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Ordering in spinels—A Monte Carlo study

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ABSTRACT

We have extended a recently developed Monte Carlo technique which includes explicit exchange as well as movement of ions to systems involving heterovalent exchange. These Monte Carlo computer simulations, based on analytical inter-atomic potentials, are capable of providing detailed quantitative information concerning the thermodynamics of ordering of spinel ($MgAl_2O_4$), gahnite ($ZnAl_2O_4$), hercynite ($FeAl_2O_4$), $NiAl_2O_4$, and magnesioferrite ($MgFe_2O_4$) over a range of pressures and temperatures. At all temperatures and pressures ionic relaxation, lattice vibrations, and pressure are *explicitly* taken into account. Each compound has a larger expansion coefficient and smaller bulk modulus in the normal than in the inverse spinel structure. We predict only a small variation of order parameter with pressure, and that this will be more pronounced for inverse than normal spinels. We examine, briefly, the consequences of our results for the kinetics of cation ordering in these solids.