American Mineralogist, Volume 89, pages 1148, 2004

COMMENT

Ordering in spinels—A Monte Carlo study: Discussion

GIOVANNI B. ANDREOZZI,[1,*] FRANCESCO PRINCIVALLE,[2] HENRIK SKOGBY,[3] AND ANTONIO DELLA GIUSTA[4]

[1]Dip. di Scienze della Terra, Università di Roma "La Sapienza", P.le A. Moro 5, I-00185, Roma, Italy
[2]Dip. di Scienze della Terra, Università di Trieste, Via E. Weiss 8, I-34127, Trieste, Italy
[3]Dept. of Mineralogy, Swedish Museum of Natural History, Box 50007, S-104 05 Stockholm, Sweden
[4]Dip. di Mineralogia e Petrologia, Università di Padova, Corso Garibaldi 37, I-35137, Padova, Italy

Lavrentiev et al. (vol. 88, 1522–1531, 2003) extends Monte Carlo computer simulations to the thermodynamics of spinel ordering over a range of *T* and *P*. Starting with $MgAl_2O_4$, several spinel end-members are considered, and experimental data from recent literature are processed.

The authors state that "a contentious issue is the thermal expansion of spinels. For example, for $MgAl_2O_4$, Andreozzi et al. (2000) reported that the lattice parameter actually decreases between 600 and 1100 °C, in contradiction, as shown in Figure 2a, to the results of..."

There is no contradiction here at all, since the structural data reported in Andreozzi et al. (2000) were collected at room temperature after quenching from high temperature. Obviously, as a consequence of this type of experimental technique, only the effect of intracrystalline disorder (and not thermal expansion) on the lattice parameter was measured by Andreozzi et al. (2000) for samples quenched from 600 to 1100 °C. The results were as they must be—that is, the lattice parameter of $MgAl_2O_4$ decreases when intracrystalline disorder increases.

The above-mentioned authors erroneously compared these data to those measured "in situ" at high temperature, when decrease in the lattice parameter is greatly exceeded by thermal expansion.

In spite of this erroneous comparison, the correct comparison of results from these two different approaches allows us to distinguish between the positive contribution to the lattice parameter, due to thermal expansion, and the negative contribution, due to intracrystalline disorder. This was discussed in Andreozzi et al. (2000) on page 1169. Careful inspection of the latter paper would also have revealed that specific thermal expansion coefficients for the T and M sites were obtained, from which a very accurate lattice thermal expansion coefficient could be calculated.

Lastly, Lavrentiev et al. (2003) ambiguously ascribe the differences of ordering in $MgAl_2O_4$ reported by Redfern et al. (1999) with respect to Andreozzi et al. (2000) to "...difficulties in preparing stoichiometric samples and in the experimental determination of the order parameter." It should be noted that both Andreozzi et al. (2000) and Redfern et al. (1999) discussed the problem of synthetic spinel stoichiometry, and the lattice parameters of their samples are certainly ascribable to spinels with extremely low, if any, vacancy content [see, for comparison, the non-stoichiometric samples studied by Lucchesi and Della Giusta (1994)]. In any case, the stoichiometry of the single crystal used by Andreozzi et al. (2000) was ascertained with the highest degree of confidence by means of both microchemical and structural investigations. Concerning order determination by different techniques, a detailed discussion may be found in Andreozzi et al. (2000), in which it is highlighted that different techniques, or even different experimental procedures adopted when using the same technique, may give embarrassingly different results. A solution is, obviously, not simple, and is certainly beyond the scope of this Letter.

REFERENCES CITED

Andreozzi, G.B., Princivalle, F., Skogby, H., and Della Giusta, A. (2000) Cation ordering and structural variations with temperature in MgAl2O4 spinel: an X-ray single crystal study. American Mineralogist, 85, 1164–1171.

Lavrentiev, M.Y., Purton, J.A., and Allan, N.L. (2003) Ordering in spinels—A Monte Carlo study. American Mineralogist, 88, 1522–1531.

Lucchesi, S. and Della Giusta, A. (1994) Crystal chemistry of non-stoichiometric Mg-Al synthetic spinels. Zeitschrift für Kristallographie, 209, 714–719.

Redfern, S.A.T., Harrison, R.J., O'Neill, H.St.C., and Wood, D.R.R. (1999) Thermodynamics and kinetics of cation ordering in $MgAl_2O_4$ spinel up to 1600°C from in situ neutron diffraction. American Mineralogist, 84, 299–310.

MANUSCRIPT RECEIVED NOVEMBER 18, 2003
MANUSCRIPT ACCEPTED FEBRUARY 20, 2004
MANUSCRIPT HANDLED BY LEE GROAT

* E-mail: gianni.andreozzi@uniroma1.it