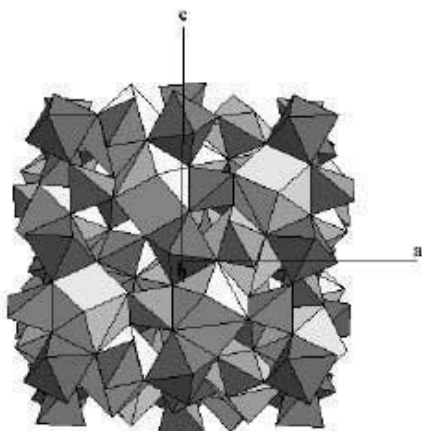


**s11.m1.p13** **Charge density study of synthetic grossular garnets** Y. Dusausoy<sup>1</sup>, F. Porcher<sup>1</sup>, C. Lecomte<sup>1</sup>, H. Lega<sup>2</sup>, J. M. Gaité<sup>3</sup>, H. Rager<sup>4</sup>, <sup>1</sup>L.C.M.<sup>3</sup>B. Université H. Poincaré, Nancy, France <sup>2</sup>C.N.R.S. Bellevue – Brest, France. <sup>3</sup>C. R. M. D., Université d'Orléans, France <sup>4</sup>Institut of Mineralogy-Crystallography, Universität Marburg, Germany.

Keywords: mineralogy, charge density, garnet.

The garnets  $X_3^{2+} Y_2^{3+} [Z_4^{4+} O_4^{2-}]_3$  crystallize in cubic space-group  $Ia\bar{3}d$  with cubic (X), octahedral (Y) and tetrahedral sites. The substitution of cation<sup>3+</sup> in octahedral site induces a framework relaxation and a modification of local electric field at site Y. In order to have an estimation of these later phenomena, we started a study of various Y<sup>3+</sup> substituted garnets by X ray diffraction and local spectrometric probes.

The charge density of synthetic garnets (grossular type) has been studied by high resolution X ray diffraction on single crystals. Data collections were performed at room temperature with Ag(K $\alpha$ ) radiation on Nonius CAD4 and Kappa CCD diffractometers. The electron density in the crystals was modeled using the program Molly<sup>1</sup>. The first results on electrostatic properties (electron distribution, atomic charges ...) will be presented on the poster.



**s11.m1.p14** **The vibrational behaviour of eight-coordinated atoms in pyralispite garnets: anharmonicity or disorder?** C.M. Gramaccioli *Dip.to di Scienze della Terra, Università, via Botticelli 23, I-20133 Milano, Italy*, T. Pilati, *Centro C.N.R. per lo studio delle relazioni tra struttura e reattività chimica, via Golgi 19, I-20133 Milano, Italy*, F. Demartin, *Dip.to di Chimica strutturale e stereochimica inorganica, Università, via Venezian 21, I-21033 Milano, Italy*.

Keywords: mineralogical crystallography.

Garnets such as pyrope, Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> and almandine Fe<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> have long been known to show an unusual behaviour. Such a situation clearly appears in the values of thermodynamic functions such as the heat capacity and entropy, as well as in the crystallographic ADP's of the Mg or Fe atoms, whose distribution often requires higher cumulants. The values are higher than usual, including theoretical (lattice-dynamical) estimates<sup>1</sup>.

To explain such a behaviour, the presence of either "dynamic" or "static" disorder has been claimed. However, for these two minerals and for spessartine Mn<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> at all temperatures a rigid-ion harmonic lattice-dynamical model extended to the whole Brillouin zone together with the assumption of "static" disorder and that of a chemical equilibrium at low temperatures between the "ordered" and "disordered" phase provide good agreement with all the presently available experimental data, including Raman- and IR-vibrational spectra, crystallographic ADP's as well as thermodynamic functions such as entropy and the heat capacity. Moreover, evidence against the "static" disordered model has not been provided yet on quantitative basis.

The notable disagreement concerning the ADP's of the O atoms observed for a natural sample of spessartine can be accounted for by the heretofore unsuspected presence of notable amounts of fluorine, in line with recent discoveries<sup>2</sup>.

In conclusion, whereas the presence of anharmonicity cannot be denied, harmonic lattice dynamics, even as a "pure mathematical hypothesis" is good enough to interpret such phenomena satisfactorily. The advantages of such a procedure, even in spite of its approximations, is relevant especially concerning the correlation between the motion of the different atoms in the crystal structure, as well as zero-point effects, which are not negligible in minerals where all the atoms are strongly bonded.

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