Quantum Mechanical Simulation of the Vibrational Properties of Garnets

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Structural, vibrational and electronic properties of pyrope, grossular and andradite have been simulated with the periodic *ab initio* CRYSTAL [1] program, that adopts a local variational basis set ("Atomic Orbitals") to build the crystalline orbitals. An *all-electron* basis and the B3LYP hamiltonian have been used.

The full spectrum at the Γ point (97 frequencies) [2] and the IR intensities have been evaluated, along with the symmetry of the modes, which is automatically determined. The eigenvectors of the dynamical matrix have been analyzed with different tools, including direct inspection, isotopic substitution, animations; classification-interpretation questions raised by previous studies are discussed.

The 17 IR and 25 RAMAN active modes are compared with available experimental data [3], [4]. The agreement is excellent in most of the cases (6-8 cm^{-1} the mean absolute difference).

[1] Saunders V.R., Dovesi R., Roetti C., Orlando R., Zicovich-Wilson C., Harison N.H. Doll K., Civalleri B., Bush I.J., D'Arco Ph., Llunell M., *CRYSTAL2003 user's manual. University of Torino, Torino,* 2003. [2] Pascale F., Zicovich-Wilson C., Orlando R., Dovesi R., *J. Phys. Chem.*, 2005, ***in press***. [3] Kolesov B., Geiger C., *Phys. Chem. Min*, 2000, **27**, 645. [4] Hofmeister A., Chopelas A., *Phys. Chem. Min*, 1991, **17**, 503.

Keywords: ab-initio calculations, garnets, vibrational frequencies