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Structural and Dynamical Aspects of Structural Phase Transitions on Incommensurate A_2BX_4 compounds

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At high temperature, the A_2BX_4 crystals exhibit $P6_3/mmc$ structure. With temperature decreasing, a rich diagram of structural phases and phase transitions are observed, including different incommensurate phases. Ordering of the BX_4 tetrahedra orientation in the unit cell drives the transitions, and they can be well described by an Ising model with competing interactions. Raman and infrared spectroscopy, differential scanning calorimetry (DSC) and thermogravimetry (TGA) are used to characterize the phase transitions in Cs_2HgBr_4 and Rb_2WO_4 crystals.

Keywords Incommensurate; phase transition; Raman; infrared; DSC

1. Structural Phases and Phase Transitions in A_2BX_4 Crystals

In the A_2BX_4 compounds, the B and X atoms form tetrahedral molecules (BX_4^{2-}) making ionic bounds with the A^+ atoms. Exception from the crystals formed by small radius cations (e.g. Li_2SO_4, Na_2SO_4, etc.), the structural phases of the A_2BX_4 compounds can be obtained from the hexagonal $P6_3/mmc$ structure presented by the prototype α-K_2SO_4, as shown in Fig. 1(a). At high temperatures, the orientation of the BX_4^{2-} tetrahedra is completely undetermined and they exhibit up/down orientational disorder, as well as planar disorder.

By decreasing the temperature, the up/down orientation is frozen, leading the crystal to different symmetries depending on the neighbouring up/down ordering, as displayed in Fig. 1(b). The phase transitions can be all mediated by incommensurate phases depending on competing forces during the orientation process, and these incommensurate phases are indicated in the Fig. 1(b) diagram by dashed blocks. Further temperature decreasing results on planar orientation of the BX_4^{2-} tetrahedra, leading to the appearance of a rich diagram of structural phases and phase transitions [1].

In this work we will focus on the experimental study of Rb_2WO_4 and Cs_2HgBr_4 crystals that exhibit incommensurate phases, as indicated in Fig. 1(b). The phase transitions are shown to exhibit an order-disorder character, the first one related to the up/down ordering of the BX_4^{2-} tetrahedra, and the second one related to the planar orientation of the tetrahedra.

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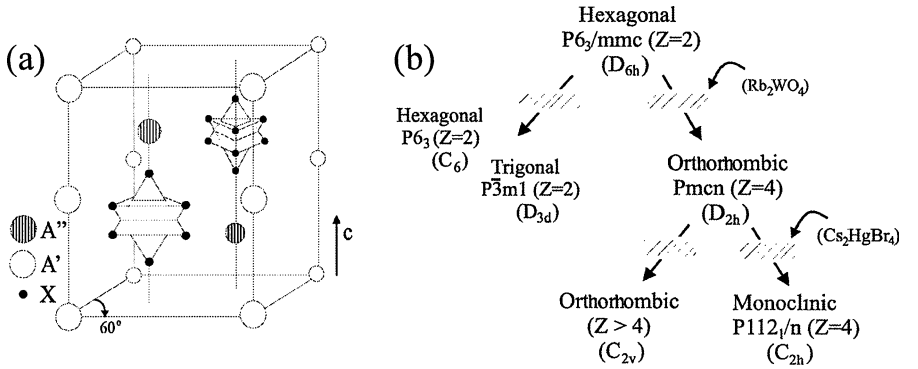

FIGURE 1 (a) Unit cell structure for the prototype α-K_2SO_4. (b) Temperature phase diagram for A_2BX_4 compounds. The structural phase transitions can be intermediated by incommensurate phases. The incommensurate phases observed for Cs_2HgBr_4 and Rb_2WO_4 are indicated.

We also present an Ising-like theoretical model to describe the different phase transitions observed from the hexagonal $P6_3/mmc$ structure, including the incommensurate phase in the basal plane of A_2BX_4 crystals.

2. Basal-Plane Incommensurate Phases in hcp Structures

In this section we discuss the use of a mean-field approximation to study the Ising model on the hexagonal-close-packed (hcp) lattice, where frustration is uniquely related to the topology of the lattice and is provided by the in-plane NN anti-ferromagnetic interaction. The development of the model is presented in Ref. [2], and here we only point some interesting aspects.

Figure 2 shows the phase diagram of the hcp-Ising model as a function of the nearest-neighbour (NN) and next-nearest-neighbour (NNN) interaction parameters $\kappa = J_{out}/J_{in}$ and $\lambda = J'_{out}/J_{in}$, where J_{in} ,J_{out} andJ'_{out} represents the Ising interactions for the NN in-plane sites, NN out-of-plane sites and NNN out-of-plane sites, respectively. The κ and the λ parameters are functions of the c/a crystallographic properties of the several A_2BX_4

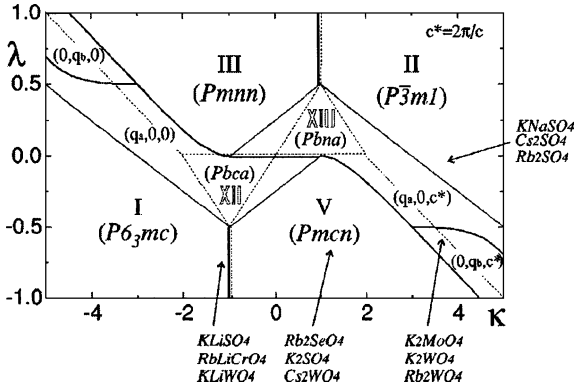

FIGURE 2 Phase diagram of the hcp-Ising model as a function of the NN (κ) and NNN (λ) interaction parameters.

compounds and, therefore, they can be located at Fig. 2, with good agreement between theory and experimental observations for the structural phases.

Figure 2 can be used to predict the crystallographic phase observed for the different A_2BX_4 compounds below the hexagonal $P6_3/mmc$ structure, as well as to predict the observation of phase transitions by applying, for example, uniaxial pressure to change the c/a ratio of a given crystal. The occurrence of basal-plane incommensurate phase, differently from the usual incommensurate phase with modulation along the higher symmetry c axis, is predicted. Basal-plane incommensurate phase is observed for the Rb_2WO_4 crystals as discussed below.

3. High Temperature Phase Transition in Rb_2WO_4 Crystal

Rb_2WO_4 was studied by Raman spectroscopy and calorimetric measurements (DSC and TGA) [3], and we obtained information about the incommensurate ($T_I = 746$ K) and lock-in ($T_C = 664$ K) phase transitions. The observation of first-order phase transitions peaks in the DSC curve with large entropy jumps ($\Delta S/R\log 2 = 0.3$ at T_C and 0.2 at T_I) clearly show their strong order-disorder characteristic. The value goes to $R\log 2$, the value expected for a complete lock-in of the up/down degree of freedom for the BX_4^{2-} tetrahedra. The incommensurate phase is, therefore, related to a dynamic up/down modulation of the tetrahedra orientation along the basal plane of the Rb_2WO_4 structure.

The presence of a lower temperature orthorhombic-monoclinic phase transition is also observed, but it is shown to be due to the presence of water in the structure, that decreases the crystal symmetry at room temperature [3].

4. Low Temperature Phase Transitions in Cs_2HgBr_4

Cs_2HgBr_4 crystals were studied by Raman [4] and infrared spectroscopy [5]. This crystal exhibits four phase transitions below room temperature, one of them being incommensurate [6]. Observation of Raman mode forbidden by symmetry and analysis of the Raman frequencies (see Figs. 3(a) and (b)) indicate that the planar disorder of the tetrahedra orientation

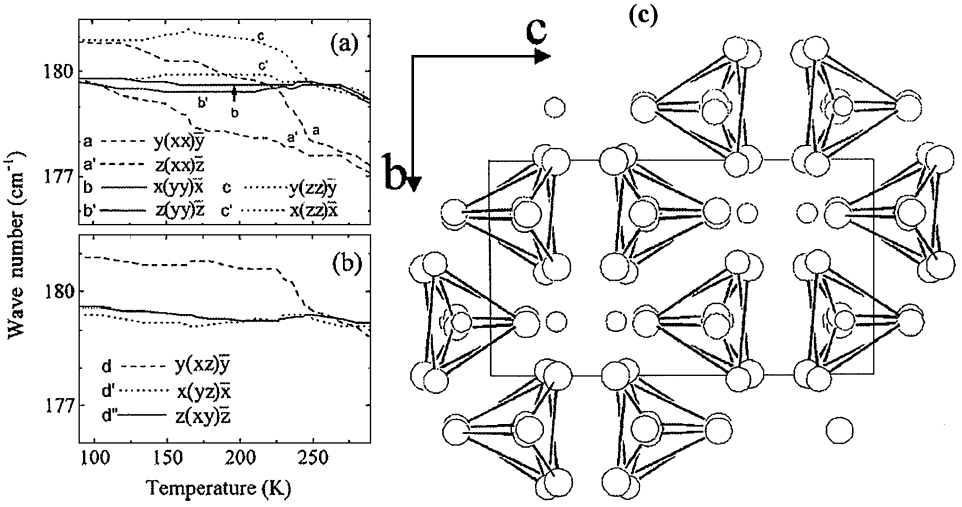

FIGURE 3 (a) and (b) Temperature dependence of the frequency of the peak associated with ν_1 mode in nine different backscattering geometries. (c) Projection along the a axis of the disordered room-temperature A_2BX_4 structure of Cs_2HgBr_4.

occurs in the room temperature phase (see Fig. 3(c)), decreases at the incommensurate ($T_I = 245$ K) and lock-in ($T_C = 232$ K) phase transitions, and disappears below the phase transition at $T_{L1} = 165$ K.

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