



Article scientifique

Article

1984

Accepted version

Open Access

This is an author manuscript post-peer-reviewing (accepted version) of the original publication. The layout of the published version may differ .

---

## Optical rotatory dispersion (ORD), circular dichroism (CD), absorption and spontaneous birefringence ( $\Delta n_s$ ) in the langbeinite $K_2Co_2(SO_4)_3$

---

Brezina, Bohuslav; Rivera, Jean-Pierre; Schmid, Hans

### How to cite

BREZINA, Bohuslav, RIVERA, Jean-Pierre, SCHMID, Hans. Optical rotatory dispersion (ORD), circular dichroism (CD), absorption and spontaneous birefringence ( $\Delta n_s$ ) in the langbeinite  $K_2Co_2(SO_4)_3$ . In: Ferroelectrics, 1984, vol. 55, n° 1, p. 177–180. doi: 10.1080/00150198408015362

This publication URL: <https://archive-ouverte.unige.ch/unige:30823>

Publication DOI: [10.1080/00150198408015362](https://doi.org/10.1080/00150198408015362)

OPTICAL ROTARY DISPERSION (ORD), CIRCULAR DICHROISM (CD),  
ABSORPTION AND SPONTANEOUS BIREFRINGENCE ( $\Delta n_s$ ) IN THE  
LANGBEINITE  $K_2Co_2(SO_4)_3$

BOHUSLAV BREZINA\*, JEAN-PIERRE RIVERA and HANS SCHMID  
Laboratory of Applied Chemistry, University of Geneva,  
CH-1211 Geneva 4, Switzerland

Abstract - ORD, CD and absorption of  $K_2Co_2(SO_4)_3$  have been measured in the cubic phase ( $P2_13$ ) between 430 and 700nm. In the orthorhombic phase ( $\leq T_t = 125K$ )  $\Delta n_s$  of one of the three indicatrix sections has been measured down to 5K. On a second principal section ORD is visually observable down to 4K.

INTRODUCTION

The langbeinite sulphates  $A_2B_2(SO_4)_3$  (A stands for  $K^+$ ,  $NH_4^+$ ,  $Rb^+$ , etc. and B for  $Mg^{++}$ ,  $Ni^{++}$ ,  $Co^{++}$ , etc.) are reported to have prototype space group  $P2_13$  and phase transitions to one or more of the potential subgroups  $P2_1$ ,  $P1$ ,  $P2_12_12_1$  and  $R3$ <sup>1</sup>. In  $K_2Co_2(SO_4)_3$  (=KCS) one of the authors (B.B.) discovered a first order transition at 125K to a potentially ferroelectric phase<sup>2</sup> which was claimed to be non-polar ( $2_12_12_1$ )<sup>3</sup>. With a view to clarifying this transition, cleaved or cut and polished (100)<sub>c</sub> platelets of Bridgman-grown single crystals have been studied at room temperature (ORD, CD and absorption in the  $P2_13$  - phase) and between 4 and 300K (domains,  $\Delta n_s$ ) in an optical helium-flow cryostat under the microscope.

EXPERIMENTS

ORD, CD and absorption in the cubic phase. Ivanov and Koňiak<sup>4</sup> have measured ORD in the cubic phase of the langbeinite  $Cd_2(NH_4)_2(SO_4)_3$  (CAS) and found it normal, i.e. it could be described by a single term Chandrasekhar equation,  $\rho = K\lambda^2/(\lambda^2 - \lambda_0^2)^2$  with  $K=0.115 \text{ deg } \mu^2/\text{mm}$  and  $\lambda_0 = 0.1583 \mu$ . In contrast to the relatively weak specific rotation,  $\rho$ , and normal dispersion of CAS ( $\rho$  is decreasing from  $\sim 2.5 \text{ deg.cm}^{-1}$  at 700nm)<sup>4</sup> and of  $K_2Cd_2(SO_4)_3$  ( $\rho \sim 15.6 \text{ deg.cm}^{-1}$  at 632.8nm along an optic axis of the  $222$  - phase)<sup>5</sup>, KCS has a high  $\rho$  and strong "anomalous" ORD in the visible that can be seen, e.g. on a 1 mm thick platelet by decrossing slightly the crossed polars symmetrically: vivid contrast between red-orange and violet-blue! Measurement of the absorption spectrum of a 1 mm thick crystal under the microscope (with photomultiplier and interference filter) and of a 58 $\mu$ m thick crystal with a spectrophotometer Unikon 820

\* On leave of absence from the Institute of Physics, Academy of Sciences, Prague.

(Fig. 1a),) show a strong peak at 545nm ( $18350\text{ cm}^{-1}$ ) and a shoulder due to a weaker peak at  $\sim 485\text{nm}$  ( $20620\text{ cm}^{-1}$ ). In analogy to the langbeinite  $\text{K}_2\text{Cd}_2(\text{SO}_4)_3$ , in which  $\text{Cd}^{++}(1)$  and  $\text{Cd}^{++}(2)$  have trigonally distorted oxygen octahedral environment <sup>6,7</sup>,  $\text{Co}^{++}$  is certainly similarly coordinated in KCS. Above 4.2K KCS is paramagnetic with  $\text{Co}^{++}$  in the high spin state <sup>8</sup>. Therefore the peak at  $\sim 18350\text{ cm}^{-1}$  can be assigned to the  ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$  transition of high spin  $\text{Co}^{++}$ . For  $\text{CoCl}_2$  a similar spectrum due to  $\text{Co}^{++}$  - with a shoulder - is found <sup>9</sup>. Using an ORD/CD- spectropolarimeter (JASCO-J-20A), ORD and CD of KCS have been measured at 18°C. Figures 1b, and 1c, show the results and demonstrate that the crystal field transition of  $\text{Co}^{++}$  is responsible for the "anomalous" dispersion. The peaks of CD (at 562nm) and the inversion of the slope of ORD coincide fairly well with the absorption peaks. The CD-spectrum of one of the KCS crystals showed, at 18°C, sharp fine structure peaks with  $170\text{ cm}^{-1}$  intervals starting at  $16530\text{ cm}^{-1}$  on the low frequency side of the band and extending to the high frequency side. A structure determination of KCS, providing accurate details of the  $\text{Co}^{++}$  environment, would be needed to explain the details of the absorption and CD spectra (compare with comments in <sup>9</sup>). The strong rotation due to  $\text{Co}^{++}$  is superimposed on a weaker one of the same order of magnitude as the one of CAS <sup>4</sup>, with normal dispersion and being due to the structure's basic framework.

#### STUDY OF THE LOW TEMPERATURE PHASE

Attempts at poling the domains below  $T_t = 125\text{K}$  by cooling in a field through  $T_t$  and field reversal below  $T_t$  failed in fields as high as  $40\text{ kV cm}^{-1}$ . Heating in zero field showed no evidence of charge development (electrometer Keithley 616) at  $T_t$ . These findings, together with the observation of parallel extinction ( $\parallel <100>$ ) only (see below), demonstrate that the low temperature phase is orthorhombic( $2_12_12_1$ ) and hence ferroelastic as concluded earlier <sup>3</sup>. Spontaneous birefringence,  $\Delta n_s$ . On a 58 m thick  $(100)_c$  platelet two of the three possible domain orientations - all of them have indicatrix principal sections parallel to  $(100)_c$  - have been observed (Fig. 2) : one of them (clear area on picture) had extinction parallel to  $[100]_c$ . Its  $\Delta n_s$  has been measured at 643nm (minimum of absorption) between 125K and 4K (Fig. 3). The transition is of first order. The temperature dependence of  $\Delta n_s$  possibly reflects that of the order parameter, but the decrease of  $\Delta n_s$  of KCS, on approaching  $T_t$ , is at variance with the reported increase of  $|\Delta n_s|$  in two principal sections and its temperature independence in the third one of the 222 - phase of  $\text{K}_2\text{Mn}_2(\text{SO}_4)_3$  <sup>10</sup>. A second kind of domain orientation appeared dark in any direction between crossed polars (Fig.2), but ORD was visually observable on it (see above) from 125K down to 4K. More precisely, the visually observable ORD in the cubic phase between 300K and 125K did not undergo a drastic change at  $T_t$ .

Because class 222 allows maximal rotation along the 2-axes <sup>11</sup>, superposition of birefringence and rotation necessarily occurs. The observation of ORD on the latter domain indicates, however, a very high ratio of rotation to birefringence indicating a very acute bisectrix or quasi-uniaxial optical axis perpendicular to the surface. On a second crystal the third potential orientation showed extinction parallel to [100] at 90° to the first one, however, its poor quality, did not allow a measurement of  $\Delta n$ .

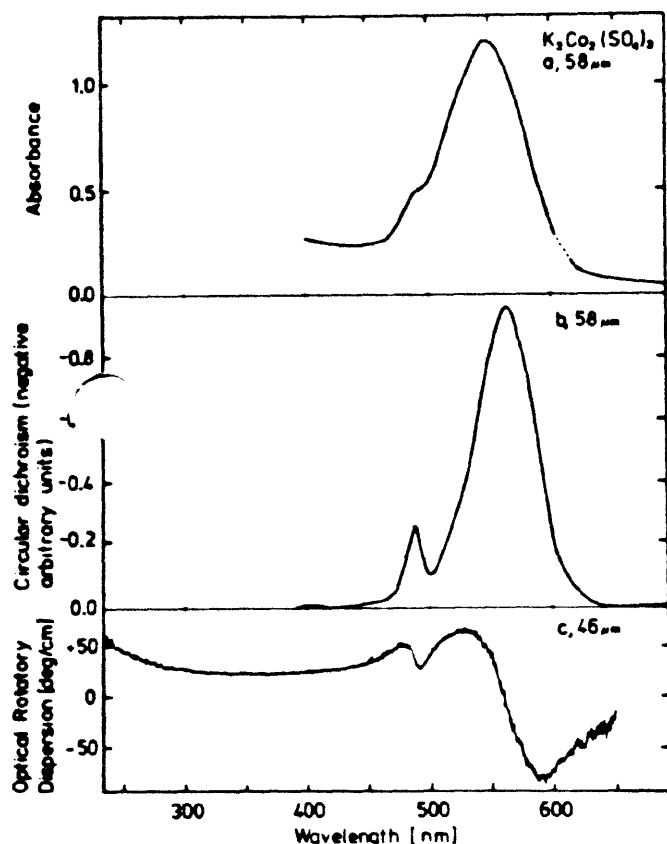


FIGURE 1 Absorbance (a) CD (b) and ORD (c) of  $K_2Co_2(SO_4)_3$  at room temperature



FIGURE 2 Domain pattern of a 58  $\mu m$  thick (100)-cut platelet at 30K. Clear region : domain in 45° position, dark region : domain with visible ORD. ( $D = 2 mm$ )

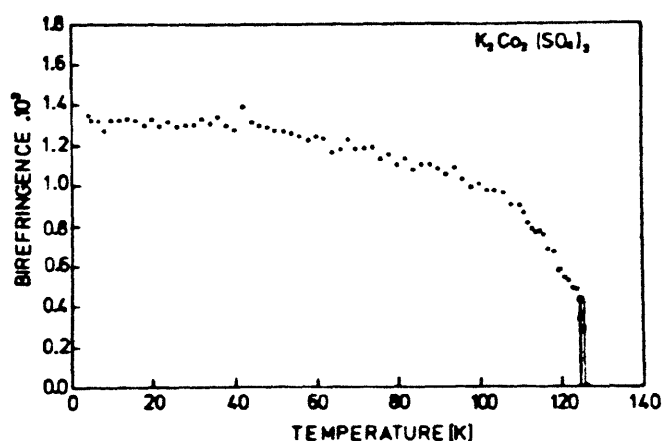


FIGURE 3 Spontaneous birefringence versus temperature of the clear domain of Figure 2 ( $\lambda = 643 nm$ )

## CONCLUSIONS

On the basis of the extinction properties of the domains and the unsuccessful attempts at poling ( $\rightarrow 40 \text{ kV cm}^{-1}$ ) it is concluded that the phase below 125K is orthorhombic and ferroelastic with Aizu species 23F222. A more detailed analysis of the strong ORD and CD due to  $\text{Co}^{++}$  ions in the cubic and orthorhombic phases is very desirable. However, a careful characterization of the indicatrix of the orthorhombic phase - in which strong rotation is superimposed on birefringence - would be required previously.

## ACKNOWLEDGEMENT

One of the authors (B. Brezina) is grateful to Battelle Geneva Research Laboratory for a grant. Thanks are extended to Dr. B. Schwendimann (Biochemistry Dept.) for his advice and willingness in putting the spectropolarimeter at our disposal, to Mr. Joly (Organic Chemistry Dept.) for taking an absorption spectrum, to R. Cros, R. Boutellier and E. Burkhardt for technical help and to Mrs O. Hirth for typing the manuscript.

## REFERENCES

1. V. Dvořák, phys.stat.sol. (b) 52, 93 (1972)
2. B. Brezina, 5.Frühjahrsschule der SAG Ferroelektrizität, DDR - Graal - Müritz, 11/15 April 1977, pp. 22/32
3. T. Mikita, S. Sekiguchi, T. Ikeda, J.Phys.Soc.Jap., 43, 1327 (1977)
4. N.R. Ivanov and Č. Koňák, Kristallographiya, 19, 1216 (1974) [Sov.Phys.-Crystallogr., 19, 755 (1975)]
5. O.G. Vlokh and L.A. Lažko, this conference (EMF-5)
6. F. Lissalde, S.C. Abrahams, J.L. Bernstein and K. Nassau, J.Appl.Phys., 50, 845 (1979)
7. S.C. Abrahams, F. Lissalde and J.L. Bernstein, J.Chem.Phys., 68, 1926 (1978)
8. J.V. Waszczak, Magnetism Letters, 1, 97-101 (1978)
9. C. Bailar Jr. et al. (ed.), Comprehensive inorganic chemistry, (Pergamon Press, Oxford, 1973) Vol. 3, p. 1089
10. N. Yamada, Y. Chubachi and T. Ikeda, J.Phys.Soc.Japan, 45, 1638 (1978)
11. J.F. Nye, Physical properties of crystals, (Clarendon Press, Oxford, 1957)