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An optical anomaly possibly due to optical activity in some uniaxial opaque ore minerals

A. J. HALL

Department of Applied Geology, University of Strathclyde, James Weir Building,
75 Montrose Street, Glasgow G1 1XJ

B. D. CERVELLE

Laboratoire de Minéralogie-Cristallographie, associé au C.N.R.S., Université Pierre et Marie-Curie,
Tour 16, 4, place Jussieu, 75230 Paris Cedex 05

AND

P. R. SIMPSON

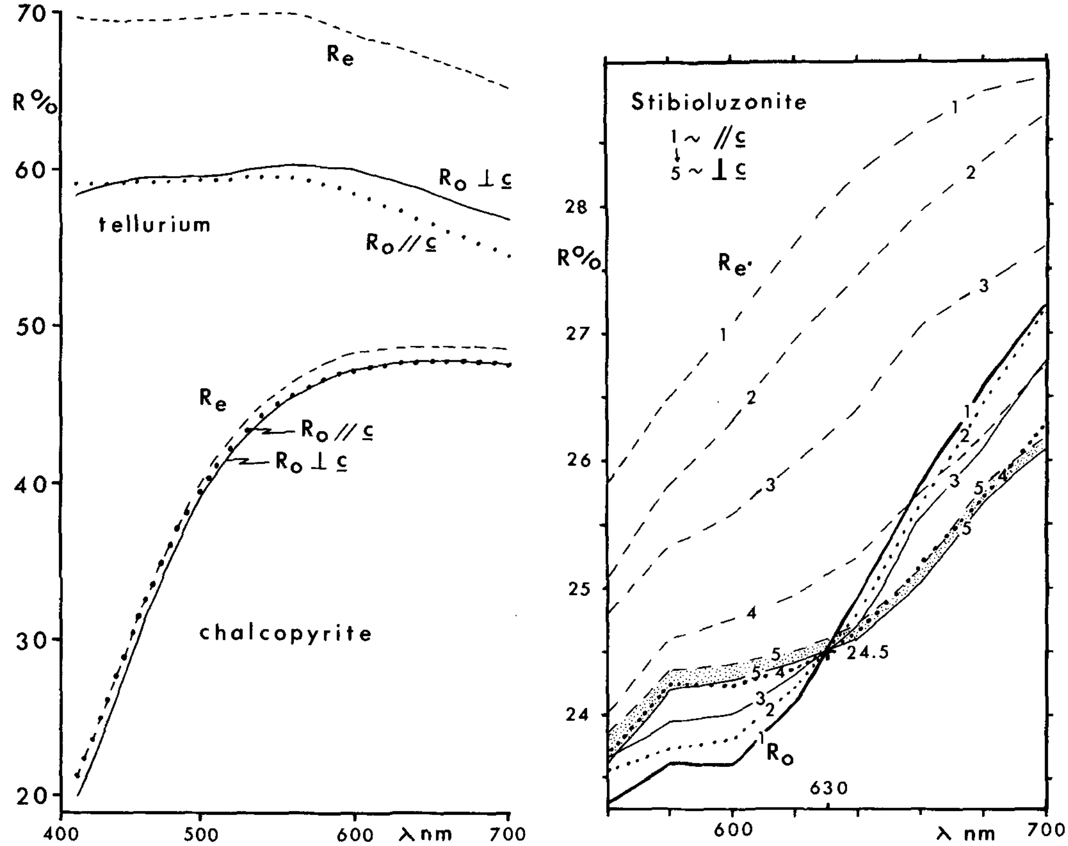
Institute of Geological Sciences, 64/78 Gray's Inn Road, London WC1X 8NG

SUMMARY. Spectral reflectance measurements on three uniaxial ore minerals, tellurium, chalcopyrite, and stibioluzonite, which are opaque at least in the visible part of the spectrum have revealed that the reflectance curve of the ordinary ray varies with crystallographic orientation of the polished section. The three minerals possess symmetries capable of exhibiting optical activity in *transmitted light*. A possible explanation, therefore, of the anomalous behaviour is that the optical constants, i.e. the refractive index and the absorption coefficient, and thus also the reflectance, of the ordinary ray may differ for sections cut normal to *c* where optical activity probably has its maximum effect and for sections cut parallel to *c* where there is probably little or no complication due to optical activity. There would therefore appear to be a need to extend the theory of reflection from absorbing media to include reflection from optically active absorbing minerals.

DETAILED spectral reflectance measurements on three uniaxial absorbing minerals (tellurium, Te—Cervelle and Lévy, 1976; chalcopyrite, $CuFeS_2$—Araya *et al.*, 1977; and stibioluzonite, Cu_3SbS_4—Hall, unpublished) have revealed that the reflectance curve of the ordinary ray is not independent of the crystallographic orientation of the polished section. Oriented sections cut parallel and normal to the *c*-axes of tellurium (fig. 1) and chalcopyrite (fig. 1) give different spectral curves for $R_0(/\!/ c)$ and $R_0(\perp c)$ while randomly oriented sections of stibioluzonite (fig. 2) show a systematic change in the R_0 curve from grains showing maximum bireflectance ($/\!/ c$) to grains showing zero bireflectance ($\perp c$).

The crystallographic symmetries of the three minerals (tellurium—hexagonal, class 32; chalcopyrite—tetragonal, class $\bar{4}2m$; and stibioluzonite—tetragonal, class $\bar{4}2m$) indicate that the three minerals belong to the group of symmetries capable of optical activity (enantiomorphic—classes 1, 2, 222, 3, 32, 4, 422, 23, 432, 6, and 622 and non-enantiomorphic—classes *m*, *mm*, $\bar{4}$, and $\bar{4}2m$). Optical activity in classes $\bar{4}2m$ and $\bar{4}$ remains a theoretical possibility (Wooster, 1949, p. 156) and, if confirmed for stibioluzonite and chalcopyrite, these will be the first examples.

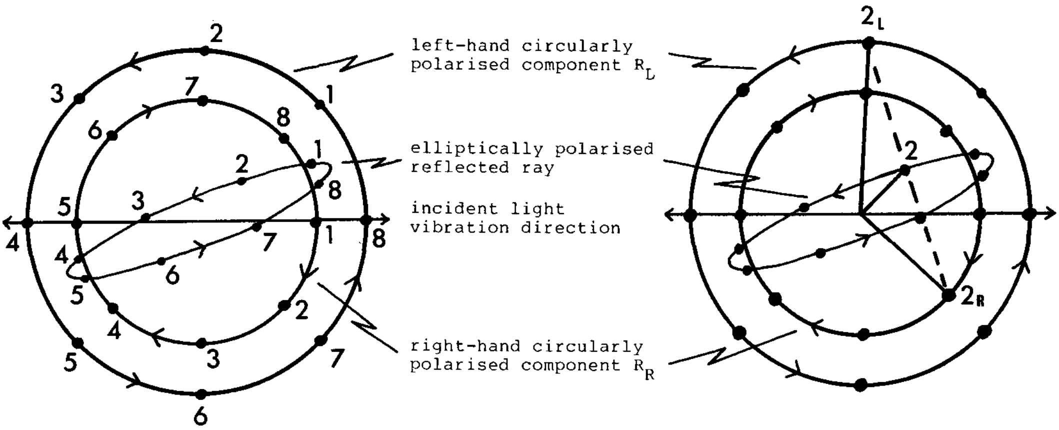
The structure of tellurium consists of spiral chains of atoms in angular twofold coordination; as $R_e > R_o$ this suggests a greater absorption for light vibrating parallel to the *c*-axis and the spiral chains. Chalcopyrite has a sphalerite-based structure but is slightly 'compressed' and has a higher conductivity (Shuey, 1975) along the *c*-axis. Stibioluzonite also has a sphalerite-based structure but with a *c*:*a* ratio of almost exactly 2:1; replacement of some Cu by Ag (Hall, 1971) or Sb by As (towards the luzonite end-member) results in a significant change in the ratio and a 'compression' along the *c*-axis. Both chalcopyrite and stibioluzonite have $R_e > R_o$ indicating a slightly higher absorption for light vibrating parallel to the *c*-axis in the direction of 'closer' chemical bonding. The spiral chains of tellurium and distortions of the cation tetrahedral sites in chalcopyrite and stibioluzonite could result in optical activity according to the theory of Born (in Jenkins and White, 1976, pp. 593-4). Compression alone of tetrahedra probably cannot account



FIGS. 1 and 2. FIG. 1 (*left*). Spectral reflectance curves of single crystals of natural chalcopyrite (Araya *et al*., 1977) and synthetic tellurium (Cervelle and Lèvy, 1976) measured on vertical (// *c*) and basal (⊥ *c*) sections. FIG. 2 (*right*). Spectral reflectance curves of randomly oriented grains of synthetic stibioluzonite. Five grains illustrating the systematic change in R_o from near isotropic (~ ⊥ *c*) to strongly anisotropic (~ // *c*) sections have been selected to show the change in R_o with change in crystallographic orientation. The curves have been adjusted to give $R_o = 24.5$ at 630 nm in order to emphasize the systematic nature of the change. This is also necessary because of the measurement technique which involves measuring the complete spectrum of intensities of the standard, then the two spectra of the grain followed by a repetition of the standard. An accurate reproducible curve shape is obtained with the estimated precision in the comparison of R_o and R_e of a single grain approximately 0.5% relative. The absolute values of R_o and R_e pairs can be compared with less precision. The systematic change in curve shape was reproducible using several polished samples. Stibioluzonite is stoichiometric so compositional variation is ruled out and in any case a compositional variation could not explain the *systematic* change in bireflectance of the section. It is difficult to envisage any instrumental factor that could account for the systematic change.

for optical activity but the compression results from distortion of the tetrahedral co-ordination, especially of Cu, in tetrahedral sites; such co-ordination polyhedra are only approximately symmetrical in these and many other sulphide structures. Tellurium is in fact known to be optically active for transmitted infra-red light (Nomura, 1960).

Optical activity in transparent minerals, e.g. quartz, is the rotation of linearly polarized light as it travels parallel to the optic axis. The amount of rotation varies with the wavelength of light and depends on the distance traversed. The explanation of the phenomenon by Fresnel is that plane-polarized light entering a crystal along the optic axis is decomposed into two circularly polarized vibrations rotating in opposite directions with the same frequency. The two vibrations travel at different velocities and recombine on leaving the crystal to form a slightly rotated plane-polarized vibration. There are therefore two refractive indices for the ordinary ray—one corresponding to clockwise circularly polarized light and one to anticlockwise circularly polarized light. Light passing through quartz at an angle to the *c*-axis is split into two elliptically polarized vibrations but the



FIGS. 3 and 4. FIG. 3 (*left*). Reflection from a basal section of an absorbing optically active uniaxial mineral. The diagram is constructed for a 45° phase difference between the ordinary-ray components R_L and R_R. Following the Fresnel model of optical activity in transparent media, the incident linearly polarized light is separated, on the polished surface, into two circularly polarized components. The difference in the amplitude of the components, represented by differing radii of circles, would result from the differing n and k values of the two components. The relationship between the components of the reflectance, R_L and R_R and the optical constants, $n_L k_L$ and $n_R k_R$ is given by the Fresnel equation, $R\% = 100 \times \{(n-1)^2+k^2\}/\{(n+1)^2+k^2\}$. However, the Fresnel equation is strictly applicable only to the case of linearly polarized light. If, as is assumed, $k_L \neq k_R$ the two components of the reflectance would have a phase difference and this would cause rotation and ellipticity of the vibration direction. The reflectance value measured and the degree of ellipticity and rotation would be dispersed due to dispersion of n and k. In conclusion, it seems plausible that $R_o \perp c$ need not equal $R_o /\!/ c$. FIG. 4 (*right*). Construction of fig. 3. Rotated and elliptically polarized-light is obtained by the combination of the two out-of-phase left-hand and right-hand circularly polarized components. This takes place *on* the polished surface. At a given instant, the vibrating point (A) is attempting to move towards 2_L and 2_R; the result is a movement towards point 2 on the ellipse. If there was no phase difference, i.e. $k_L = k_R$, there would be no rotation nor ellipticity and a linearly polarized reflected ray would result.

ellipticity is very small. The difference between the two values of the refractive index of the ordinary ray is very small compared with their difference from the refractive index of the extraordinary ray, resulting in the optical activity being confined essentially to beams travelling along the c-axis (Jenkins and White, 1976). A small rotation due to optical activity has been determined in sections oblique and even parallel to the c-axis in quartz (Szivessy, 1937), and is zero only at an angle of 56° 10′ to that axis. Because the rotary effect depends on distance travelled, the direction of vibration of normally incident linearly polarized light reflected from a section of quartz cut normal to the c-axis should not be rotated.

In the theoretical case of optically active uniaxial absorbing minerals, if the clockwise and anti-clockwise circularly polarized components of the ordinary ray had different absorption coefficients then the resulting phase difference would cause the rotation of the plane of vibration of linearly polarized light on reflection from sections cut perpendicular to c and this would occur *without* significant penetration in a similar way to the reflection of rotated elliptically polarized light from, for example, a (100) section of a uniaxial absorbing mineral in the 45° orientation. In strongly absorbing substances the reflectance is high and the transmission is so low that the effect of optical activity on the transmitted light cannot be measured. Figs. 3 and 4 demonstrate how rotated and elliptically polarized light could result from reflection of linearly polarized incident light by a basal section of an absorbing optically active uniaxial mineral.

Thus a *possible* explanation of the anomalous behaviour of the three minerals is that due to optical activity the optical constants for the 'ordinary' ray depend on crystallographic orientation and differ for sections cut normal to c where optical activity probably has its maximum effect and sections cut parallel to c where there is probably little or no complication due to optical activity. The relative values of $R_o(/\!/ c)$ and $R_o(\perp c)$ depend on their associated optical constants which in turn depend on the anisotropic nature of the chemical bonding.

While the theory of optical activity in transparent media and the effects of absorption bands on optical activity have been studied in detail

(Lowry, 1935) and the theory of reflection from transparent and absorbing media is now well established (Galopin and Henry, 1972) the results of reflectance measurements on tellurium, chalcopyrite, and stibioluzonite suggest that there is a need to extend the theoretical studies to include reflection from optically active absorbing materials.

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