Lattice-dynamical evaluation of thermodynamic properties and atomic displacement parameters for beryl using a transferable empirical force field

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ABSTRACT

Using empirical potentials derived from fitting the vibrational frequencies of a group of silicates and oxides, and crystallographic information, a Born-von Karman rigid-ion lattice-dynamical model has been applied to the whole Brillouin zone in beryl. The Raman and infrared spectra are satisfactorily reproduced and interpreted by these calculations; there is also very good agreement with atomic displacement parameters derived from accurate crystal-structure refinement by various authors and with experimental values of thermodynamic functions for the anhydrous phase at different temperatures. The agreement of our calculations with experimental data of independent origin and nature demonstrates the potential of such a procedure.

INTRODUCTION

Following our interest in the field, which started from molecular crystals (e.g., Gramaccioli 1987 and references therein), we have tried to extend our harmonic lattice-dynamical calculations to minerals (Pilati et al. 1990, 1993a, 1993b, 1994, 1995, 1996a, 1996b, 1997). For such purposes, the Born-von Karman procedure has been adopted, using a rigid-ion model extended to the whole Brillouin zone.

The initial scope of our calculations was concerned with theoretical evaluation of atomic displacement parameters (ADP) and their comparison with corresponding results obtained from crystal-structure refinement. Then we began interpreting vibrational spectroscopy data, such as Raman and infrared spectra, and especially estimating the values of thermodynamic functions.

The first systematic attempt to derive thermodynamic properties for a whole series of different minerals from spectral data, using statistical-mechanical procedures, is that of Kieffer (1979a, 1979b, 1979c, 1980, 1982). However, a Born-von Karman lattice-dynamical model is more accurate; no fit is needed for several experimental data specific for a single phase, and there is an immediate connection with force fields. The possibility of wide application of Born-von Karman lattice-dynamical models to minerals, using empirical valence force-field (VFF) parameters is supported by several authors who also used the rigid-ion model, such as Rao et al. (1988), Dove et al. (1992), Kihara 1993, and Ghose et al. (1994). An important advantage of such lattice-dynamical models is that spectroscopic information is helpful for deriving these empirical force-field parameters only, on a best-fit basis to experimental values; if the force fields are transferable, such information may not even be essential for each particular compound (e.g., Pilati et al. 1996a, 1996b). The need to know all possible information concerning the vibrational frequencies for each particular compound could be a serious drawback, because, apart from the problem of selecting the fundamentals, many of these frequencies are often missing in the experimental measurements of Raman or infrared spectra, either because their intensity is too weak or because they are not active due to symmetry. A significant example occurs for garnets; because of symmetry, more than 50% of the modes at the origin of the Brillouin zone are both Raman and IR inactive.

Successful applications of Born-von Karman lattice dynamics to minerals using more elaborate schemes, such as shell models or the quasi-harmonic approximation, are due to several authors such as Price et al. (1987a, 1987b), Winkler et al. (1991), and Patel et al. (1991). In most of these works, good agreement was achieved with the experimental values of some thermodynamic functions such as the specific heat and entropy at different temperatures, and the possibility of using transferable empirical force fields for such purposes has been confirmed also. However, the inadequacy of the rigid-ion model with respect to these more advanced models is generally evident for the highest frequencies only. In most cases, the lowest vibrational energy levels are reproduced with comparable accuracy, and the contribution of these low levels is usually the overwhelming one in accounting for thermodynamic functions and ADP. Rigid-ion models similar to ours were used recently and successfully by several authors, such as Dove et al. (1992) and Catti et al. (1993) to derive physical properties of calcite and aragonite, and Keskar and Chelikowsky (1995) to calculate thermodynamic properties of silica polymorphs.

Unfortunately, for minerals in general there are very...