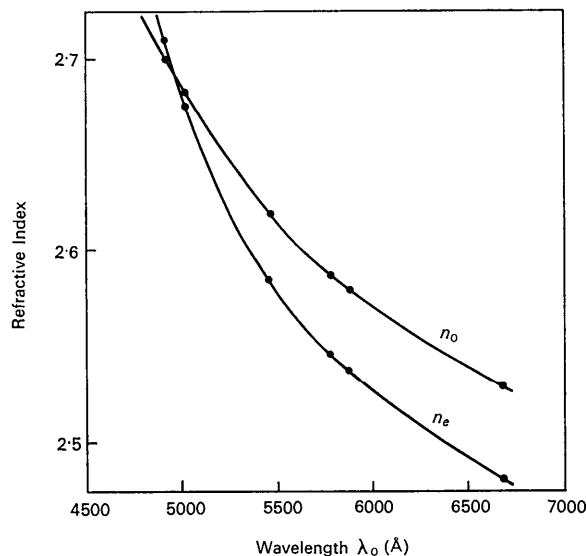


Fig. 1. The refractive indices of AgGaS₂ at 20°C .

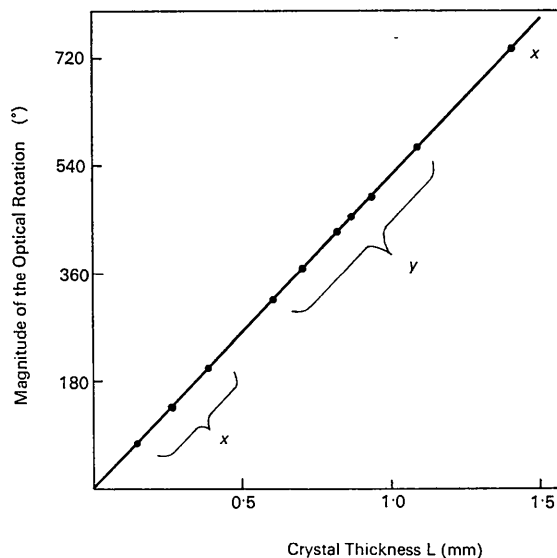


Fig. 2. Magnitude of the optical rotation in degrees for various thicknesses of AgGaS₂ in the form of polished plates. Data points x refer to specimens cut perpendicular to one diad axis and y to those cut perpendicular to the other diad axis. The rotation for x and y specimens was of the opposite hand.

Table 1. *The refractive indices and birefringence of AgGaS₂ at 20°C for various wavelengths in the visible spectrum*

The birefringence changes sign at 4974 Å, at which point the crystal is optically isotropic.

λ_0 (Å)	n_o	n_e	$n_e - n_o$
6678	2.529	2.481	-0.048
5876	2.579	2.537	-0.042
5780	2.587	2.546	-0.041
5461	2.619	2.585	-0.034
5016	2.683	2.676	-0.007
4916	2.700	2.710	+0.010

The rotation of the plane of polarization in these plates was measured with monochromatic light at 4974 Å using a linear polarizer and analyser. By reducing the thickness of these plates it was possible to show, without ambiguity, that the rotatory power was 522 deg.mm⁻¹, the sense of rotation being opposite for the x and y plates. Fig. 2 shows the rotation measured with these plates. To simplify the presentation, the magnitudes of the rotations have been given; it is to be understood that the senses of rotation for the x and y plates were opposed. It was observed in a z -cut plate that there was no rotation along the c axis.

These observations are in agreement with the predictions based on equation (4), thereby verifying the gyration tensor for this class and providing the first known example of optical activity in a non-enantiomorphous crystal. The magnitude of g_{11} is 3.88×10^{-3} at 4974 Å. The rotatory power for silver thiogallate is very much greater than that of quartz but is comparable to that of cinnabar; it corresponds to a difference in refractive index for the two modes of propagation of 1.31×10^{-3} .

The appearance of this crystal under the polarizing microscope is somewhat unusual. With monochromatic light at 4974 Å, a rotation of the plane of polarization is observed in certain directions as described above; there is no conoscopic figure owing to the absence of birefringence. Orthoscopic examination of silver thiogallate with white light illumination shows an incomplete extinction due to a band of blue radiation transmitted in the region of 4974 Å (see below). The conoscopic figure in white light shows pale blue fringes on a yellow-orange background. These arise from the fact that in the orange and red parts of the visible spectrum the birefringence is approximately proportional to the wavelength* (see Fig. 1), which gives an achromatic conoscopic figure of dark fringes on a yellow-orange background. These dark fringes appear pale blue owing to the light transmitted at about 4974 Å. The appearance of this crystal under the polarizing microscope with monochromatic

* The linear relationship between birefringence and wavelength, mentioned above, could be of use in the construction of achromatic quarter-wave plates and similar optical components. In the range 5800 Å to 6800 Å, $(n_e - n_o)/\lambda_0$ is constant to $\pm 1\%$.

green, yellow, or red illumination is indistinguishable from that of a uniaxial crystal with no optical activity.

The principle of superposition of optical rotation and birefringence at wavelengths close to 4974 Å has been demonstrated by the following experiment. Linearly polarized white light was passed normally through a 0.61 mm thick y -cut plate of AgGaS₂, oriented with the c axis in the plane of polarization. The emerging light was passed through a crossed analyser and focused on the slit of a spectrograph. Had the crystal been birefringent but not optically active the light would have propagated in the crystal as an extraordinary wave and would have been rejected by the analyser. The simultaneous presence of optical activity and birefringence alters the modes of propagation and the emerging light is, in general, elliptically polarized. The light passed by the analyser gave the spectrogram shown in Fig. 3.

Suppose the ellipticity of the modes of propagation at a given wavelength be k . The incident radiation, linearly polarized in the z direction (c axis) gives rise to two contra-rotating elliptically polarized waves with complex amplitudes:

$$(1+k^2)^{-1}[\mathbf{z} + ik\mathbf{x}] \quad \text{and} \quad (1+k^2)^{-1}[k^2\mathbf{z} - ik\mathbf{x}], \quad (8)$$

where \mathbf{x} and \mathbf{z} are unit vectors. It can be seen that both waves have ellipticity k , they are polarized with the opposite sense of rotation, and their sum is the unit vector \mathbf{z} , corresponding to the incident wave. After propagation through a crystal of length L there is a relative phase retardation between these waves of LA , where A is given by equation (5). At the exit surface the amplitude of the sum of the components in the x direction is

$$ik(1+k^2)^{-1}[\exp(+iLA/2) - \exp(-iLA/2)]. \quad (9)$$

So the fractional transmitted intensity passed by the analyser is given by

$$I/I_0 = 4k^2(1+k^2)^{-2} \cdot \sin^2(LA/2). \quad (10)$$

From equations (6), (7) and (10) it can be shown that

$$I/I_0 = \{(G/\bar{n})^2 / [(n_e - n_o)^2 + (G/\bar{n})^2]\} \cdot \sin^2(LA/2). \quad (11)$$

The second term shows that there will be dark fringes when $LA = 2\pi N$. The first term is an envelope function with value 1 when the birefringence is zero, and tends to zero as $(n_e - n_o) \gg G/\bar{n}$. It has a value $\frac{1}{2}$ when $(n_e - n_o) = G/\bar{n}$, that is, when the birefringence due to optical activity is equal to the ordinary birefringence. Equation (11) explains the appearance of Fig. 3. In the small spectral region where this banded pattern occurs G/\bar{n} can be assumed constant and $(n_e - n_o)$ is a linear function of wavelength. Using equation (11), and putting $G/\bar{n} = 1.31 \times 10^{-3}$ and $d(n_e - n_o)/d\lambda = 1.6 \times 10^4 \text{ cm}^{-1}$, with $L = 0.61 \text{ mm}$, an adequate representation of Fig. 3 is obtained.

The wavelength for optical isotropy in AgGaS₂ is 4974 Å at 20°C. As the temperature rises this wave-

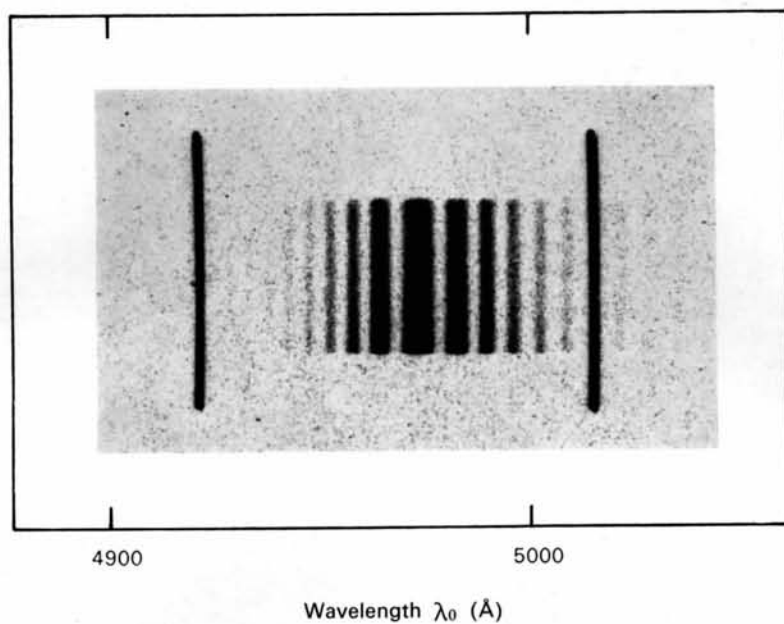


Fig. 3. A banded spectrum found in AgGaS_2 in the vicinity of 4974 \AA due to the simultaneous presence of optical activity and birefringence. The He emission lines at 4922 \AA and 5016 \AA are also shown for calibration.

length increases initially at the rate of 0.2 Å/°C. At higher temperatures the rate of increase is greater and by 200°C the wavelength for isotropy is 5030 Å.

Conclusion

Direct observation of optical activity substantiates the theory of optical activity based upon the gyration tensor for the crystal class $\bar{4}2m$. This positive observation provides the first recorded instance of optical activity in a non-enantiomorphous crystal.

I wish to thank D.S. Robertson and H.A. Chedzey for growing the crystals and K.F. Hulme and W.A. Wooster for their encouragement and helpful comments. This paper is contributed by permission of the Director of R.R.E. Copyright Controller H.B.M.S.O.

Acta Cryst. (1968). A24, 680

The Structures and Phase Transformations in β -AuCd Alloys

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(Received 24 January 1968 and in revised form 21 March 1968)

An X-ray powder diffraction and single-crystal study of the structures and phase transformations existing in the 50 at.% region of the gold-cadmium system has been carried out. The transformation β_1 (cubic) \rightarrow β' (orthorhombic) occurring in the range 47–48.5 at.% Cd is confirmed. At higher cadmium content, 49–52 at.%, the cubic β_1 phase transforms to a structure possessing hexagonal symmetry rather than the previously suggested tetragonal structure. The X-ray diffraction patterns of this hexagonal structure can be interpreted in terms of a unit cell of 27 atoms, which is structurally similar to the ζ phase of the AgZn system.

Introduction

Above 80°C gold-cadmium alloys of around 50 at.% composition have an ordered body-centred cubic structure ($a=3.3126$ Å), the β_1 phase. Below 80°C, the β_1 phase is subject to two possible structural modifications. Alloys in the range 47–48.5 at.% Cd transform to give a product phase β' which is said to have an orthorhombic structure (Ölander, 1952*a, b*; Chang, 1951). At higher cadmium content, 49–52 at.%, alloys transform to a phase β'' which is reported to have a tetragonal structure by Köster & Schneider (1940) and Chen (1954).

The transformations take place on cooling at 60°C and 30°C and on heating at approximately 80°C and 40°C respectively.

The structure of the β' phase is fairly well established. Ölander was able to show that most of the X-ray powder diffraction lines could be explained on the basis of an orthorhombic structure, having cell parameters $a=3.144$, $b=4.851$, $c=4.745$ Å.

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The structure of the β'' phase is less certain. Köster & Schneider gave tetragonal cell parameters for the β'' phase as: $a=5.074$, $c=4.487$ Å. This was supported by Chen, who was uncertain of the actual lattice parameters but suggests the unit cell is large, with the possible parameters shown in Table 1.

There has been considerable interest in the mechanisms of the transformations, which possess some unusual features. The phase changes take place athermally and the product phases indicated are those resulting from slow or moderately slow cooling rates from the parent phase. The transformation mode, and in certain cases the transformation product, may be altered by suitable heat treatment of the parent phase. A number of investigations have been carried out using resistivity and elastic moduli data to study these effects (Wechsler, 1957; Subramanya, Baker, Lieberman & Read, 1961; Zirinsky, 1956; Class & Lieberman, 1961; Birnbaum, 1959). The results of these investigations are summarized below:

(1) Following severe quenching, alloys in the range 47–48.5 at.% Cd transform to produce resistivity and elastic data similar to those recorded during the transformation $\beta_1 \rightarrow \beta''$. From this observation, it was concluded that the $\beta_1 \rightarrow \beta'$ transformation is inhibited by