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Ab-initio thermal physics and Cr-isotopic fractionation of $MgCr_2O_4$

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ABSTRACT

Ab-initio thermophysical properties and isotopic separative effects in $MgCr_2O_4$ were computed with the CRYSTAL03 code. All calculations were carried out within the LCAO approach (Linear Combination of Atomic Orbitals) by using the Hartree-Fock and the hybrid B3LYP density functional methods. Vibrational frequencies have been computed at the long-wavelength limit corresponding to the center of the Brillouin zone ($\mathbf{k} \rightarrow 0$). Since thermodynamic functions depend on the phonon dispersion relation, the ab-initio based vibrational analysis of the optical modes has been coupled with the semiempirical Kieffer model for the acoustic modes, which is based on a sine wave dispersion equation. All computed magnitudes (zero point energy, internal energy, Helmholtz free energy, optical vibrational modes, thermal corrections to internal energy, enthalpy and Gibbs free energy, thermal pressure, bulk modulus and its *P* and *T* derivatives, entropy, isochoric and isobaric heat capacity, and isotopic separative effects) are consistent with direct observations and/or reasonable estimates, within the accuracy of the method. The computed separative effects are similar to those observed in other Cr^{3+}-bearing substances. The crystal field seems to have no influence on the separative effect for an isotopomeric couple with respect to an isolated gaseous couple with Cr^{3+} as central cation.

Keywords: Ab-initio thermochemistry, picrochromite, Cr-isotopes, Cr-fractionation, vibrational properties, thermal physics