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Structural properties and lattice dynamics of $RbMnCl_3$ crystal

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Abstract

Energies and lattice dynamics of cubic and hexagonal phases of $RbMnCl_3$ crystal have been calculated non-empirically within a modified Gordon–Kim model. At normal pressure the crystal has been demonstrated to have a six-layer hexagonal structure. Above 1.1 GPa $RbMnCl_3$ is found to transform into the cubic phase. Calculated lattice vibrational frequencies are compared with available experimental data.

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1. Introduction

$RbMnCl_3$ crystal belongs to the family of perovskite-like ABX_3 structures. Crystals of this family may form several structural polytypes with different packing of BX_6 octahedra. Most oxide and fluoride ABX_3 compounds including Rb–Mn fluoride crystallize into a cubic perovskite structure (Fig. 1a), while compounds with highly polarizable anions (like Cl, Br) have a hexagonal structure (Fig. 1b). Structural properties and lattice dynamics of cubic perovskites have been well studied in many ways, including ab initio methods. These methods based on Kohn–Sham equations for wave functions are computationally intensive for crystals of more complex hexagonal structures. The Gordon–Kim approach in its traditional form has been used [1] for the lattice vibration spectrum of hexagonal $RbMnCl_3$. These results qualitatively disagree with experimental Raman data [2]. This work is an attempt to improve the Gordon–Kim model taking into account dipole and quadrapole density distortions [3–5], and applying it to calculate the structure and lattice dynamics of $RbMnCl_3$ crystal and to study its stability under hydrostatic pressure.

2. Calculation of total energy

Under normal conditions the structure of $RbMnCl_3$ crystal is hexagonal ($P6_3/mmc$ space group with $Z = 6$, Fig. 1b). Every type of ion in the unit cell has two crystallo–graphically non-equivalent positions, and some ions have free coordinates. Table 1 gives calculated and experimental values of the unit cell parameters and ionic coordinates. Calculated structural parameters agree with experimental values within 5% precision that is typical for this method (see [3–5] for detail). Free parameter values calculated in [1] within the framework of the Gordon–Kim model with spherical ions are also presented there, but in this case the cubic structure is more stable than the hexagonal one and disagrees with the experimental data.

The total energy values, calculated in the generalized Gordon–Kim model and individual contributions to the total energy for the hexagonal and cubic structures are shown in Table 2. Formation of hexagonal structures in

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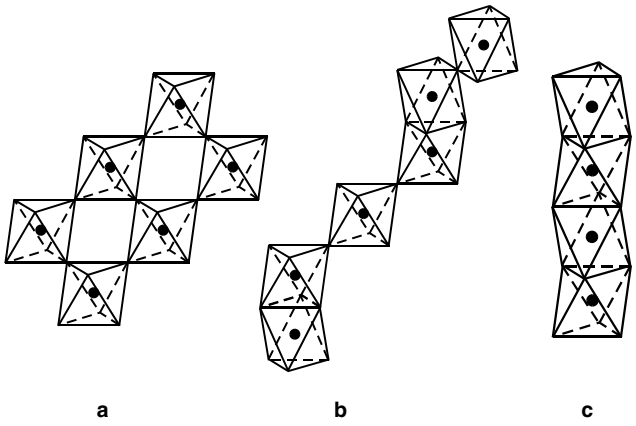

Fig. 1. The arrangement of octahedra in different polytypes of ABX_3: (a) cubic (perovskite) structure, (b) six-layer hexagonal structure, and (c) two-layer hexagonal structure.

Table 2
Calculated values (per molecules) of the total energies and of individual contributions

$E - E^{self}$, eV	Hexagonal phase	Cubic phase, $a = 5.14$ Å
E^c	−33.8317	−34.6722
E^s	2.8239	2.9107
E^c_{d-d}	−0.8318	0.0
E^s_{d-d}	0.1261	0.0
E^c_{q-q}	−0.4500	−0.6357
E^s_{q-q}	0.4072	0.6341
E^c_{d-q}	−0.0850	0.0
E^s_{d-q}	0.0563	0.0
E_{total}	−31.7850	−31.7631

E^c—Madelung energy, E^s—energy of short-range spherically symmetric ion–ion interactions, $E^c_{d-d}, E^c_{q-q}, E^c_{d-q}$—energies of long-range dipole–dipole, quadrapole–quadrapole and dipole–quadrapole interactions, respectively, $E^s_{d-d}, E^s_{q-q}, E^s_{d-q}$—short-range parts of these interactions, respectively. E^{self}—self-energy of an ion.

the rigid ion model was found to be less favorable in terms of energy: because the Mn^{2+} ions are too close to each other there is a loss in the Madelung energy, while the energy of the short-range interactions for both structures is almost equal. The hexagonal structure is stabilized by the polarization energy associated with the interactions between induced dipole and quadrapole moments of ions placed into non-centrosymmetrical positions in this structure. As seen from Table 2, the competition between the long-range Coulomb interaction of point multipoles and the short-range interaction of extended multipoles is very important for lattice stabilization. It should be noted that the hexagonal structure of $RbMnCl_3$ is stabilized by the quadrapole–quadrapole interactions. In compounds with more polarizable anions, such as Br^- in $RbMnBr_3$, the hexagonal structure is stabilized by the energy of dipole–dipole interactions only [6].

The energies of hexagonal and cubic structures are very close and from Fig. 2 which shows the pressure dependence of the difference between the enthalpies of hexagonal and cubic structures it is apparent that under the hydrostatic pressure the structural phase transition from hexagonal to cubic phase is predictable. The calculated transition pressure 1.1 GPa is in good agreement with experimental value 0.7 GPa [2,7]. During this transition the volume of the unit cell decreases, and the resultant cubic unit cell parameter 5.09 Å likewise agrees well with the experimental value of 5.06 Å [7].

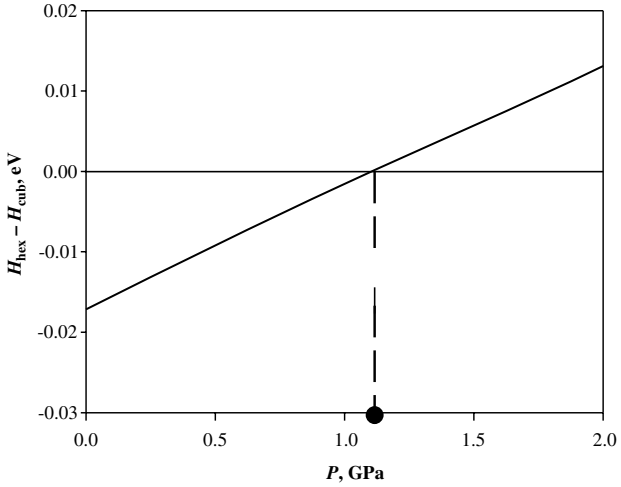

Fig. 2. The pressure dependence of the difference between the enthalpies of hexagonal and cubic structures for $RbMnCl_3$ crystal.

Table 1
Unit cell parameters and coordinates of ions in hexagonal structure

$a = b$, Å				c, Å					
Calc.		Expt. [7]		Calc. [1]			Calc.	Expt. [7]	Calc. [1]
7.09		7.16		7.22			19.04	17.80	18.03
	x/a			y/b			z/c		
	Calc.	Expt. [7]	Calc. [1]	Calc.	Expt. [7]	Calc. [1]	Calc.	Expt. [7]	Calc. [1]
Rb(2b)	0	0	0	0	0	0	1/4	1/4	1/4
Rb(4f)	1/3	1/3	1/3	2/3	2/3	2/3	0.8690	0.9112	0.8920
Mn(2a)	0	0	0	0	0	0	0	0	0
Mn(4f)	1/3	1/3	1/3	2/3	2/3	2/3	0.1543	0.1603	0.1649
Cl(6h)	0.5008	0.4928	0.4925	0.4992	0.5072	0.5230	1/4	1/4	1/4
Cl(12k)	0.1456	0.1616	0.1626	0.8544	0.8384	0.8374	0.1000	0.0820	0.0877