Optical rotatory dispersion (ORD), circular dichroism (CD), absorption and spontaneous birefringence (Δns) in the langbeinite K2Co2(SO4)3

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Abstract

The ORD, CD, and absorption spectra of K2Co2(SO4)3 were measured in the cubic phase (P213) at 430-700 nm. In the orthorhombic phase (≤ Tt = 125 K), Δns of 1 of the 3 indicatrix sections was measured down to 5 K. On a 2nd principal section, ORD is visually observable down to 4 K. [on SciFinder(R)]


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OPTICAL ROTARY DISPERSION (ORD), CIRCULAR DICHROISM (CD),
ABSORPTION AND SPONTANEOUS BIREFRINGENCE (Δnₜ) IN THE
LANGBEINITÉ K₂Co₂(SO₄)₃

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Abstract - ORD, CD and absorption of K₂Co₂(SO₄)₃ have been
measured in the cubic phase (P2₁3) between 430 and 700nm. In
the orthorhombic phase (≤ Tₖ = 125K) 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 sulpha tes A₂B₂(SO₄)₃ (A stands for K⁺, NH₄⁺, Rb⁺,
etc. and B for Mg²⁺, Ni²⁺, Co²⁺, etc.) are reported to have proto-
type space group P2₁3 and phase transitions to one or more of the
potential subgroups P2₁, P1, P2₁2₁2₁ and R3 ¹. In K₂Co₂(SO₄)₃ (=KCS)
one of the authors (B.B.) discovered a first order transition at
125K to a potentially ferroelectric phase ² which was claimed to be
non-polar (2₁2₁2₁) ³. With a view to clarifying this transition,
cleaved or cut and polished (100) c platelets of Bridgman-grown
single crystals have been studied at room temperature (ORD, CD and
absorption in the P2₁3 - phase) and between 4 and 300K (domains,
Δnₜ) in an optical helium-flow cryostat under the microscope.

EXPERIMENTS
ORD, CD and absorption in the cubic phase. Ivanov and Koniak ⁴ have
measured ORD in the cubic phase of the langbeinite Cd₂(NH₄)₂(SO₄)₃
(CAS) and found it normal, i.e. it could be described by a single
term Chandrasekhar equation, ρ = Kλ²(λ²-λ₀²)² with K=0.115 deg u²/mm
and λ₀ = 0.1583 μ. In contrast to the relatively weak specific ro-
tation, ρ, and normal dispersion of CAS (ρ is decreasing from
~ 2.5 deg.cm⁻¹ at 700nm) ⁴ and of K₂Cd₂(SO₄)₃ (ρ ~ 15.6 deg.cm⁻¹
at 632.8nm along an optic axis of the 222 - phase )⁵, KCS has a high
ρ 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 58μm thick crystal with a spectrophotometer Unikon 820

* On leave of absence from the Institute of Physics, Academy of
Sciences, Prague.
show a strong peak at 545nm (18350 cm$^{-1}$) and a shoulder due to a weaker peak at $\sim$ 485nm (20620 cm$^{-1}$). In analogy to the langbeinite $K_2Cd_2(SO_4)_3$, in which Cd$^{++}(1)$ and Cd$^{++}(2)$ have trigonally distorted oxygen octahedral environment, Co$^{++}$ is certainly similarly coordinated in KCS. Above 4.2K KCS is paramagnetic with Co$^{++}$ in the high spin state. Therefore the peak at $\sim$ 18350 cm$^{-1}$ can be assigned to the $^{4}T_{1g} \rightarrow ^{4}T_{1g}(P)$ transition of high spin Co$^{++}$. For CoCl$_2$ a similar spectrum due to Co$^{++}$ - with a shoulder - is found. 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 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 cm$^{-1}$ intervals starting at 16530 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 Co$^{++}$ environment, would be needed to explain the details of the absorption and CD spectra (compare with comments in 9). The strong rotation due to Co$^{++}$ is superimposed on a weaker one of the same order of magnitude as the one of CAS, with normal dispersion and being due to the structure's basic framework.

STUDY OF THE LOW TEMPERATURE PHASE

Attempts at poling the domains below $T_t = 125K$ by cooling in a field through $T_t$ and field reversal below $T_t$ failed in fields as high as 40 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 ($/\langle 100\rangle$) only (see below), demonstrate that the low temperature phase is orthorhombic($2_12_12_3$) and hence ferroelastic as concluded earlier. 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 $K_2Mn_2(SO_4)_3$. 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 $T_t$. 

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(Fig. 1a),) show a strong peak at 545nm (18350 cm$^{-1}$) and a shoulder due to a weaker peak at $\sim$ 485nm (20620 cm$^{-1}$). In analogy to the langbeinite $K_2Cd_2(SO_4)_3$, in which Cd$^{++}(1)$ and Cd$^{++}(2)$ have trigonally distorted oxygen octahedral environment, Co$^{++}$ is certainly similarly coordinated in KCS. Above 4.2K KCS is paramagnetic with Co$^{++}$ in the high spin state. Therefore the peak at $\sim$ 18350 cm$^{-1}$ can be assigned to the $^{4}T_{1g} \rightarrow ^{4}T_{1g}(P)$ transition of high spin Co$^{++}$. For CoCl$_2$ a similar spectrum due to Co$^{++}$ - with a shoulder - is found. 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 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 cm$^{-1}$ intervals starting at 16530 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 Co$^{++}$ environment, would be needed to explain the details of the absorption and CD spectra (compare with comments in 9). The strong rotation due to Co$^{++}$ is superimposed on a weaker one of the same order of magnitude as the one of CAS, with normal dispersion and being due to the structure's basic framework. 

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Because class 222 allows maximal rotation along the 2-axes, 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 Δn.

FIGURE 1 Absorbance (a) CD (b) and ORD (c) of K₂Co₂(SO₄)₃ at room temperature

FIGURE 2 Domain pattern of a 58μm 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 (λ = 643 nm)
CONCLUSIONS

On the basis of the extinction properties of the domains and the unsuccessful attempts at poling (+ 40 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 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.

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