Ionic solids at elevated temperatures and high pressures: MgF_2

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A combination of periodic Hartree–Fock theory, quasiharmonic lattice dynamics, and molecular dynamics is used to study the behavior of MgF_2 at elevated temperatures and/or high pressures. Particular attention is paid to the pressure-induced transition from the rutile to the fluorite structure in view of earlier theoretical estimates of the transition pressure, which differ widely. It is shown that previously reported potentials obtained by fitting to empirical data fail to reproduce thermodynamic properties. To rectify this, a new set of consistent two-body potentials has been derived from *ab initio* periodic Hartree–Fock calculations. Lattice dynamics calculations in the quasiharmonic approximation based on these potentials has been used to study the two phases of MgF_2 at high T and P. The resulting transition pressure and that obtained *directly* from Hartree–Fock calculations in the static limit are both $\leqslant 30$ GPa, which is close to the experimental value but appreciably lower than a previous molecular dynamics value of over 130 GPa. The variation of quantities such as $(\partial P/\partial T)_V$ which play a central role in the formulation of approximate equations of state is also considered. © *1997 American Institute of Physics.* [S0021-9606(97)51035-X]

INTRODUCTION

It is now widely accepted that computational techniques provide an attractive approach for investigating the behavior of solids at high pressure and temperature. This is an important aspect of condensed matter chemical physics in areas ranging from the modeling of explosives to geophysics. A number of studies have been reported of the B1–B2 transition in the alkali halides and alkaline-earth oxides,[1–4] with rather less attention paid to tetragonal and other noncubic systems, which often represent a step forward in the study of crystal complexity. In particular, the rutile–fluorite transition in MgF_2 has been studied by Nga and Ong[5] using molecular dynamics techniques and an empirical Born–Mayer potential fitted by Catti *et al.* to the lattice parameters and elastic constants of the rutile phase.[6] Although there was some indication that this interionic potential might not lead to a stable fluorite structure, the molecular dynamics results[6] gave the rutile phase as stable up to pressures of about 85 GPa, followed by an intermediate phase of ill-defined structure, with the fluorite phase becoming established at about 135 GPa. This is over four times the experimental value[7] of about 30 GPa and approximately three times an earlier theoretical estimate.[8] In an attempt to clarify this situation, Allan *et al.*[9] recalculated the transition pressure using both lattice statics and quasiharmonic lattice dynamics based on the Catti potential, and also from *ab initio* periodic Hartree–Fock calculations in the static limit at $P=0$. Estimates of the transition pressure from static calculations using $P_t \approx -(\Delta E/\Delta V)_{P=0}$ gave $P_t \approx 25$ GPa for both the Catti potential and electronic structure calculations. Extrapolation of the lattice dynamics results led to a value of P_t in the range 30–40 GPa. However, above ~ 23 GPa, imaginary frequencies at certain **q**-vectors were found for the rutile structure, indicating the lattice was unstable; no such instability was detected for the fluorite structure at these pressures. The discrepancies between the results from lattice dynamics and from molecular dynamics simulations were surprising, because previous simulations[10,11] of MgO and Li_2O over a very wide range of pressure and/or temperature indicated a remarkable degree of agreement between the two approaches.

Further (unpublished) calculations by the present authors with the Catti potential, using finer grids of vectors in the Brillouin zones of the two phases than those previously employed,[9] have revealed imaginary frequencies not only for the rutile structure but also for the fluorite structure at all pressures up to at least 50 GPa, thus confirming Nga and Ong's earlier suggestion.[5] This not only prohibits lattice dynamical calculations, but also implies that both structures are unstable. The Catti potential does indeed predict a minimum in the static energy with respect to changes of lattice parameter (so-called ''mechanical'' stability) for the rutile and fluorite structures, but the instability now revealed with respect to more general displacements renders the use of the Catti potential invalid, not only for calculations at nonzero temperature, but even in the static limit itself.

The failure of the Catti potential necessitates the generation of an alternative for high temperature studies, since elec-

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tronic structure methods cannot easily be used directly other than in the static limit. Accordingly, in this paper we present a new set of potentials derived from *ab initio* periodic Hartree–Fock calculations.[12,13] Our approach is similar to that used for Li_2O (Ref. 11), for which dynamically stable structures up to the fast-ion transition temperature were obtained. As before,[11] these new potentials are entirely theoretical, with no empirical input, and have been constructed by sampling parts of the (Hartree–Fock) energy hypersurface that are relevant to high temperatures and pressures. They appear to lead to dynamically stable rutile and fluorite structures, and hence can be used to investigate the properties of MgF_2 at high pressures and temperatures. We use them and the greater computational resources now available to us, first to resolve the apparent discrepancy between transition pressures obtained from lattice dynamics and molecular dynamics, and then to examine other temperature and pressure dependent properties in some detail. In the calculation of minimum (Gibbs) free energy structures we also report, for the first time, a comparison of results obtained from analytic derivatives of the dynamical matrix[14] with those obtained from numerical derivatives of the Helmholtz free energy,[1,2] and show them to be identical. Further, we examine critically the effect on the results of employing the zero static internal stress approximation (ZSISA),[15] a widely used approximation in which the total free energy is minimized only with respect to external strains (lattice parameters), while internal strains are determined by minimizing simultaneously only the static contribution. Finally, we consider briefly the variation with T and P of some thermodynamic quantities of importance to approximations used in geophysics and explosives modeling.

TECHNIQUES

Hartree–Fock calculations

The all-electron *ab initio* LCAO Hartree–Fock method for periodic systems and its computational implementation in the CRYSTAL 92 code have been described in detail previously.[12,13] The calculations reported here use extended Gaussian basis sets for MgF_2 derived previously by Catti *et al.*[6] The numerical values of the tolerance parameters involved in the evaluation of the infinite bielectronic Coulomb and exchange series were identical to those in a recent study,[16] and chosen, as previously, to ensure high numerical accuracy. A detailed account of the effect of these tolerances has been given elsewhere.[17] Since our study required the comparison of energies for very different crystal configurations and structures, very high accuracy was necessary, and so all bielectronic integrals were calculated explicitly. The reciprocal space integration utilized the Monkhorst–Pack sampling scheme[18] with a shrinking factor of 8 (i.e., 144 points in the irreducible part of the Brillouin zone for rutile, and 29 for fluorite). The self-consistent-field (SCF) convergence criterion was taken to be changes in the total energy of less than 10^{-8} Hartree.

TABLE I. The potential parameter set for MgF_2 derived in this work. For each pairwise interaction $V(r)=A\ \exp(-r/\rho)-Cr^{-6}$, with a cut-off of 8 Å. The charge on Mg is 1.808e.

Interaction	A/eV	ρ/Å	C/eV Å^6
Mg^{2+}/F^-	5971.77	0.212 726	8.959 64
F^-/F^-	224 00.8	0.191 711	−24.8042

Lattice statics and quasiharmonic lattice dynamics

To calculate free energies we have used the quasiharmonic approximation, and assumed the Helmholtz free energy of a crystal, A, at a temperature, T, can be written as the sum of static and vibrational contributions

$$A=\Phi_{\text{stat}}+A_{\text{vib}}, \tag{1}$$

where Φ_{stat} is the potential energy of the static lattice and A_{vib} the vibrational contribution given by the Born expression:

$$A_{\text{vib}}=\sum_{\mathbf{q},j}\ \{\tfrac{1}{2}h\nu_j(\mathbf{q})+kT\ \ln[1-\exp(-h\nu_j(\mathbf{q})/kT)]\}, \tag{2}$$

where the $\nu_j(\mathbf{q})$ are the normal mode frequencies for wave vector $\mathbf{q}$ and k is Boltzmann's constant. The $\nu_j(\mathbf{q})$ are evaluated from the dynamical matrix in the usual way, and so are explicit functions of the crystallographic parameters, but not of the temperature T. We sum over uniform grids of $\mathbf{q}$-vectors,[19] using successively finer grids until convergence is achieved.

For the fluorite structure there is only one independent parameter a giving the size of the cubic unit cell. For the rutile structure[20] there are three parameters: a and c give the dimensions of the tetragonal cell, but a further ''internal'' parameter, u, is needed to determine the positions of the fluoride ions. For such a crystal, it is simplest to treat the internal strain as a thermodynamic variable on the same footing as macroscopic strain.[14,21,22] Thus the equilibrium structure at applied pressure P can be found by minimizing the Gibbs energy $(A+PV)$ simultaneously with respect to a, c, and u. To achieve this, we have used a standard conjugate gradients technique.[23] For this it is necessary to calculate the strain derivatives of G, which are evaluated using analytic derivatives of the dynamical matrix in first-order perturbation theory.[24] Results obtained in this way are in excellent agreement with derivatives obtained numerically using finite increments of 10^{-5} in the strains.

Molecular dynamics

To check the quasiharmonic approximation we have carried out molecular dynamics simulations at constant pressure and temperature based on an extended system as described in Ref. 25. The same interionic potentials were used as for the lattice dynamics calculations. The initial configuration for each phase was generated by arranging (i) 192 Mg and 384 F ions in a box of sides 4×4.52, 4×4.52, and 6×3.09 Å (rutile); (ii) 256 Mg and 512 F ions in a cubic box of side

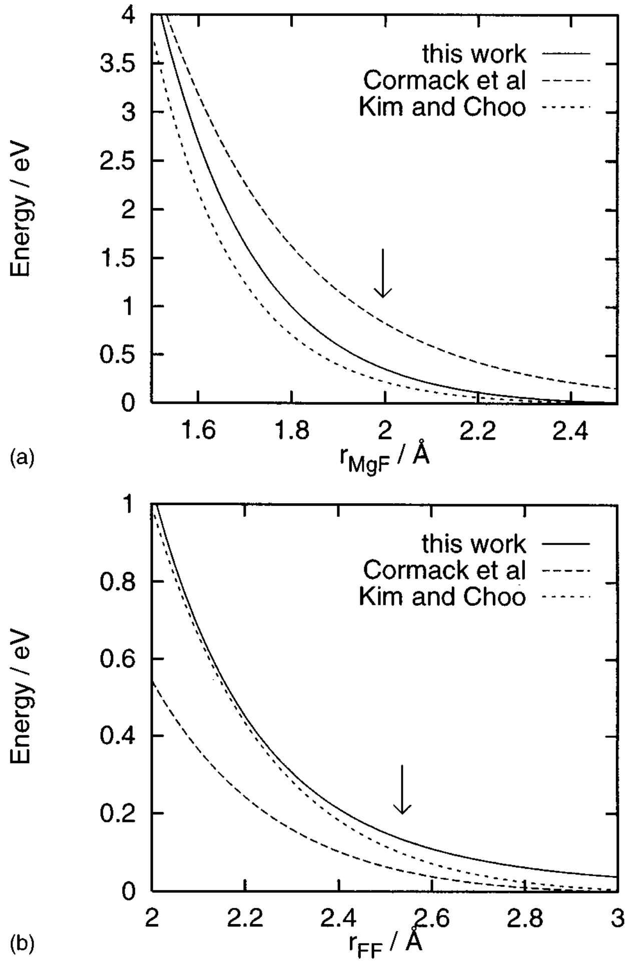

FIG. 1. A comparison of (a) Mg–F (b) F–F potentials for MgF_2. The arrows denote the closest Mg–F and F–F separations at 300 K.

length 4×4.95 Å (fluorite). Constant NVE runs of 10 ps gave initial configurations. This configuration was used as the starting point for equilibration runs of 10 ps, followed by production runs of 10 ps at constant NPT for each pressure and temperature considered. The temperature and pressure were kept constant by using an extended system with thermostat and barostat relaxation times of 1 and 0.5 ps, respectively. The reliability of the results was checked by selected further runs with simulation times longer than 10 ps.

RESULTS

Potentials

The approach we have used to derive (pair) potentials directly from Hartree–Fock energies differs somewhat from that employed previously[11] for Li_2O; all the potential parameters were fitted simultaneously to the energies of a set of different configurations instead of displacing each sublattice relative to the other and fitting each potential in turn. Energies were calculated solely for the rutile phase, as follows: (i) the lattice parameter a was varied from 4.1 to 5.1 in steps of 0.1 Å, keeping c and the internal degree of freedom u constant at their equilibrium values at $P=0$, c_0 and u_0; (ii) next, the lattice parameter c was varied from 2.5 to 3.7 in steps of 0.1 Å, keeping $a=a_0$ and $u=u_0$; (iii) last, u varied from 0.25 to 0.35 in steps of 0.01, keeping $a=a_0$ and $c=c_0$. The short-range interionic potentials fitted simultaneously to all these energies were assumed to be of the Buckingham form, giving total pair potentials

$$Z_aZ_b/r+V_{ab}(r)=Z_aZ_b/r+A_{ab}\ \exp(-r/\rho_{ab}) - C_{ab}r^{-6}. \tag{3}$$

Here a and b refer to the ion type and r is the interionic distance. Z_{Mg} and Z_{F} were put equal to the Mulliken charges of 1.808 and $-0.904\,e$, respectively, for the Hartree–Fock optimized rutile phase at $P=0$. For simplicity, the Mg–Mg interaction was assumed to be purely Coulombic. The remaining parameters were then obtained by fitting V_{MgF} and V_{FF} simultaneously with a cut-off of 8 Å for both. The final potential parameters are listed in Table I.

It is instructive to compare our fitted potentials with some other recent sets in the literature. In Fig. 1 we plot the non-Coulombic contributions to the Mg–F and F–F potentials derived in this work and those developed by empirical fitting by Cormack *et al.*,[26] and by Kim and Choo.[27] There are large differences between the various potentials, particularly at the nearest neighbor Mg–F (≈2.0 Å) and F–F distances (≈2.5 Å). In particular, the Mg–F potential due to Cormack *et al.*[26] is more repulsive than the others and their F–F potential less so. The Coulombic contributions to the potentials are also very different; Ref. 26 assumes full ionicity while Ref. 27 assigns a charge of only 1.56 e to Mg.

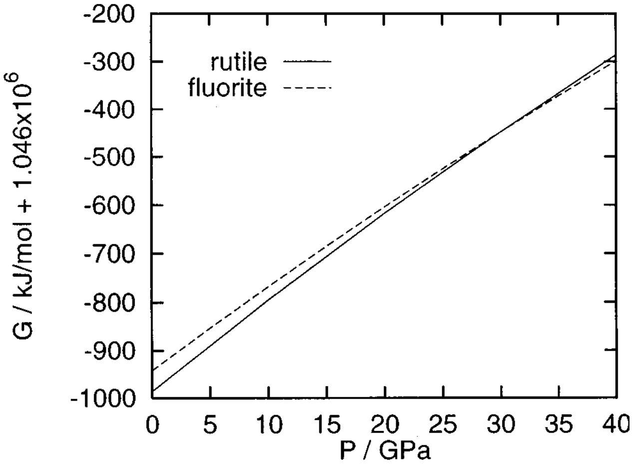

FIG. 2. Gibbs energy (kJ mol^{-1}) vs pressure (GPa) for the rutile and fluorite phases of MgF_2 calculated in the static limit using periodic Hartree–Fock calculations and the basis set listed in Ref. 6.

Transition pressure

We now present results for a range of properties which are traditionally difficult to calculate accurately. We start with the static equilibrium structure of MgF_2 at high pressure. Figure 2 shows the variation of G with P for both phases in this limit (in which $G=H=\Phi_{\mathrm{stat}}+PV$), calculated *directly* using the CRYSTAL 92 code.[13] For the fluorite phase, the electronic energy Φ_{stat} was determined for a range of volumes and the corresponding pressure from $-(d\Phi_{\text{stat}}/dV)$, evaluated numerically. For the rutile phase, for a given volume, the structure was found by minimizing the electronic energy with respect to the ratio of the lattice parameters a and c and to the internal coordinate u, and the pressure determined as for the fluorite phase. In the static limit the Hartree–Fock transition pressure is found to be 30 GPa, in good agreement with the experimental value.[7] A corresponding periodic Hartree–Fock study of the B1–B2 transition in NaCl by Aprà *et al.*[3] suggests that the inclusion of electron correlation effects, at least applied *a posteriori*, is unlikely to change this value by more than a few percent. In contrast, the transition pressure estimated from zero pressure data, i.e., from $P_t \approx -(\Delta E/\Delta V)_{P=0}$, is only 23 GPa, too low by $\approx 25\%$.

To estimate the temperature dependence of the transition pressure, we have used lattice dynamics in the quasiharmonic approximation. For this purpose we can use our new two-body potentials because, unlike those of Catti *et al.*, they give no imaginary frequencies for either crystal structure over the relevant range of geometrical configurations. With these potentials we obtain a transition pressure in the static limit of ≈ 12 GPa, of the same order of magnitude but considerably lower than the 30 GPa given by the direct comparison of Hartree–Fock energies for the two structures. The two-body potentials are, of course, unable to reproduce exactly the Hartree–Fock energies, and the transition pressure is sensitive to small changes in the energy because ΔG remains small over a large range of pressures.

Figure 3 shows the total Gibbs free energy as a function of pressure (GPa) for the rutile and fluorite phases of MgF_2 at 300 K, calculated using quasiharmonic lattice dynamics with the new potential. The model still gives $P_t \approx 12$ GPa; the vibrational effects on P_t, which can be calculated either directly, or from $dP_t/dT = \Delta S/\Delta V$, are negligible ($|dP_t/dT| \leqslant 0.001$ GPa K^{-1}). Furthermore, the inclusion of a shell model for F^-, with an associated polarizability of 1.07 Å^3, also made little difference to P_t. The value of $P_t \approx 12$ GPa may be compared with those of ≈ 8 and ≈ 20 GPa obtained using the empirical sets of pair potentials reported in Refs. 26 and 27, respectively (plotted in Fig. 1), showing that in this respect they perform as well as the new potential.

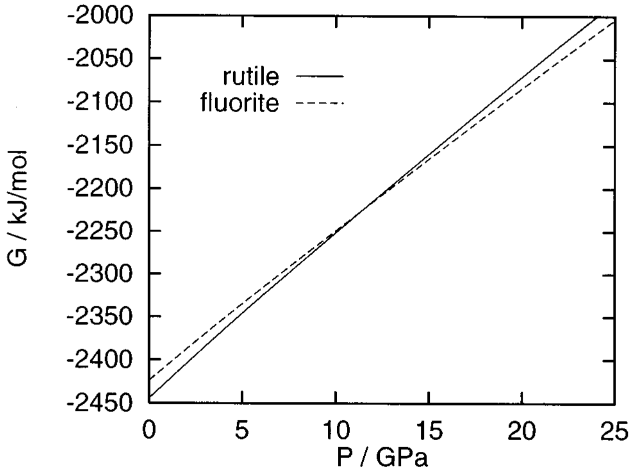

FIG. 3. Gibbs energy (kJ mol^{-1}) at 300 K vs pressure (GPa) for the rutile and fluorite phases of MgF_2 calculated using lattice statics and dynamics and the potential derived in this work listed in Table I. A grid of 27 **q**-points was used.

Taken as a whole, the results of all these calculations suggest a transition to the fluorite structures in the range 10–30 GPa, which is over 100 GPa less than that suggested by Nga and Ong.[5] Thus we find no evidence from any of the different types of calculations presented here that the thermodynamic transition pressure, at any temperature, between the rutile and fluorite phases of MgF_2, is much in excess of the apparent experimental value[7] of ≈ 30 GPa. It might well be that the molecular dynamics result arises from an activation barrier to the transition, similar to that observed in the B1–B2 transition for the alkali halides.[4] Calculations investigating the kinetics and mechanism of the transition are currently in progress.

Thermal expansion

We now consider in more detail selected thermodynamic properties of the two phases, considering first the lattice pa-

TABLE II. Hartree–Fock optimized geometries for the rutile and fluorite phases of MgF_2 obtained using the basis set tabulated in Ref. 6. u refers to the internal degree of freedom, such that in the asymmetric unit there is a fluorine ion at $(u,u,0)$ (fractional coordinates). The experimental geometry at 300 K is also given (Ref. 35). For the rutile phase we also give the values predicted at 300 K and zero pressure by quasiharmonic lattice dynamics and the potentials obtained in this work. For details of the ZSISA and CISPA approximations see the text.

Parameter	Hartree–Fock	Experiment (300 K)	Lattice dynamics (300 K)	Lattice dynamics+ ZSISA (300 K)	Lattice dynamics+ CISPA (300 K)	Molecular dynamics (300 K)
Rutile						
a/Å	4.637	4.628	4.615	4.615	4.615	4.611
c/Å	3.087	3.045	3.135	3.136	3.135	3.131
u	0.3032	0.3030	0.305	0.306	0.306	
Fluorite						
a/Å	4.931		4.940			

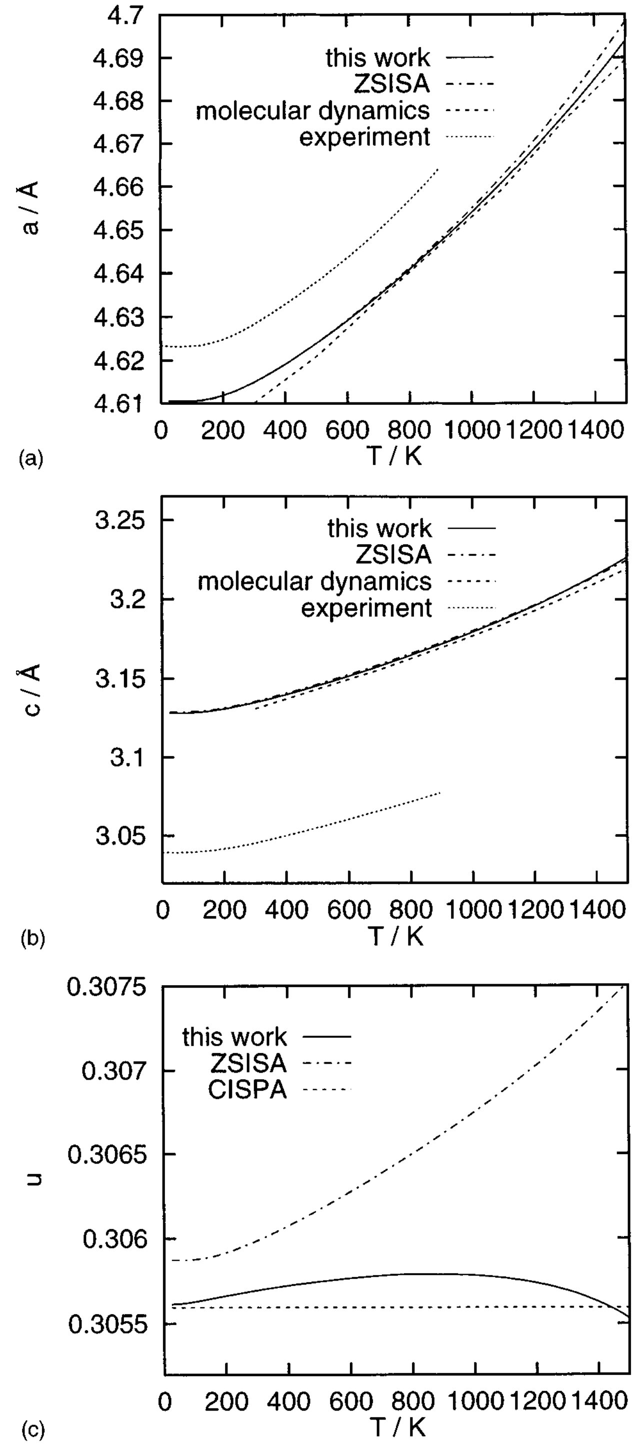

FIG. 4. Calculated variation of a, c, and u with temperature for the rutile phase of MgF$_2$.

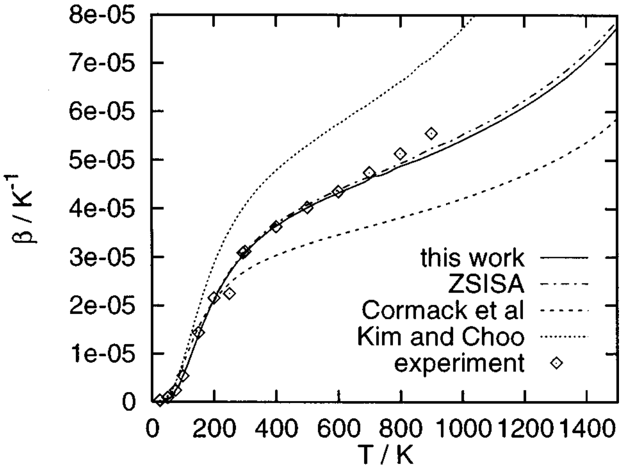

FIG. 5. Calculated and experimental thermal expansion of the rutile phase of MgF$_2$.

rameters and thermal expansion of the rutile phase of MgF$_2$ at zero pressure. It is well-known that the Hartree–Fock method generally overestimates lattice parameters,[12,13] and for MgF$_2$ the Hartree–Fock lattice parameters a and c are slightly larger than experiment[28] (Table II). Figures 4(a) and 4(b) show the same is true of the values predicted using the new potential obtained by fitting to the Hartree–Fock energies. However, the variation with T of the lattice parameters a and c, calculated from both lattice dynamics (LD) and molecular dynamics (MD), is very close to experiment [as shown in Figs. 4(a) and 4(b)], surprisingly even at temperatures quite close to the melting point (1520 K). At low temperatures the MD values for a and c are lower than the LD values because only the latter takes account of quantum effects (zero-point vibration) which expand the lattice by a small amount; but the effect of zero-point energy is much less important for MgF$_2$ (estimated dilations at $T=0$ are $\delta a = 0.017$ and $\delta c = 0.014$ Å) than for the lighter Li$_2$O considered previously.[11] At high temperatures the MD results serve as a check of the validity of the quasiharmonic approximation. The LD results show a characteristic divergence of slope from the MD results for $T \geqslant 1300$ K, indicating that this approximation is beginning to break down.

The variation with temperature of the volumetric thermal expansion coefficient $\beta\,(=(\partial V/\partial T)_P/V)$ is shown in Fig. 5, where LD results obtained using various two-body potentials are compared. Using the potential derived in this work, agreement between experiment[28] and quasiharmonic lattice

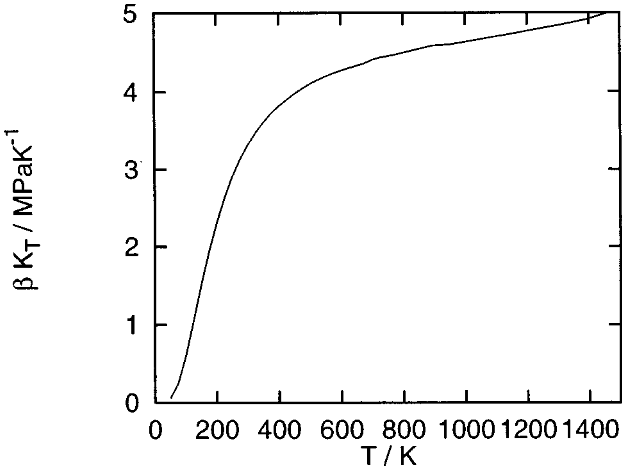

FIG. 6. βK_T(MPa K^{-1}) vs T(K) for the rutile phase of MgF$_2$ at zero pressure.

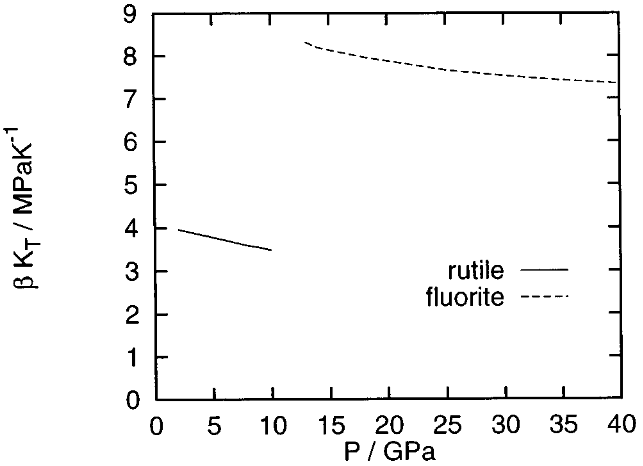

FIG. 7. βK_T(MPa K^{-1}) vs P(GPa) for the rutile and fluorite phases of MgF$_2$ at 500 K.

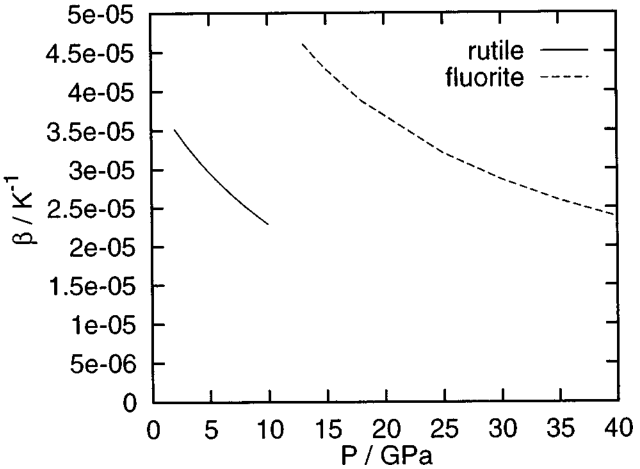

FIG. 8. Calculated variation of the thermal expansion coefficient β with pressure for the rutile and fluorite phases of MgF$_2$ at 500 K.

dynamics is excellent. The rapid increase in the expansion coefficient for $T \geqslant 1300$ K predicted by the lattice dynamics again reflects the failure of the quasiharmonic approximation at these high temperatures. Figure 5 also shows that the newly derived potentials perform better here than those from Refs. 26 and 27.

Last, in this section we comment on a common approximation used in lattice dynamics at elevated temperatures, namely, the zero static internal stress approximation (ZSISA).[15] In determinations of equilibrium structures above 0 K, this approximation can reduce the computational effort considerably. The free energy at each temperature is minimized with respect to external strains only, simultaneously determining the internal strains by minimizing the *static* lattice energy, requiring

$$\left(\frac{\partial G}{\partial a}\right)_{c,u} = \left(\frac{\partial G}{\partial c}\right)_{a,u} = \left(\frac{\partial \Phi_{\text{stat}}}{\partial u}\right)_{a,c} = 0,$$

instead of minimizing the total free energy G with respect to *both* external *and* internal strains. Although this may give an incorrect internal strain, it gives to first order the correct external strain at each temperature. An even cheaper approximation is CISPA (constant internal strain parameter approximation), which fixes the internal strains at those calculated in the static limit; with our choice of u as internal strain coordinate, CISPA thus requires that the fractional coordinates of the basis atoms do not vary with temperature.

For MgF$_2$ the use of either of these two approximations makes little difference to any of the properties calculated in this paper, as is clear from the values listed in Table II and the relevant curves in Figs. 4 and 5. For example, a full minimization gives values of 4.614 97, 3.135 03, and 0.305 69 Å for a, c, and u, respectively, for the rutile phase at 300 K; the corresponding results from ZSISA are 4.614 94 Å, 3.135 76 Å, and 0.305 99 and CISPA 4.614 99 Å, 3.134 77 Å, and 0.305 60. CISPA assumes u is not a function of temperature; ZSISA predicts an increase in u with temperature, while a full minimization indicates an increase at low temperatures followed by a decrease at higher temperatures (Fig. 4c). Nevertheless these changes are very small. For the temperature variation of the lattice parameters a and c, and hence thermodynamic properties, CISPA happens, for MgF$_2$, to give values closer to those from the complete minimization than ZSISA itself. This is because the fully minimized u goes through a maximum over the range of temperatures considered and hence varies very little, so that a constant value as assumed by CISPA turns out to be a good approximation.

Approximate models

We conclude our study by examining the temperature and pressure dependence of some quantities of importance to approximations used, for instance, in geophysics. For example, it is often assumed that the partial derivative $(\partial P/\partial T)_V$, which is equal to βK_T, the product of β and the isothermal bulk modulus K_T, is effectively independent of T at and above the debye temperature Θ, i.e., that the ''thermal pressure'' varies linearly with T. The agreement of our model with experiment both for β (Fig. 5) and for the bulk modulus at 300 K (107.5 compared with the measured[29] 106.2 GPa) encourages its use at temperatures and pressures where experimental data are not available. Accordingly, Fig. 6 shows that βK_T for the rutile phase of MgF$_2$ rises only slowly with temperature for $T \geqslant \Theta$, as calculated for the B1 and B2 oxides and halides considered previously.[1,2]

It is also often assumed that βK_T is independent of volume at high pressures, although Anderson[30] has pointed out that for some solids it decreases with pressure. For the two phases of MgF$_2$, Fig. 7 shows a small decrease in βK_T with increasing pressure. This effect is similar to that noted for MgO over a similar compression range.[30] More dramatically, βK_T is more than doubled at the transition from the rutile to the fluorite phase. These results call into question the uncritical use of common assumptions used in formulating approximate equations of state. We note also that at the phase transition the bulk modulus of the fluorite phase (≈ 165 GPa at 500 K) is larger than that of the rutile phase (≈ 152 GPa at 500 K), consistent with our earlier work on the B1–B2 transition, but contrary to the suggestion by Heinz and Jeanloz[31] of a marked decrease in K_T at such a phase transition.

Another quantity widely used in geophysical approximations is the isothermal Anderson–Grüneisen function, δ_T, given by

$$\delta_T = -(\partial \ln K_T/\partial \ln V)_P = -(\partial \ln \beta/\partial \ln V)_T .$$

We find that for the rutile phase over its entire pressure range, β is approximately proportional to V^t at 300 K, where $t \approx 7$, thus giving δ_T a constant value of 7. In contrast, for the fluorite phase δ_T decreases with pressure from ≈ 5.7 at the transition to ≈ 4.7 at 80 GPa, still higher than the value of $\delta_T \approx 3$ deduced by Anderson[32] from seismic data for the lower mantle, but in agreement with the observation of O. L. Anderson that δ_T decreases at high pressures. For comparison, the corresponding theoretical[2] and experimental[33] value for MgO is $t \approx 6$. For MgF_2 the calculated value of β is larger in the fluorite phase than in the rutile phase. At 500 K, β increases by over a factor of 2 at the phase transition. Consequently, because of the phase change, there is no marked decrease of β with pressure for MgF_2 (Fig. 8) (cf. MgO, where there is no phase transition over the range of pressures considered here). The implications of large values of δ_T for minerals have been discussed, for example, by Chopelas and Boehler.[34]

DISCUSSION

In this paper we have presented a range of computed thermodynamic properties of MgF_2 based on four distinct procedures, namely, lattice statics, lattice dynamics, molecular dynamics, and *ab initio* electronic structure calculations. Of these, the *ab initio* periodic Hartree–Fock method for electronic structures has proved particularly versatile, in that it has provided both a simple estimate of the rutile to fluorite transition pressure in the static limit (which is apparently close to the experimental value) and also a straightforward practical route to the calculation of interionic pair potentials which can be used in atomistic simulation studies. In studies of this type, the transition pressure and thermal expansion coefficient are highly sensitive to the potentials used, and of the four sets examined in this study, only those derived from Hartree–Fock calculations give values for both the transition pressure and the thermal expansion in reasonable agreement with experiment. It is evident from the results that computations involving lattice dynamics put considerably more demands on the reliability of interionic potentials than do static calculations, and here there would appear to be a need for representations of interionic interactions beyond pair potentials, even for systems as ionic and as relatively simple as MgF_2.

A further feature of the results presented here is the good agreement up to about 80% of the melting point between lattice dynamics and molecular dynamics calculations based on identical potentials for properties such as the thermal expansion. This confirms that quasiharmonic lattice dynamics, which has suffered some neglect in recent years, can be a useful technique for studying systems even at elevated temperatures, particularly bearing in mind that molecular dynamics simulations can be orders of magnitude more expensive. Reasons for the utility of lattice dynamics are that the results are often simpler to interpret than those from molecular dynamics simulations and that high precision is readily achieved; that quasiharmonic lattice dynamics is particularly useful at low temperatures where molecular dynamics simulations fail below the classical region; that, as observed previously,[10] lattice dynamics can also be remarkably robust at elevated temperatures; and that it provides an extremely sensitive test for interatomic potentials, such as those used originally by Nga and Ong,[5] in a way that would be very difficult for molecular dynamics.

To sum up, this study has led to a consistent picture of the rutile–fluorite transition pressure in MgF_2; the *ab initio* calculations and lattice dynamics predict a thermodynamic transition under pressure between the rutile and fluorite phases within the range 12–30 GPa, which is consistent with the reported experimental value[7] but much lower than a previous molecular dynamics estimate of over 130 GPa. Furthermore, the change in transition pressure with temperature is predicted to be very small indeed. We have also derived thermal expansion coefficients in good agreement with experiment, and derived other thermodynamic quantities such as $(\partial P/\partial T)_V$ which are crucial to approximate equations of state. In conclusion, we believe that the simple approach to the treatment of ionic solids at elevated temperatures and pressures presented here has proved sufficiently robust to justify its wider use, and in particular its extension to more complex systems.

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