RESEARCH ARTICLE

The bulk modulus of cubic spinel selenides: an experimental and theoretical study

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It is argued that mainly the selenium sublattice determines the overall compressibility of the cubic spinel selenides, AB_2Se_4 , and that the bulk modulus for these compounds is about 100 GPa. The hypothesis is supported by experiments using high-pressure X-ray diffraction and synchrotron radiation, and by first-principles calculations using density functional theory.

Keywords: Bulk modulus; equation of state; spinel arrangement; X-ray diffraction; density functional theory

1. Introduction

Finger et al. [1] first observed that cubic spinel oxides with chemical formula AB_2O_4 respond in a similar way to hydrostatic pressure. In particular, the zero-pressure bulk modulus for all of these compounds is about 200 GPa. Later, Pendás et al. [2] and Recio et al. [3] have theoretically justified this behavior. Essentially, the physical explanation is based on two facts: (i) the oxygen ions are forming a nearly close-packed substructure, accounting for most of the crystal volume, and (ii) the cations A and B are low-compression chemical species. Therefore, mainly the oxygen sublattice is determining the overall bulk compressibility.

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In previous work, we have studied the high-pressure behavior of several cubic spinel oxides [4] and of the selenide CdCr_2Se_4 [5]. Using similar arguments as above, one may assume that mainly the selenium sublattice is determining the bulk modulus of the cubic spinel selenides, AB_2Se_4 . The present study is an attempt to verify this hypothesis. Wyckoff [6] is listing three selenides with the cubic spinel arrangement, CdCr_2Se_4 , CuCr_2Se_4 and ZnCr_2Se_4 , and we have made an experimental and theoretical study of these compounds.

2. Experimental procedure

Room temperature, high-pressure powder x-ray diffraction spectra were recorded at HASYLAB-DESY in Hamburg, Germany, using synchrotron radiation. The diffractometer, working in energy-dispersive mode, has been described elsewhere [7]. High pressures were obtained in a Syassen-Holzapfel type diamond-anvil cell [8]. A fine powder and a ruby chip were placed in a hole with diameter 200 μm in an Inconel gasket, pre-indented to a thickness of 60 μm . A 16:3:1 methanol: ethanol: water mixture was used as the pressure-transmitting medium. The pressure was determined by the ruby luminescence method, using the non-linear pressure scale of Mao et al. [9]. The Bragg angle of each run was calculated from a zero-pressure spectrum of sodium chloride (NaCl).

At each pressure, values for the lattice parameter and the unit-cell volume were derived from the diffraction spectrum (cf. Fig. 1) and refined using the PURUM code [10]. The compression curve was then described by the Birch-Murnaghan equation of state [11]:

$$P = \frac{3}{2} B_0 (x^{-7/3} - x^{-5/3}) [1 - \frac{3}{4} (4 - B_0') (x^{-2/3} - 1)], \quad (1)$$

where $x = V/V_0$, V is the volume at pressure P , and V_0 is the volume at zero pressure. B_0 is the bulk modulus and B_0' its pressure derivative, both parameters evaluated at zero pressure. Values of B_0 and B_0' were obtained by a non-linear least-squares fit of equation (1) to the experimental pressure-volume data points.

3. Theoretical calculations

The ability of the ABINIT code [12] to deal with open shell systems has allowed an accurate description of the ferromagnetic character of the normal spinel structure of CuCr_2Se_4 and ZnCr_2Se_4 at zero pressure. CuCr_2Se_4 behaves like a ferromagnetic metal with a Curie temperature of 444 K [13], but ZnCr_2Se_4 is an antiferromagnetic semiconductor with a Néel temperature of 20 K [14]. The ferromagnetic state was

simulated by spin-polarized calculations that were started from a number of unpaired electrons fixed according to the d^3 and d^9 electronic configuration of Cr^{3+} and Cu^+ , respectively. Calculations, based on the local density approximation (LDA) as well as the generalized gradient approximation (GGA), were carried out using Hartwigsen-Goedecker-Hutter pseudopotentials [12]. The $3d$ electrons of Cu, Cr and Zn were treated as valence electrons.

After convergence studies in the semiconductor ZnCr_2Se_4 and in metallic CuCr_2Se_4 , we have chosen a kinetic energy cut-off of 80 (60) hartree for the plane wave expansion and a $2 \times 2 \times 2$ ($4 \times 4 \times 4$) Monkhorst-Pack [15] grid of special $\mathbf{k}$ -points for the Brillouin zone integration (parameters in brackets are for CuCr_2Se_4). Energy (E)-volume (V) curves were computed after fitting numerical and analytical standard functions to the set of calculated (E , V) points for fully optimized unit cells of both crystals, thus providing theoretical values of the lattice parameter a_0 , the oxygen position u , the bulk modulus B_0 , and the pressure derivative B_0' [16].

4. Results and discussion

Figure 1 shows an energy dispersive X-ray diffraction spectrum of CuCr_2Se_4 at 10.6 GPa. Experimental and theoretical results for the cubic spinel selenides are summarized in Table 1. It is seen that the experimental bulk modulus is about 100 GPa. Within the same type of calculation, the B_0 values cluster around 115 GPa (LDA) and 75 GPa (GGA). Thus, the LDA and GGA results differ by as much as 40 GPa. However, it is known that the LDA and GGA values represent the upper and lower limits of the experimental bulk modulus. Moreover, the GGA approximation is more appropriate for magnetic materials [17]. In that respect, our GGA results for B_0 should be a better description of the experimental high-pressure behavior.

It is interesting to notice that in previous work we have found that the bulk modulus of the super-hard cubic spinel Si_3N_4 is about 300 GPa, a value that is mainly determined by the nitrogen sublattice [18, 19]. However, the binary nitrides exhibit a more diverse response to high pressure, the bulk modulus varying from 231 GPa (Ge_3N_4) to 415 GPa (C_3N_4) [20]. This is due to the fact that nitrogen is the less compressible chemical specie in these crystals.

Although more computational work is needed for improving the description of the pressure behavior of magnetic selenides, the present experimental and theoretical results allow us to conclude that, in analogy with the cubic spinel oxides, mainly the selenium sublattice is determining the bulk modulus of the cubic spinel selenides.

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Table 1. Experimental and theoretical results for cubic spinel selenides. B_0 is the bulk modulus, a_0 is the lattice parameter, and u is the oxygen parameter. The first and second values of the calculated properties for CuCr_2Se_4 and ZnCr_2Se_4 represent LDA and GGA calculations, respectively.

Compound	$a_0, \text{expt.}$ (Å)	$B_0, \text{expt.}$ (GPa)	$a_0, \text{calc.}$ (Å)	u_{calc}	$B_0, \text{calc.}$ (GPa)	Ref.
CdCr_2Se_4	10.721	101(3)	10.574	0.265	92.0	[5]
CuCr_2Se_4	10.357	96(3)	9.982–10.308	0.257–0.258	112.4–69.1	Present work
ZnCr_2Se_4	10.443	–	10.265–10.572	0.260–0.261	119.7–79.0	Present work

Figure Caption

Figure 1. Energy dispersive X-ray diffraction spectrum of CuCr_2Se_4 at 10.6 GPa. The Bragg angle is $\theta=3.54^\circ$, e = escape peaks, W = tungsten fluorescence peak.

Fig. 1.