Calculated pressure-induced phase transition in MgF_2

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Relatively little attention has been paid to pressure-induced phase transitions in the Group II halides in contrast to the volume of work on the $B1$–$B2$ transition in the alkali halides and alkaline-earth oxides. However, recently the rutile to fluorite transition in MgF_2 has been the subject of a paper by Nga and Ong,[1] in which they studied this transition by molecular dynamics simulation based on a Born–Mayer potential derived by Catti *et al.*[2] Their theoretical transition pressure at 300 K of ~130–140 GPa, is greatly in excess of the measured value of ~30 GPa reported by Ming and Manghani,[3] which is somewhat puzzling in view of the accuracy with which the potential used reproduces the experimental lattice structure of MgF_2.[2] To investigate this point further, and as part of a wider study of ionic materials at elevated temperatures and high pressures,[4,5] we have carried out a combined lattice statics and lattice dynamics simulation of the two phases of MgF_2 based on the same potential and here report our calculated transition pressures. In part, our study has been prompted by a recent comparison of lattice dynamics and molecular dynamics simulations of MgO at high temperature and pressure[6] which showed remarkable agreement between the two approaches.

As elsewhere,[4,5] our approach is based on the direct calculation of the Helmholtz free energy $A(V,T)$, which is obtained from the potential energy of the lattice, E_L, and the normal mode frequencies, $\nu_j(\mathbf{k})$, which in turn are obtained from the lattice dynamics of the system. In the quasiharmonic approximation, $\nu_j(\mathbf{k})$ are independent of the temperature, T, but not the volume, V. $A(V,T)$ is given by

$$A=E_L+k_BT\sum_{\mathbf{k},j}\{\beta_j(\mathbf{k})/2+\ln(1-\exp[-\beta_j(k)])\},\tag{1}$$

where

$$\beta_j(\mathbf{k})=h\nu_j(\mathbf{k})/k_BT,\tag{2}$$

k_B is Boltzmann's constant and the sum over $\mathbf{k}$ vectors is evaluated at the Chadi–Cohen special points.[7] The pressure, $p=-(\partial A/\partial V)_T$, is obtained from numerical differentiation of A with respect to V, while the entropy, $S=-(\partial A/\partial T)_V$, is obtained directly from the normal mode frequencies

$$S=-k_B\sum_{\mathbf{k}j}\{\beta_j(\mathbf{k})(\exp[\beta_j(\mathbf{k})]-1)^{-1}+\ln(1-\exp[-\beta_j(\mathbf{k})])\}.\tag{3}$$

The Gibbs free energy, $G(p,T)$, can then be calculated from $A(V,T)$ and pV. An additional point of note is that, for the rutile phase at a given volume V, the structure and corresponding value of A are obtained by minimizing A with respect to the lattice constants a and c and the internal atomic coordinate u.

As a first approximation, the transition pressure can be estimated from the strain-free lattice energies and volumes of the two phases, $p_t=\Delta E_L/\Delta V$, which is the hypothetical value in the athermal limit. From the values of ΔE_L and ΔV given in Table I, this first estimate of p_t is 26 GPa, which compares with the experimental estimate of ~30 GPa.[3] Figure 1 shows the calculated pressure dependence of the Gibbs free energy of the rutile and fluorite phases of MgF_2 at 296 K. The fluorite phase is found to be stable throughout the pressure range, in contrast to the rutile phase which, as expected, shows mode softening leading to imaginary frequencies and a structural instability at approximately 23 GPa. Thus we cannot locate the exact pressure at which $\Delta G=0$, unlike the $B1$ to $B2$ transition in NaF, for example, where similar calculations have found both phases to be stable through the transition pressure.[6] An approximate value of the transition pressure can be obtained from polynomial fits to $G(p)$ for the rutile phase followed by extrapolation to pressures beyond 23 GPa and from these we estimate p_t to be in the range ~30–40 GPa, which is close to the static value. This is similar to what has been found for the $B1$–$B2$ transition in NaF[6] and NaCl,[8] but in marked contrast to the $B1$–$B2$ transition in the alkaline-earth oxides, for which the phonon contribution to the transition pressure has been found to be appreciable.[8]

The present transition pressures may be compared with a previous athermal value of ~43 GPa reported by Muhlhausen and Gordon[9] based on a two-body potential derived from their electron-gas theory of ionic crystals and also that obtained from *ab initio* Hartree–Fock calculations. For the latter we have reoptimized the basis set for

TABLE I. Volume and energy differences (fluorite–rutile) ΔV (Å^3) and ΔE (eV), in the athermal limit, based on Catti *et al.* potentials (Ref. 2) and Hartree–Fock calculations.

	Catti *et al.* potentials	Hartree–Fock
ΔV	−2.088	−3.083
ΔE	0.344	0.470
p_t	26	24

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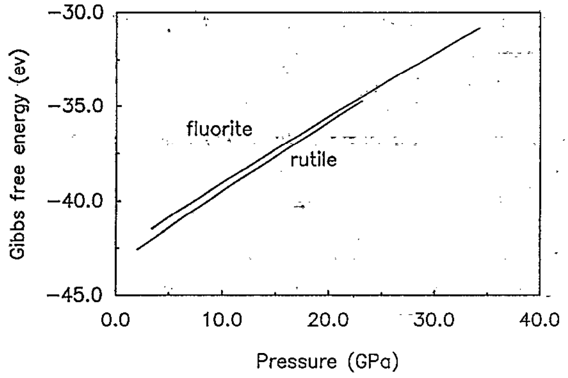

FIG. 1. Gibbs free energy (eV) vs pressure (GPa) for the rutile and fluorite phases of MgF_2.

MgF_2 used by Catti *et al.*[2] at the experimental rutile structure and used this to calculate the Hartree–Fock structures and total ground state energies, E_T, of both phases using the CRYSTAL 92 code.[10] The corresponding values of ΔE_T and ΔV are given in Table I, from which the athermal Hartree–Fock transition pressure is found to be 24 GPa. A recent *ab initio* study of the $B1$–$B2$ transition in NaCl by Aprà *et al.*[11] suggests that the inclusion of electron correlation effects, at least *a posteriori*, is unlikely to change this value by more than a few percent.

In summary, we find the transition pressure for the rutile to fluorite transition in MgF_2 based on the two-body potentials of Catti *et al.*[2] to be much lower than that reported recently by Nga and Ong[1] from molecular dynamics simulations and in good agreement with both the experimental pressure and other theoretical estimates. A previous study of the $B1$–$B2$ transition in alkali halides by Ruff *et al.*[12] reported difficulties in obtaining acceptable transition pressures using molecular dynamics simulations and we suggest this may also have been the case for MgF_2.

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