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

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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 ($\leq$ Tt = 125K) Δn_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 [1]. 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 [2] which was claimed to be non-polar ($2_12_12_1$) [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 $P2_13$ - phase) and between 4 and 300K (domains, Δn_s) in an optical helium-flow cryostat under the microscope.

EXPERIMENTS

ORD, CD and absorption in the cubic phase. Ivanov and Koňiak [4] 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 deg μ^2/mm and λ_0 = 0.1583 μ. In contrast to the relatively weak specific rotation, ρ, and normal dispersion of CAS (ρ is decreasing from $\sim$ 2.5 deg.cm^{-1} at 700nm) [4] and of $K_2Cd_2(SO_4)_3$ ($\rho \sim$ 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

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(Fig. 1a),) show a strong peak at 545nm (18350 cm^{-1}) and a shoulder due to a weaker peak at ∿ 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 [6,7], Co^{++} is certainly similarly coordinated in KCS. Above 4.2K KCS is paramagnetic with Co^{++} in the high spin state [8]. Therefore the peak at ∿ 18350 cm^{-1} can be assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition of high spin Co^{++}. For $CoCl_2$ a similar spectrum due to Co^{++} - with a shoulder - is found [9]. 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 [4], 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 (//<100>) only (see below), demonstrate that the low temperature phase is orthorhombic($2_1 2_1 2_1$) and hence ferroelastic as concluded earlier [3]. Spontaneous birefringence, Δn_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 Δn_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 Δn_S possibly reflects that of the order parameter, but the decrease of Δn_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 $K_2Mn_2(SO_4)_3$ [10]. 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 [11], 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.

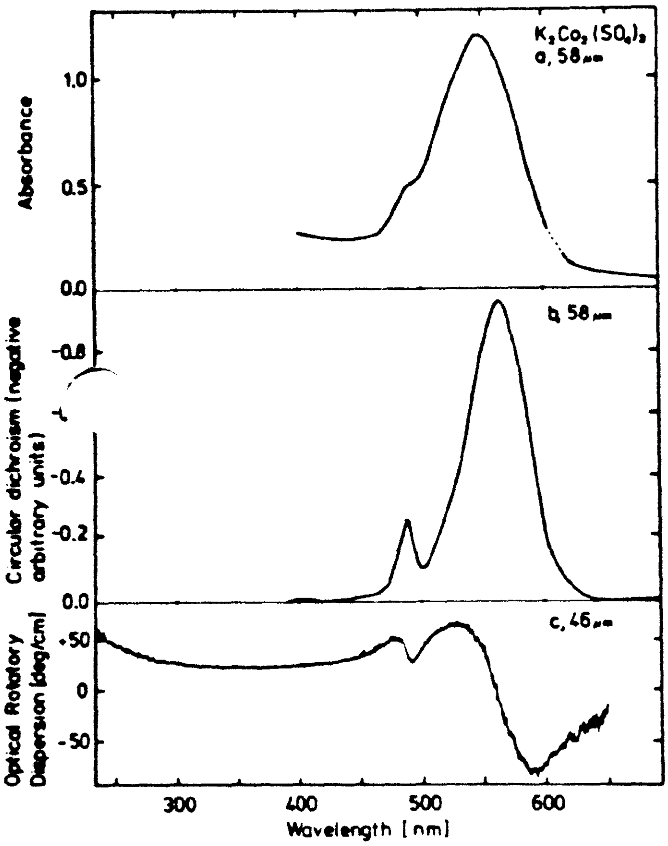

FIGURE 1 Absorbance (a) CD (b) and ORD (c) of K$_2$Co$_2$(SO$_4$)$_3$ at room temperature

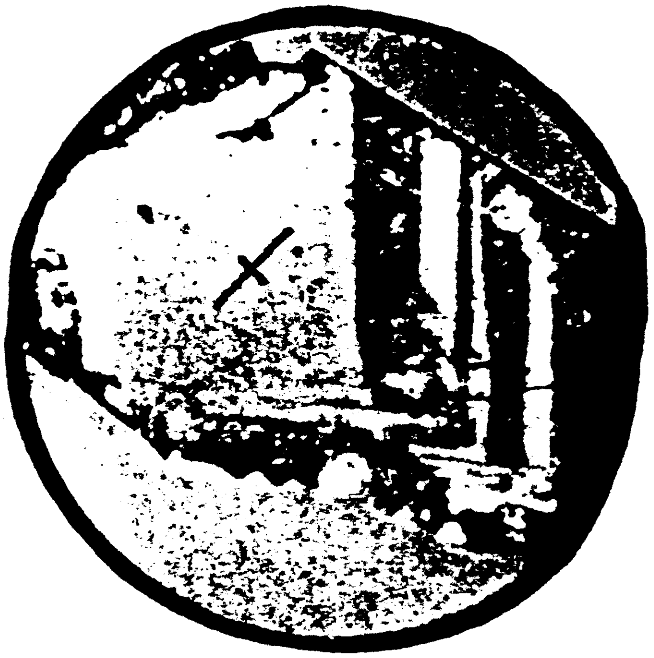

FIGURE 2 Domain pattern of a 58μm thick (100)-cut platelet at 30K. Clear region : domain in 45° position, dark region : domain with visible ORD. (D : 2mm)

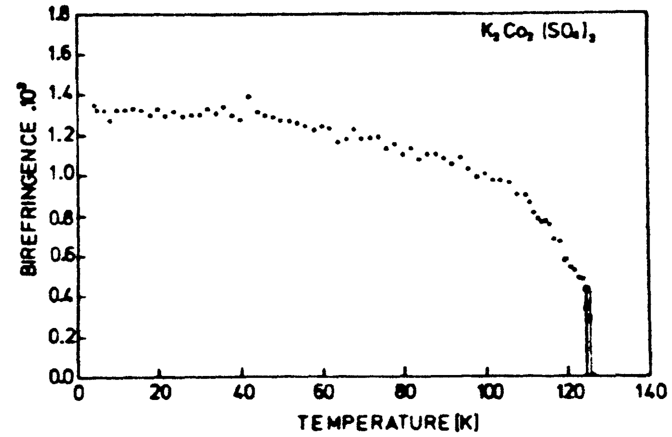

FIGURE 3 Spontaneous birefringence versus temperature of the clear domain of Figure 2 (λ = 643 nm)

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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