

1 Revision 2

2 **High pressure behavior of thiospinel CuCr_2S_4**

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15 **Abstract**

16 This study reports for the first time the lattice parameters and the complete crystal
17 structure evolution with increasing pressure for a thiospinel with composition $\text{CuCr}_{1.7}\text{V}_{0.3}\text{S}_4$
18 (space group $Fd-3m$) measured by single-crystal X-ray diffraction as a function of pressure up to
19 7 GPa. The P - V data are adequately described to a 4th order Birch-Murnaghan equation of state
20 with the following coefficients: $V_0 = 947.86(6) \text{ \AA}^3$, $K_{T0} = 88(1)$ and $K' = 6.3(9)$, $K'' = -1.1(4)$.
21 This is the first time that an equation of state for a spinel structure has been described by a 4th
22 order Birch-Murnaghan equation of state. The unit-cell volume shows a compression of about
23 6.3% over the entire pressure range investigated. The crystal structure evolution clearly indicates
24 that the main compression mechanism is related to the compression of the CuS_4 tetrahedron
25 which is significantly greater than the CrS_6 octahedron. The tetrahedral volume decreases by
26 7.8% over the pressure range studied while the octahedral volume decreases by 5.5%. The
27 change in the octahedral volume is accompanied by a decrease in the angular distortion of the
28 CrS_6 octahedra.

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30 **KEYWORDS:** thiospinel; high pressure; single-crystal X-ray diffraction;

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Introduction

35 CuCr_2S_4 belongs to the thiospinel group and crystallizes in the cubic spinel structure
36 (space group Fd-3m). It is a normal spinel with Cu^{2+} occupying the tetrahedrally coordinated
37 sites and the Cr^{3+} occupying the octahedrally coordinated sites. In the last decade, this class of
38 compounds has attracted great interest because of their unusual optical, electrical and magnetic
39 properties (Berry et al. 2007; Dmitrieva et al. 2007; Haacke and Beegle 1968; Ito et al. 2005; Ito
40 et al. 2006; Koroleva et al. 1991; Lotgering 1964; Masrour et al. 2011; Nogues et al. 1979; Saha-
41 Dasgupta et al. 2007; Samokhvalov et al. 1976a; Siberchicot 1993; Snyder et al. 2001; Tewari et
42 al. 2010; Tressler and Stubican 1968; Zub 1983). Many phases belonging to the thiospinel group,
43 with the same symmetry as CuCr_2S_4 , (Fd-3m), have shown interesting structure-property
44 changes under extreme high-temperature and high-pressure conditions. For example, it was
45 demonstrated that some thiospinels undergo structural phase transitions at high pressure that are
46 correlated changes in their magnetic properties (i.e. Garg et al. 2007; Ito et al. 2003; Nakamoto
47 et al. 2005). It is therefore crucial to investigate the structural evolution of such important
48 materials which closely correlate with their unusual material properties.

49 In particular CuCr_2S_4 has always been considered to be a good candidate as a base
50 material for the production of magneto-optical devices and as cathodes for Li-secondary batteries
51 (Imanishi et al. 1993; Saha-Dasgupta et al. 2007). Because of its unique features involving
52 magnetic phase transitions (i.e. higher ferromagnetic, metal-insulator and semiconductor-metal
53 phase transitions), CuCr_2S_4 has been investigated under low and high temperature conditions in

54 order to better understand how resistivity, conductivity, and ferromagnetic properties are affected
55 under non-ambient conditions (Albers and Rooymans 1965; Banus and Lavine 1969; Ito et al.
56 2003; Samokhvalov et al. 1976a; Samokhvalov et al. 1976b; Tressler et al. 1968). In this study
57 we present results of the elastic properties and crystal structure evolution of CuCr_2S_4 as a
58 function of pressure in order to evaluate how chemical composition variations affect the high-
59 pressure behavior in the thiospinel group.

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Experimental methods

61 The natural crystal investigated in this study was selected from the same crystal batch
62 studied by Reznitsky et al. (2011) who determined the following composition:
63 $(\text{Cu}_{0.98}\text{Fe}_{0.02}\text{Zn}_{0.01})_{1.01}(\text{Cr}_{1.65}\text{V}_{0.34}\text{As}_{0.01})_{2.00}\text{S}_{3.99}$ (hereafter abbreviated as $\text{CuCr}_{1.7}\text{V}_{0.3}\text{S}_4$). The
64 crystal studied under high-pressure conditions (size $0.130 \times 0.090 \times 0.060$ mm) was selected on
65 the basis of its size, absence of twinning, and X-ray diffraction profiles. The crystal was loaded
66 in an ETH-type diamond-anvil cell (DAC, Miletich et al. 2000) using a steel gasket (T301) pre-
67 indented to a thickness of 90 μm and with a hole of 250 μm in diameter. A single crystal of
68 quartz was used as an internal diffraction pressure standard (Angel et al. 1997) and a 4:1 mixture
69 of methanol:ethanol was used as pressure medium, which remains hydrostatic throughout the
70 entire pressure range investigated (Angel et al. 2007). The unit-cell parameters were determined
71 by single-crystal X-ray diffraction using a Huber four-circle diffractometer (non-
72 monochromatised $\text{Mo-K}\alpha$ radiation) operating at 50 kV and 40 mA, automated by the SINGLE
73 software (Angel and Finger 2011). The unit cell parameters were measured at 13 different
74 pressures up to 6.73 GPa by centering not less than 20 reflections in the 2θ range between 10°
75 and 30° for each high-pressure data point. Typical half-widths of reflections were between 0.05°
76 and 0.08° in ω and no broadening was detected at any pressure. Full details of the instrument and

77 the peak-centering algorithms are provided by Angel et al. (1997). During the centering
78 procedure the effects of crystal offsets and diffractometer aberrations were eliminated from
79 refined peak positions by the eight-position centering method of King and Finger (1979).
80 Unconstrained unit-cell parameters, obtained by vector least-squares (Ralph and Finger 1982,
81 were found to be similar, within one estimated standard deviation, to the symmetry-constrained
82 ones which are reported in Table 1 and Figure 1.

83 Complete intensity data collection devoted to the structural refinements were collected at
84 five different pressures on an Xcalibur-1 Oxford Diffraction diffractometer equipped with a CCD
85 detector (kappa-geometry, graphite-monochromatised Mo- $K\alpha$ radiation). Integrated intensity
86 data were then corrected for absorption effects due to the crystal and the DAC using the
87 ABSORB computer program (Angel 2004; Angel and Gonzalez-Platas 2013) and averaged with
88 the computer program WinAve (by Ross J. Angel).

89 Anisotropic structure refinements were performed with the SHELX-97 software
90 (Sheldrick 2008) starting from the atomic coordinates reported by Reznitsky et al. (2011) using
91 neutral scattering factors for Cr, Cu and S, fixing the occupancies to those obtained from the
92 chemical analysis (see Reznitsky et al. 2011). Details of the structure refinements, sulphur
93 atomic coordinates, atomic displacement parameters, bond distances and angles are reported in
94 Table 2, 3, (the CIF files relative to the five structure refinements were deposited as
95 supplementary material).

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Results and discussion

101 *Equation of state and high pressure crystal structure evolution*

102 The f_E - F_E plot, for the unit-cell volume, with F_E normalized stress defined as
103 $F_E = P/3f_E(1+2f_E)^{5/2}$ for the Birch-Murnaghan equation of state (BM-EoS), and the finite Eulerian
104 strain f_E defined as $[(V/V_0)^{2/3}-1]/2$ (see Angel 2000 for details), is shown in Figure 2. The plot
105 clearly indicates that the pressure – volume data should be fit to a 4th order Birch-Murnaghan
106 Equation of State (BM4) due to the clear upward convex trend of the data. For comparison in
107 Table 4 the fitting results (V_0 , K_{T0} , K' and K'') and the significant statistical fit parameters (i.e.
108 ΔP_{\max} and χ^2) obtained with the two approaches (BM4 and BM3) are reported. The need of a
109 higher order EoS shown by the f_E - F_E plot is firstly confirmed by the behavior of the calculated
110 pressures (used as the dependent variable) as a function of the unit-cell volume. As shown in
111 Figure 3, ΔP (difference between observed and calculated pressure for each volume data point)
112 shows an unreasonable trend with high deviations from zero over the entire dataset in the case of
113 the BM3 approach with values larger than the actual e.s.d.'s in our dataset; on the contrary the
114 ΔP obtained for the BM4 approach is constantly in the order of the dataset standard deviation.
115 The ΔP_{\max} (maximum difference between observed and calculated pressure among the whole
116 dataset) for the BM3 approach (0.021 GPa) is two times bigger than the largest e.s.d.'s on the
117 measured dataset (0.011 GPa), while the ΔP_{\max} calculated for the BM4 approach (0.005 GPa) is
118 as small as the smallest e.s.d.'s in the whole dataset (0.005 GPa). The sensible reduction of the
119 ΔP_{\max} when the truncation order is increased to the 4th makes clear that the 4th order Birch-
120 Murnaghan Equation of State is more representative of the entire dataset. The same evidence is
121 testified by the large reduction of χ^2 from 1.35 (for the BM3 approach) to 0.13 (for the BM4
122 approach). Moreover the BM4 K'' differs 2.5 e.s.d.'s from the one implied with the BM3

123 Equation of State with only a slight decrease in the correlation between K_{T0} and K' from 95.92 to
124 95.69 for the BM3 and the BM4 respectively, providing the last evidence for an increased order
125 in the fitting.

126 Therefore our experimental P - V data were fitted to a BM4-EoS providing the following
127 coefficients: $V_0 = 947.86(6) \text{ \AA}^3$, $K_{T0} = 88(1)$ and $K' = 6.3(9)$, $K'' = -1.1(4)$. It should be remarked
128 that this is the first time that the equation of state of a spinel structure is described by a BM4-
129 EoS. As mentioned above the 3rd order Birch-Murnaghan Equation of State fit [$V_0 = 947.79(6)$
130 \AA^3 , $K_{T0} = 91.6(4)$ and $K' = 3.7(1)$] has been reported in Table 4 solely for purpose of comparison
131 with our BM4 results and with the literature data. In Table 4 are also reported the results of
132 previous elasticity measurements on other thiospinel compounds (see Table 5). Data fit have
133 been performed with EoSFit7c program (Angel et al. 2014).

134 Cuprokalinitite (ideally CuCr_2S_4) has a spinel structure that is described by three
135 symmetry independent sites: (i) the tetrahedrally coordinated site T (in our sample occupied by
136 Cu with coordinates: 0.125, 0.125, 0.125); (ii) the octahedrally coordinated site O (for our
137 sample occupied by Cr and V with coordinates: 0.5, 0.5, 0.5); (iii) an S atom-bearing site (with
138 coordinates $u = x = y = z$). Therefore, the cubic spinel structure has only two structural variables:
139 the unit-cell parameter a and the anion positional parameter, u , with only two unique bond
140 distances, Cr – S and Cu – S.

141 Our data show that the Cr – S bond distances decrease by about 1.4% (see Fig. 4 and
142 Table 3) while the shorter Cu – S compress by about 2.7% (see Fig. 4 and Table 3). Such
143 behavior is the consequence of the variation of the S atomic coordinates [$u = 0.25735(7)$ at
144 room- P] towards the perfect cubic eutaxy 0.25 (i.e. Nestola et al. 2007, Makovicky and Balić Žunić,
145 1998). The decrease in the anionic coordinate by 0.0007 from room- P to the maximum pressure

146 reached in this work (see Fig. 5 and Table 2) is in agreement with (i) the faster compression of
147 the tetrahedral volume (7.8%) with respect to the octahedral one (5.5%) and (ii) the
148 regularization of the octahedra with a volume distortion decrease from 0.0054 at room-*P* to
149 0.0044 at 6.7 GPa (see IVTON software for the definition and calculation of the volume
150 distortion of a crystallographic site, Balić Žunić and Vicković 1996). The volume-distortion
151 parameter used here quantifies the volume deficit of the polyhedron as compared to an ideal equivalent.
152 The advantage of this parameter is that it measures only distortions due to the arrangement of atoms
153 forming the vertices of the polyhedron alone, and decouples these from distortion due to the relative
154 position of the central atom and surrounding atoms (see Nestola et al. 2013).

155 The literature data available so far (i.e. Nestola et al. 2007 and Nestola et al. 2010 and
156 references therein) clearly show that the change in the anion atomic coordinate in spinels is
157 generally accompanied by a possible change in the degree of cation order between the octahedral
158 and tetrahedral crystallographic sites. However, an attempt to refine the crystal structure data for
159 our sample refining the site occupancies did not allow us to definitively demonstrate that the
160 degree of order is affected by pressure as reported for spinel s.s. (Nestola et al. 2007).

161 Concerning the octahedral bond angles, they show small but significant changes (i.e.
162 greater than 2 e.s.d.'s) over the entire range of pressure. This is in agreement with the volume
163 decrease of the tetrahedron and regularization of the octahedron. Most of the unit-cell volume
164 compression is mainly accommodated by the compression of the Cu tetrahedra undergoing a
165 volume decrease by about 7.8% with a bulk modulus of 70.5(8) GPa (obtained with a 2nd order
166 Birch-Murnaghan EoS). On the other hand, the volumes of the CrS₆ octahedra decrease only by
167 5.5% with a bulk modulus of about 106.7(5) GPa (obtained with a 2nd order Birch-Murnaghan

168 EoS). The relative compression of the polyhedral volumes centered by Cr and Cu are plotted
169 against pressure in Figure 6 with nearly linear trends for both cations.

170 *Comparison with previous works*

171 As far as we are aware, our data represent the first and only single-crystal structural
172 datasets available over a range of pressures. Therefore we can only compare our elasticity data
173 with those for selenides and thiospinel available in literature so far (see Table 5). To this aim, the
174 wide chemical variability, typical of thiospinels, and the lack of accuracy in the lattice-
175 parameters measurements at high- P makes it quite difficult to build a model to predict the bulk
176 modulus given a composition (see Table 5 for available data on selenides and thiospinel
177 available for comparison). Secondly, most of the published data for selenides do not have enough
178 accuracy to be used for comparison. For example, data obtained for the same measurement on
179 CdCr_2Se_4 are reported in three different publications (Waškowska et al. 2002; Waškowska et al.
180 2004 and Waškowska et al. 2009) with different values of K_{T0} ranging from 101 to 104 GPa, and
181 K' ranging from 3.3 to 5.2, both with large standard deviations. For CuCr_2Se_4 (Waškowska et al.
182 2009) and ZnCr_2Se_4 (Wittlinger et al. 1997), the measurements performed by the energy-
183 dispersive diffraction technique cannot be expected to have the accuracy of crystal lattice
184 parameter comparable to others. Given the lack of precision of the pressure-volume data in these
185 previous studies, is not possible to determine whether the equation of state of these thiospinels
186 are best described by a fourth-order Birch-Murnaghan EoS. We can only conclude that
187 published data for selenides and S-thiospinel show values of bulk modulus of about 100 GPa
188 (comprised between 96 and 104 GPa) and 77 GPa (comprised between 76 and 78 GPa),
189 respectively, with significant data scattering. Thus the bulk modulus of our $\text{CuCr}_{1.7}\text{V}_{0.3}\text{S}_4$ is
190 closer to the published bulk moduli of selenides rather than those found for thiospinels.

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Implications

194 In the last several decades, thiospinels have attracted great interest because of their
195 peculiar optic, electric and magnetic properties. The peculiar high-pressure unit-cell volume
196 evolution of the thiospinels here studied, $\text{CuCr}_{1.7}\text{V}_{0.3}\text{S}_4$, can be described using a 4th-order Birch-
197 Murnaghan EoS [$K_{0T} = 88(1)$ GPa, $K' = 6.3(9)$ and $K'' = -1.1(4)$]. Such a behavior is here
198 observed for the first time among the extremely high number of spinels studied so far. It is well
199 known that for any EoS the use of a correct truncation order is crucial in providing the correct
200 value of bulk modulus and its derivatives. In order to give the readers an easy example of the
201 discrepancies caused by the use of an improper EoS we calculated for our sample the total
202 volume compression up to 10 GPa using the 4th-order against the 3th-order Birch-Murnaghan
203 EoS (the latter being the most used EoS for describing the spinel high pressure volume
204 evolution). The calculation gave a unit-cell volume $V_{10\text{GPa}}$ of 861.91 \AA^3 and $V_{10\text{GPa}} = 864.32 \text{ \AA}^3$
205 calculated using the BM4-EoS and the BM3-EoS, respectively. Such difference in volume
206 corresponds to a hypothetical compression of 0.24 GPa, which is about two orders of magnitude
207 greater than the uncertainties on the pressure determination given by our experimental method
208 (see Table 1, where the pressure has an uncertainty between 0.005 and 0.011 GPa). The
209 differences in the above calculated volumes using one or another EoS could have significant
210 implications on the determination of the stability fields in mineralogy as demonstrated for some
211 important high-pressure phases (see antigorite, i.e. Nestola et al. 2010).

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356

FIGURES AND TABLES CAPTIONS

357 **Figure 1.** Unit-cell volume as a function of pressure collected during increasing and decreasing
358 pressure. E.s.d.'s are smaller than the symbols. Line represents the fitting of our data to a BM4-
359 EoS.

360 **Figure 2.** F_E-f_E plot for the unit-cell volume in the whole range of pressure investigated in this
361 work. Dashed line represents the fitting of the data to a BM4-EoS.

362 **Figure 3.** ΔP (difference between observed and calculated pressure for each volume data point)
363 for both the BM3 and the BM4 approach plotted against unit-cell volume for each pressure
364 increase.

365 **Figure 4.** Normalized bond distances (calculated with respect to the room P data) with
366 increasing pressure. Lines represent linear fitting of the data.

367 **Figure 5.** Coordinate of the sulphur against pressure.

368 **Figure 6.** Normalized volumes of polyhedra (calculated with respect to the room P data) against
369 pressure. Lines represent linear fitting of the data.

370 **Table 1.** Unit cell parameters (\AA) with increasing and decreasing pressure (GPa) for sample
371 CuCr_2S_4 up to 6.73GPa.

372 **Table 2.** Intensity data collection, structure refinement details, fractional atomic coordinates and
373 atomic displacement parameters (\AA^2) for CuCr_2S_4 sample measured upon increasing and
374 decreasing pressure up to 6.73GPa.

375 **Table 3.** Bond lengths (\AA), polyhedral volume (\AA^3) and angles ($^\circ$) for CuCr_2S_4 thiospinel. Data
376 collected with increasing and decreasing pressure up to 6.73GPa.

377 **Table 4.** Elastic parameters and statistical parameters obtained by fitting to a BM3 and BM4 EoS
378 using pressure-volume data on CuCr_2S_4 sample measured with increasing pressure up to
379 6.73GPa.

380 **Table 5.** Bulk modulus and first pressure derivative for Se and S thiospinels.

381

MANUSCRIPT TABLES

Table 1. Unit cell parameters (Å) with increasing and decreasing pressure (GPa) for sample CuCr_2S_4 up to 6.73GPa.

<i>Pressure</i> (GPa)	<i>a</i> (Å)	<i>V</i> (Å ³)
0.0001(0)	9.8231(1)	947.86(3)
0.441(5)	9.8072(2)	943.26(6)
1.211(7)	9.7805(2)	935.47(6)
2.248(6)	9.7461(2)	925.74(5)
2.290(7)*	9.7448(3)	925.37(9)
3.430(6)	9.7086(2)	915.11(7)
4.256(11)	9.6837(2)	908.07(7)
4.580(11)*	9.6737(3)	905.26(10)
5.013(6)	9.6611(3)	901.72(7)
5.701(6)	9.6409(3)	896.09(8)
6.145(9)	9.6281(3)	892.52(8)
6.210(8)*	9.6263(3)	892.01(9)
6.730(11)	9.6111(3)	887.82(7)

Note: * Data collected during pressure decrease

Table 2. Intensity data collection, structure refinement details, fractional atomic coordinates and atomic displacement parameters (\AA^2) for CuCr_2S_4 sample measured upon increasing and decreasing pressure up to 6.73GPa.

	0.0001(0)	3.430(6)	4.580(11)*	5.701(6)	6.730(11)
Space group			Fd $\bar{3}$ m		
Temperature (K)	293	293	293	293	293
<i>a</i> (\AA)	9.8231 (1)	9.7090 (2)	9.6737 (3)	9.6409(3)	9.6111(3)
<i>V</i> (\AA^3)	947.86 (2)	915.1 (3)	905.27 (5)	896.09(5)	887.81 (5)
<i>Z</i>			8		
μ (mm^{-1})	10.52	10.78	10.86	10.94	11.06
Crystal size (mm)			0.130×0.090×0.060		
Diffractometer	Oxford Diffraction XCalibur, Point Detector		Oxford Diffraction XCalibur, CCD Detector		
Absorption correction			Absorb 6.0		
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	287,114,90	344, 125, 79	339, 102, 60	354, 118, 71	331, 110, 64
R_{int}	0.072	0.073	0.09	0.06	0.073
Refinement software			Shelxl-97		
$R[F_2 > 2\sigma(F_2)]$, $wR(F^2)$, <i>S</i>	0.037, 0.068, 1.15	0.037, 0.076, 0.80	0.045, 0.096, 0.92	0.064, 0.158, 1.13	0.043, 0.125, 0.87
No. of reflections	114	125	102	118	110
No. of parameters	8	8	8	8	8
No. of restraints	0	0	0	0	0
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e \AA^{-3})	1.23, -0.79	0.78, -0.65	0.59, -1.08	0.84, -1.19	0.91, -0.98
S					
$u = x=y=z$	0.25735 (7)	0.25696 (11)	0.25668 (15)	0.25676 (18)	0.25665 (17)
$U_{\text{iso}}^*/U_{\text{eq}}$	0.0132 (3)	0.0128 (4)	0.0128 (6)	0.0236 (8)	0.0263 (8)
Cr					
$x=y=z$	0.5	0.5	0.5	0.5	0.5
$U_{\text{iso}}^*/U_{\text{eq}}$	0.0161 (3)	0.0158 (5)	0.0165 (6)	0.0278 (9)	0.0298 (8)
Cu					

$x=y=z$	0.125	0.125	0.125	0.125	0.125
$U_{\text{iso}}^*/U_{\text{eq}}$	0.0158 (3)	0.0147 (5)	0.0150 (7)	0.0256 (9)	0.0286 (8)
S					
U^{11}	0.0132 (3)	0.0128 (4)	0.0128 (6)	0.0236 (8)	0.0263 (8)
U^{12}	-0.0005 (2)	-0.0001 (4)	-0.0015 (6)	-0.0002 (8)	0.0004 (7)
Cr					
U^{11}	0.0161 (3)	0.0158 (5)	0.0165 (6)	0.0278 (9)	0.0298 (8)
U^{12}	0.0024 (2)	0.0029 (5)	0.0047 (7)	0.0047 (8)	0.0038 (7)
Cu					
U^{11}	0.0158 (3)	0.0147 (5)	0.0150 (7)	0.0256 (9)	0.0286 (8)

Note:* Data collected during pressure decrease; Pressures units are GPa. $U^{11}=U^{22}=U^{33}$ and $U^{12}=U^{13}=U^{23}$ for symmetry reasons (where $U^{12}=U^{13}=U^{23}=0$ for the tetrahedrally coordinated site); the tetrahedrally coordinated cations are at (1/8, 1/8, 1/8) and the octahedrally coordinated cations are at (1/2, 1/2, 1/2).

Table 3. Bond lengths (Å), polyhedral volume (Å³) and angles (°) for CuCr₂S₄ thiospinel. Data collected with increasing and decreasing pressure up to 6.73GPa.

	0.0001(0)	3.430(6)	4.580(11)*	5.701(6)	6.730(11)
Cu – S	2.2518(11)	2.2189(19)	2.206(3)	2.200(3)	2.192(3)
Cr - S	2.3858(6)	2.3616(12)	2.3556(14)	2.3468(16)	2.3406(15)
V_{CuS4}	5.860	5.608	5.512	5.466	5.402
V_{CrS6}	18.01	17.48	17.35	17.16	17.02
V_{distortion**}	0.0054	0.0049	0.0045	0.0046	0.0044
Cu - S - Cr	122.81(2)	122.95(4)	123.04(5)	123.01(6)	123.05(6)
Cr - S - Cr	93.41(3)	93.23(5)	93.10(7)	93.14(8)	93.09(8)
S - Cr - S	93.52(3)	93.32(5)	93.18(8)	93.23(9)	93.17(8)
S - Cr - S	86.48(3)	86.68(6)	86.82(8)	86.77(9)	86.83(8)

Note: * Data collected during pressure decrease; ** Volume distortion have been calculated with IVTON software following Balić Žunić and Vicković 1996; Pressures are in GPa.

Table 4. Elastic parameters and statistical parameters obtained by fitting to a BM3 and BM4 EoS using pressure-volume data on CuCr₂S₄ sample measured with increasing pressure up to 6.73GPa.

	BM3	BM4
V_0 (Å ³)	947.79(6)	947.86(6)
K_{T0} (GPa)	91.6(4)	88(1)
K'	3.7(1)	6.3(9)
K''	-0.04*	-1.1(4)
ΔP_{\max}	-0.021	-0.005
χ^2	1.35	0.13

*Value implied for the BM3 fitting;
Standard deviations are given in parenthesis.

Table 5. Bulk modulus and first pressure derivative for Se and S thiospinels.

Composition	Bulk modulus, K_{T0} (GPa)	First pressure derivative, K'	Reference
CdIn ₂ S ₄	78(4)	3.1(8)	Santamaría-Pérez et al. 2012
MgIn ₂ S ₄	76(3)	2.8(7)	Santamaría-Pérez et al. 2012
MnIn ₂ S ₄	78(4)	3.2(1)	Santamaría-Pérez et al. 2012
ZnCr ₂ S ₄	76(9)	12(4)	Wittlinger et al. 1997
CuCr _{1.7} V _{0.3} S ₄	91.6(4)	3.7(1)	This study
CdCr ₂ Se ₄	101(3)	3.3(1.9)	Waskowska et al. 2002
CuCr ₂ Se ₄	96(3)	n.a.	Waskowska et al. 2009
ZnCr ₂ Se ₄	98(3)	n.a.	Waskowska et al. 2009

n.a. = not available; the EoS for our sample refers to a BM3 fitting of our data. Wittlinger et al. 1997 has not been taken into account for our comparison because such high K' value (12) is not reliable for this structural type and considering the high correlation between K_{T0} and K' the miscalculation of the K' will lead to a completely unreliable K_{T0} value.











