ABSORPTIONS- AND RAMAN SPECTROSCOPIC INVESTIGATIONS OF SYNTHETIC COBALT-BOUSSINGAULTITE (PICROMERITE GROUP), $(NH_4)_2Co(SO_4)_2.6H_2O$: REFINEMENT OF SUPERPOSITION MODEL (SM) PARAMETERS FOR Co^{2+}

by

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Crystals of cobalt-boussingaultite $(NH_4)_2Co(SO_4)_2.6H_2O$ up to several mm in size were obtained by controlled evaporation of an aqueous solution of an equimolar mixture of $(NH_4)_2SO_4$ and $CoSO_4$ at 293K. The transparent crystals are orange-red in colour and exhibit weak pleochroism in polarized light.

Cobalt-boussingaultite belongs to the picromerite group, $A^+_2Me^{2+}(SO_4)_2.6H_2O$, with A^+ = NH_4^+, K, Cs, Tl and Me^{2+} = Mg, Co, Ni. Fe, Cu, Zn, V and Cd, crystallising in space group $P2_1/a$. The Me^{2+} cations are sixfold coordinated to oxygen atoms of the water molecules. A recent structure refinement of $K_2Co(SO_4)_2.6H_2O$ by KIRFEL et al. [1] reveals that the Co^{2+} cation is [2+4] coordinated, thus forming a pseudo-tetragonal compressed octahedron, whereas the SO_4 tetrahedron is only slightly distorted.

Corresponding polyhedral distortions could also be detected in $(NH_4)_2Co(SO_4)_2.6H_2O$ by spectroscopic methods: single crystal Raman measurements in the range 100 to 4000 cm^{-1} were conducted with a Renishaw RM 1000 spectrometer equipped with a Leica DMLM series microscope. The spectra were exited with the Ar^+ 488 nm line. Raman lines (in cm^{-1}) caused by the SO_4 group are observed at 455 (v_2), 622 (v_4), 982 (v_1), and in the range 1068 - 1150 (v_3). Bands at 1425 and 1675 cm^{-1} are assigned to the normal modes v_4 and v_2, respectively, of the ammonium ion. Its fundamentals v_1 and v_3 are superimposed by stretching frequencies of the water molecules in the spectral range 3100 to 3400 cm^{-1}.

IR absorption powder spectra were measured in the spectral range 350 to 4000 cm^{-1} under vacuum using a Bruker IFS 66v/S FTIR-spectrometer. Bands were assigned as follows: 613, 639 $v_4(SO_4)$; 1097, 1143 $v_3(SO_4)$; 1400, 1428, 1470 $v_4(NH_4^+)$; 2850 $2v_4(NH_4^+)$. The fundamental $v_3(NH_4^+)$ which is expected at ~3200 cm^{-1} is again superimposed by stretching frequencies of the water molecules (3000 - 3500 cm^{-1}). The H_2O combination modes are centred around 4800 cm^{-1}.

In order to provide new Superposition Model (SM) parameters [cf. e.g. 2] for the Co^{2+} cation, polarized single crystal UV-VIS absorption spectra were measured at room temperature in the spectral range between 35000 cm^{-1} and 4000 cm^{-1} on the Bruker IFS 66v/S FTIR-spectrometer using the attached mirror optics microscope IRscopeII.

The optical spectra are characterised by two main regions of absorption around 8200 cm^{-1} and 18000–22000 cm^{-1} which are correlated predominantly with spin-allowed d-d transitions from the ground state $^4T_{1g}(^4F)$ to the $\rightarrow ^4T_{2g}(^4F)$ and $\rightarrow ^4T_{1g}(^4P)$ states in ideal octahedral O_h symmetry, respectively. A weak and broad band at ~16500 cm^{-1} is attributed to the spin-allowed $^4T_{1g}(^4F)\rightarrow ^4A_{2g}(^4F)$ transition which in the strong field limit represents an electronically forbidden two-electron jump ($t_{2g}^5 e_g^2 \rightarrow t_{2g}^3 e_g^4$) with low probability [e.g. 3]. The observed splitting and structure of the intense VIS band system indicates on one hand the tetragonal perturbation of the octahedral crystal field, on the other hand the significant contribution of intensity enhanced spin-forbidden quartet→doublet transitions and further splitting due to spin-orbit coupling.

Preliminary SM calculations, based on the octahedral geometry of the potassium compound [1], indicate that both 'intrinsic' SM parameters $\overline{B}_k$ for $(NH_4)_2Co(SO_4)_2.6H_2O$ will be comparable to those extracted previously for $Co(OH)_2$ ($\overline{B}_4 = 5320$, $\overline{B}_2 = 3900$ cm^{-1}) [4], i.e. $\overline{B}_4$ is somewhat higher than refined for $Li_2Co_3(SeO_3)_4$ ($\overline{B}_4 = 4740$ cm^{-1}) [5]. This corresponds to the expectations in that H_2O as well as OH^- molecules occupy similar positions in the spectrochemical series of ligands, whereas it has been shown that oxygen atoms of SeO_3^{2-} groups consistently have a comparatively low position within the series of oxygen based ligands [6]. In order to obtain 'correct' global SM parameters for a particular $3d^N$ cation in coordination to varying or mixed ligands, a slight modification of the Superposition Model formalism is currently proposed and tested [7].

References

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