

**SYNTHETIC COBALTOLENITE, $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$, AND RELATED Co-COMPOUNDS
AS MODEL PHASES FOR THE APPLICATION OF
THE SUPERPOSITION MODEL (SM) OF CRYSTAL FIELDS IN GEOSCIENCES**

by

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The Superposition Model (SM) of crystal fields was originally developed to separate the geometrical and physical information inherent in crystal field parameters [1, 2]. It is based on the assumption that the crystal field can be expressed as the sum of axially symmetric contributions of all i nearest neighbour ligands of the transition metal ion. The crystal field parameters B_{kq} can then be obtained from

$$B_{kq} = \sum \bar{B}_k(R_0) \left(\frac{R_0}{R_i} \right)^{t_k} K_{kq}(\Theta_i, \Phi_i)$$

where \bar{B}_k are the intrinsic parameters (related to a reference metal-ligand distance R_0), t_k are the power law exponent parameters, both for each rank k of the crystal field, R_i are the individual metal–ligand distances, and $K_{kq}(\Theta_i, \Phi_i)$ are the coordination factors calculated from the angular polar coordinates of the ligands.

Since its introduction by BRADBURY & NEWMAN [3], the SM has been applied with considerable success for the analysis of lanthanide crystal fields. Contrary, SM investigations on d-block transition elements are scarce up to date. Hence, the necessary intrinsic and power law exponent parameters for application to systems containing d-elements, e.g. in geosciences, are practically missing or were obtained from natural, dilute phases, where the local structure around the particular transition ion is not exactly known, e.g. Cr^{3+} in aluminosilicates [4, 5]. In order to provide reliable SM parameters of $3d^n$ elements for future applications in geosciences, we started to investigate inorganic model compounds, i.e. pure synthetic endmember phases, where the (local) structure is precisely known from concurrent or recent structure investigations.

The first complete SM parameter set for Co^{2+} ($\bar{B}_4 = 4740$, $\bar{B}_2 = 7000 \text{ cm}^{-1}$; $t_4 = 3.1$, $t_2 = 5.5$) was extracted from polarised electronic absorption spectra of $\text{Li}_2\text{Co}_3(\text{SeO}_3)_4$, which is characterised by a strong bond length and angle distortion of its CoO_6 polyhedra with low symmetries C_1 and C_i [6]. Subsequently, we performed SM analyses of temperature dependent polarised spectra of brucite-type $\text{Co}(\text{OH})_2$ [7], where the Co^{2+} ions occupy a high-symmetry site (D_{3d}) within a compressed hexagonal close packing of oxygen atoms. In general, the magnitude of the intrinsic B_k parameters was confirmed ($\bar{B}_4 = 5320$, $\bar{B}_2 = 3900 \text{ cm}^{-1}$; the t_k were not refined due to symmetry restrictions). On closer inspection, however, it appeared that the specific position of closely related ligands within the spectrochemical series (i.e. O_3Se^{2-} vs. OH^-) affects the intrinsic \bar{B}_k .

Therefore, especially for mixed-ligand coordinations, it might be worthwhile to apply some empirical correction factor for the ligand type in the SM equation – resembling the f -factor formerly introduced by JØRGENSEN [8] – instead of refining different SM parameter sets for each ligand type.

Consequently, we modified our program suite [9] (performing the SM calculations with varying parameter sets, preparing the input files for a modified HCFLDN2 crystal field program package by YEUNG [10], and interpreting its output files) in such a way that

$$B_{kq} = \sum_i \bar{B}_k(R_0) \left(\frac{R_0}{R_i} \right)^{t_k} K_{kq}(\Theta_i, \Phi_i) \cdot f_i$$

where f_i represents a fixed or adjustable correction factor for different ligand types, according to their position in the spectrochemical series of ligands. By default, f_i is set to unity. As a Co^{2+} model phase with a distorted mixed-ligand coordination relevant for geosciences, synthetic cobaltomenite, $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$, was chosen. There, the Co^{2+} cations are octahedrally coordinated to four oxygen atoms belonging to SeO_3 groups ($\text{Co}-\text{O} = 2.07 - 2.16 \text{ \AA}$) as well as two water molecules ($\text{Co}-\text{O} = 2.04$ and 2.19 \AA) in *cis*-position [11]. However, the calculations reveal only a marginal deviation of $f_{\text{H}_2\text{O}}$ from unity. In this case, a reason for this unexpected result might be an additional perturbation and hence complication of the crystal field due to the linkage of the CoO_6 octahedra to Co_2O_{10} dimers. Preliminary SM, $f_{\text{H}_2\text{O}}$, and interelectronic repulsion parameters for $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ are: $\bar{B}_4 = 5080 \text{ cm}^{-1}$, $t_4 = 5.4$, $\bar{B}_2 = 8000 \text{ cm}^{-1}$, $t_2 = 0$, $f_{\text{H}_2\text{O}} = 1.01$, Racah B = 800 cm^{-1} , and Racah C = 3300 cm^{-1} . With the exception of the second rank exponent t_2 , which might also be biased by the polyhedral linkage, the obtained SM and Racah parameters comply quite well with the expectations for Co^{2+} in oxygen crystal fields.

References

- [1] NEWMAN, D. J. (1971): Theory of lanthanide crystal fields. - Adv Phys, 20, 197-256.
- [2] NEWMAN, D. J. & NG, B. (1989): The superposition model of crystal fields. - Rep. Prog. Phys., 52, 699-763.
- [3] BRADBURY & NEWMAN (1967)
- [4] YEUNG, Y. Y., QIN, J., CHANG, Y. M. & RUDOWICZ, C. (1994): Correlation of spectroscopic properties and substitutional sites of Cr^{3+} in aluminosilicates: I. Kyanite. - Phys. Chem Min., 21, 526-531.
- [5] QIN, J., RUDOWICZ, C., CHANG, Y. M. & YEUNG, Y. Y. (1994): Correlation of spectroscopic properties and substitutional sites of Cr^{3+} in aluminosilicates: II. Andalusite and sillimanite. - Phys. Chem. Min., 21, 532-538.
- [6] WILDNER, M. & ANDRUT, M. (1999): Crystal structure, electronic absorption spectra, and crystal field superposition model analysis of $\text{Li}_2\text{Co}_3(\text{SeO}_3)_4$. - Z. Kristallogr., 214, 216-222.
- [7] ANDRUT, M. & WILDNER, M. (2001): Superposition Model analysis from polarised electronic absorption spectra of Co^{2+} in trigonally distorted octahedra in brucite-type $\text{Co}(\text{OH})_2$. - J. Phys. Cond. Matter (submitted).
- [8] JØRGENSEN, C. K. (1962): Absorption spectra and chemical bonding in complexes. - Oxford, Pergamon Press.
- [9] WILDNER, M. & ANDRUT, M. (1998-2001): SMM2, program suite for Superposition Model calculations. (unpublished).
- [10] CHANG, Y. M., RUDOWICZ, C. & YEUNG, Y. Y. (1994): Crystal field analysis of the $3d^N$ ions at low symmetry sites including the "imaginary" terms. - Computers in Physics, 8, 583-588.
- [11] WILDNER, M. (1990): Crystal structure refinements of synthetic cobaltomenite ($\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$) and ahlfeldite ($\text{NiSeO}_3 \cdot 2\text{H}_2\text{O}$). - N. Jb. Min. Mh., 1990, 353-362.