Supplementary Appendix II

Hålenius et al. (2007) undertook an analysis of the Racah parameters *B* and *C* and the crystal-field-splitting parameter, $\Delta = 10Dq$, by considering the spectra of a number of Mn^{2+} phases including the spinel galaxite ($Mn^{2+}Al_2O_4$). They labeled the various Mn^{2+} spin-forbidden bands, typically five in number, from ν_1 to ν_5 (see Table 4 in Hålenius et al. 2007) with increasing wavenumber and gave exact equations to calculate the energies of ν_3 and ν_5 and approximate solutions for ν_1, ν_2 and ν_4. In terms of galaxite, *B* and *C* can be calculated from their eqns. (3) and (5) and *Dq* obtained from their eqns. (1) and (2) and in doing this they obtained $B = 627$ cm^{-1}, $C = 3424$ cm^{-1} and $Dq = 592$ cm^{-1}. We note that eqns. (1) and (2) are not real in a strict sense, because if $Dq = 0$, the wavenumber of both ν_1 and ν_2 would be infinite in value, instead of the case where both would have equal energies corresponding to the electronic term ^{4}G (e.g., Burns 1993, Fig. 3.10). Taking the *B*, *C* and *Dq* values for galaxite and inserting them into their eqns. (1) and (2), one calculates $\nu_1 = 19167$ and $\nu_2 = 23389$ cm^{-1}. If, alternatively, one calculates them from the energy matrices of Tanabe and Sugano for the $^4T_1$ and $^4T_2$ states of the electronic configuration d^5 (i.e., Sviridov et al. 1976) and assuming a Trees parameter of $\alpha = 0$, one obtains $\nu_1 = 19745$ and $\nu_2 = 22145$ cm^{-1}. These values agree better with the experimental spectroscopic values for these transitions of 20300 and 22250 cm^{-1}, respectively. Note also that when $Dq = 0$, one has $\nu_1 = \nu_2 = 23390$ cm^{-1} for the electronic term ^{4}G. Similarly, the calculated wavenumber of 26529 cm^{-1} for band ν_4 (i.e, the $^6A_1(S) \rightarrow {}^4T_{2g}(D)$ transition) in galaxite, as obtained from its energy matrix, is closer to the experimental value 25970 cm^{-1} compared to the value of ~25271 cm^{-1} calculated from eqn. (4) of Hålenius et al. (2007). However, in spite of the various differences, if one considers the uncertainties associated with crystal-field and Racah-parameter

theory, we think eqns. (1), (2) and (4) give roughly similar wavenumbers to those calculated using energy matrices.

Assuming that the wavenumbers of the two field-independent electronic transitions $^6A_1 \rightarrow {}^4A_1$, ^4E (^4G) (band ν_3 of Hålenius et al. 2007), as given by the mean wavenumber value for bands i and j, and that the wavenumber value of band m (i.e., ν_5 with $^6A_1(S) \rightarrow {}^4E$ (D)) - see Table 2 - we obtain for our Mn gahnites B = 561 and C = 3530 cm^{-1}. We also calculated the wavenumber for the two field-dependent electronic transitions $^6A_1 \rightarrow {}^4T_1$(G) and $\rightarrow {}^4T_2$(G), labled ν_1 and ν_2, respectively (Hålenius et al. 2007), in the gahnites studied here, using their energy matrices (Sviridov et al. 1976). Ideally, the calculated wavenumber values of ν_1, ν_1 and ν_4 should agree with their experimental values for the same value of Dq (c.f. Burns 1993 - Fig. 3.16). This is always the case for ν_3 and ν_5, because they are field independent (i.e., a function of B and C but not of Dq) and B and C are calculated from their energies. However, we obtain an equivocal result for $^4T_1$(G) and $^4T_2$(G) that best agree with the experimental values of 20730 and 21910 cm^{-1} for rather different values of Dq, that is, 472 and 596 cm^{-1}, respectively. Adopting a mean intermediate value of Dq = 534 cm^{-1}, one calculates ν_1 = 20213 and ν_2 = 23251 cm^{-1}. They differ significantly from the experimental values of 20730 and 21910 cm^{-1} (i.e., +517 and -1305 cm^{-1}, respectively).

Concluding, we think that the noted disagreements between experiment and theory in our analysis are mainly due to the fact that the tetrahedrally coordinated Mn^{2+} in our gahnites is distorted from regular tetrahedral symmetry. This proposal is supported by the observed splitting and fine structure of the electronic bands $^6A_1 \rightarrow {}^4T_2$ and $^6A_1 \rightarrow {}^4A_1$, ^4E (^4G) shown in the spectra of Fig. 6 (see also Table 2). Therefore, the energy matrices that assume cubic symmetry (Sviridov et al. 1976) are not applicable. Moreover, we think that the Racah parameters B and C

probably cannot be determined from the wavenumbers of the strongly split $^6A_1 \rightarrow {}^4A_1$, ^4E (^4G), i.e. i and j bands, and band m (Fig. 6) assigned to $^6A_1(S) \rightarrow {}^4E$ (^4D). It is also of note that the ratio $C/B \approx 6.3$ significantly differs from the "typical value" of 3.5 obtained for various Mn^{2+}-bearing phases (e.g., Burns 1993 - Table 11.1). This indicates that the Racah parameters *B* and *C,* based on our analysis and the use energy equations for v_3 and v_5 (Hålenius et al. 2007), can not be determined quantitatively.