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Universal link of magnetic exchange and structural behavior under pressure in chromium spinels

We have conducted high-pressure x-ray diffraction studies on the MnCr2O4 and NiCr2O4 spinels at room temperature. Both compounds undergo pressure-induced structural transitions into diverse tetragonal modifications. Based on these experimental observations and our ab initio calculations, we show that the Cr-oxide spinels with magnetic A2+ cations (A2+ = Mn, Fe, Co, Ni) follow a similar trend as their chalcogenide counterparts with nonmagnetic A2+ ions, i.e., the transition pressure is proportionally related with the magnitude of the Cr-Cr magnetic exchange interactions. Therefore, we reach the conclusion that the Cr-Cr magnetic exchange interactions alone suffice to account for the high-pressure behavior of these systems. Our results clearly depict the close relationship between the structural and magnetic degrees of freedom in Cr-bearing spinels.

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I. INTRODUCTION
The series of A2+Cr3+2X4(A2+ = Mn-Zn, Cd, Hg; X = O, S, Se) spinels (SGFd3m, Z = 8) constitutes an ideal system for studying magnetic exchange interactions in solids [1–3]. The spinel structure is composed of edge-sharing Cr3+ octahedral units with six nearest neighbors/anions (the Cr3+ cations themselves form tetrahedra in a pyrochlore-type lattice, thus allowing for magnetic frustration) and relatively “isolated” A2+ tetrahedral units with four nearest neighbors (Fig. 1).

Depending on the type and size of the tetrahedrally coordinated A2+ cations and the corresponding anions, the magnetic exchange interactions can vary significantly [3,4]. As established already in the 1960s [5–8], spinels with nonmagnetic A2+ cations may exhibit either direct Cr3+-Cr3+ antiferromagnetic (AFM) or indirect ferromagnetic (FM) Cr-X-Cr interactions depending on the Cr3+-Cr3+ distance. The AFM interactions are dominant in the Cr-spinel oxides with smaller Cr3+-Cr3+ distances; on the other hand, the Cr-X-Cr FM exchange prevails in the Cr-bearing sulfide and selenide spinel series due to the larger Cr3+-Cr3+ separation distances compared to the oxides [6–8,10]. This fact alone indicates the strong coupling between magnetism and structure in these compounds. Indeed, several experimental studies have shown the enhancement of the AFM interactions upon decreasing the Cr3+-Cr3+ distances, via the reduction of the Cr-spinel volume under external compression [11,12]. In certain cases, electronic changes, e.g., insulator-to-metal [13–16] or semiconductor-to-semiconductor [17] transitions, have been reported. On the other hand, the magnetic interactions of the oxide spinels with magnetic A2+ cations are more complex, since one needs to consider also the A2+−Cr3+ and the more distant A2+−A2+ magnetic exchange interactions for interpreting accurately the respective magnetic ground states [2,4,18].

In previous works we have unraveled the close correlation between the magnetic exchange interactions and the pressure-induced structural transitions in ACr2X4 Cr-spinel chalcogenides with nonmagnetic A2+ cations (A = Zn, Cd, Hg; X = S, Se) [19,20]. In particular, we have shown that the ratio of the next-nearest-neighbor (Knnn) over the nearest-neighbor (Jnn) magnetic interactions is proportional to the structural transition pressure (PTr) from the starting cubic Fd3m phase toward a tetragonal modification [21,22]. Notable exceptions from this trend are ZnCr2Se4 [23] and CuCr2Se4 [24], as their high-pressure behavior appears to be dictated by the similar ionic radii of tetrahedrally coordinated Zn2+ and Cu2+ with the octahedrally coordinated Cr3+, and the higher covalency of the larger-sized Se anions (for a more detailed discussion see Ref. [24]). Here we expand this idea to Cr-oxide spinels with magnetic A2+ cations (A2+ = Mn-Cu). For this purpose, we have investigated the high-pressure structural behavior of MnCr2O4 and NiCr2O4 spinels by means of x-ray diffraction (XRD) and density functional theory (DFT)-based calculations. Combined with results from the literature, we could find a clear correlation between the Cr-Cr magnetic exchange interactions and PTr in these systems, as we describe below.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS
The MnCr2O4 and NiCr2O4 single-crystalline samples have been synthesized with solid-state reaction, as reported elsewhere [25,26]. The high-pressure sample environment was generated by rhenium gasketed diamond-anvil cells, equipped

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with diamonds of 300-μm culet diameter. The ruby luminescence method was employed for pressure calibration [27]. The angle-resolved high-pressure powder XRD measurements were performed at the 16BM-D beamline of the High Pressure Collaborative Access Team (MnCr₂O₄), and the 13-BMC beamline of the GeoSoilEnviroCARS (NiCr₂O₄) at the Advanced Photon Source of Argonne National Laboratory [28]. The incident monochromatic x-ray beam energies were \( E = 29.2 \text{ keV} \) (\( \lambda = 0.4246 \text{ Å}, \text{MnCr}_2\text{O}_4 \)) and \( E = 28.6 \text{ keV} \) (\( \lambda = 0.434 \text{ Å}, \text{NiCr}_2\text{O}_4 \)). Helium served as a pressure-transmitting medium in both experiments.

The majority of the measured XRD patterns were fitted with the Rietveld method. The refined parameters in each case were the lattice parameters, the atomic coordinates (Mn, Ni, and Cr reside in fixed positions in the ambient-pressure structures), and the profile parameters of the Stephens peak function [29], whereas the background was modeled with a Chebyshev polynomial. Since the diffractograms showed textured rings, we employed a spherical harmonics correction [30] in order to account for the preferred orientation of the powder particles.

Our DFT-based calculations have been performed with the Vienna Ab initio Simulation Package (VASP) [31–34], using projector-augmented wave method [35,36] with the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) [37]. The GGA + \( U \) correction scheme was used for the \( d \) orbitals of Mn, Ni, and Cr. The \( U \) values were chosen to be 3.9 eV for Mn, 6.2 eV for Ni, and 3.7 eV for Cr [38,39]. Plane-wave basis with appropriate \( k \)-point meshes and Gaussian smearing was used. We carefully constructed the cells with various magnetic configurations, including random solid solutions [40,41] provided in the Alloy Theoretic Automated Toolkit (atAT) [42,43]. In each run the cell shape and atomic positions were allowed to freely relax as in earlier works [23,44,45]. To determine the magnetic exchange interactions parameters, we have calculated the total energies of various different magnetic configurations. Detailed quantitative descriptions of the above computational methods are provided in Supplemental Material [46].

### III. RESULTS AND DISCUSSION

#### A. Cubic MnCr₂O₄ under pressure

In Fig. 2(a) we present XRD patterns of MnCr₂O₄ at selected pressures. At ambient conditions, MnCr₂O₄ crystallizes in the cubic spinel \( Fd\bar{3}m \) structure (Fig. 1). This ambient-pressure phase is retained up to \( \sim 8 \text{ GPa} \). Above this pressure, an abrupt broadening of the \( Fd\bar{3}m \) Bragg peaks is evidenced, as revealed by a change in the pressure dependence of the respective widths (Fig. S1 in Supplemental Material [46]). Since we have used helium as pressure-transmitting medium, we can most likely exclude nonhydrostatic effects at this relatively low pressure range [47]. Due to this Bragg-peak broadening, the \( Fd\bar{3}m \) phase does no longer reproduce the XRD patterns satisfactorily; a tetragonal structure, on the other hand, can reasonably index the measured diffractograms (Fig. S1 [46]). We note that upon passing from the cubic to the tetragonal structure, the majority of the \( Fd\bar{3}m \) Bragg peaks split into two or more components, thus accounting for the observed abrupt width broadening (Fig. S1 [46]). Hence, we conclude that a cubic→tetragonal distortion takes place in MnCr₂O₄ close to 8.3 GPa, similar to CoCr₂O₄ [45]. Due to this Bragg-peak broadening, we could not assign a unique space group for this high-pressure tetragonal phase.

Further compression results in the appearance of a shoulder band in the Bragg peak located at \( \sim 8^\circ \) close to 21 GPa [Fig. 2(a)]. This shoulder becomes more prominent with increasing pressure, at the expense of its adjacent Bragg peak. This observation is interpreted as a second structural transition, initiating at 21 GPa and completed at \( \sim 30 \text{ GPa} \) [Fig. 2(a)]. This second high-pressure phase can be also indexed to a tetragonal structure, with its \( c \) axis reduced by 7.5% and its \( a \) axis expanded by 4% compared to the first high-pressure tetragonal phase (Table S1 in Supplemental Material [46]). Again, due to the Bragg-peak broadening, we could not assign a unique space group for this second high-pressure tetragonal phase. Further compression above 34 GPa appears to lead to an orthorhombic distortion (not shown); the pronounced broadening of the Bragg peaks, however, does not allow for reliable XRD refinements beyond that pressure.

Due to the aforementioned Bragg-peak broadening of our XRD patterns, we performed mostly Le Bail refinements for the majority of the MnCr₂O₄ diffractograms. In Fig. 2(b) we plot the axial ratio of the tetragonal high-pressure phases of MnCr₂O₄; the respective lattice parameters are provided in Table S1 [46]. We can clearly observe that the cubic→tetragonal distortion is accompanied by a slight deviation from the cubic \( c/a \) unity value. On the other hand, the second pressure-induced tetragonal→tetragonal transition is manifested by an abrupt drop of the \( c/a \) axial ratio, owing to the sudden reduction of the tetragonal \( c \) axis at the transition point (Table S1 [46]). Such behavior is reminiscent of the documented pressure-induced structural transitions in several Cr-bearing spinels [20,48]. Nevertheless, both of the pressure-induced MnCr₂O₄ structural transitions do not show any sizable volume changes at the respective transition points [Fig. 2(c)]. The experimental \( P-V \) data were fitted with Birch-Murnaghan equations of state [49,50], with the respective results tabulated in Table 1.
FIG. 2. (a) Selected XRD patterns of MnCr$_2$O$_4$ at various pressures ($T = 300$ K, $\lambda = 0.4246$ Å). The various phases are distinguished by black ($Fd\bar{3}m$), red (HP-tetragonal I), and blue (HP-tetragonal II) colors. Orange diffractograms denote the coexistence range. Asterisks mark the strongest Bragg peaks of the Cr$_2$O$_3$ secondary phase. We also plot the (b) $c/a$ axial ratio and (c) volume per formula unit (f.u.) as a function of pressure for all phases of MnCr$_2$O$_4$ (error bars lie within the symbols). The closed and open symbols correspond to experimental and DFT data, respectively. The vertical dashed lines depict the experimental transition pressures, and the red solid lines through the symbols indicate the fitted Birch-Murnaghan equations of state [49,50]. Black circles, red triangles, and blue stars correspond to the $Fd\bar{3}m$, the tetragonal AFM-MnCr, and the tetragonal AFM-Cr phases of MnCr$_2$O$_4$, respectively, in both panels. The obtained elastic parameters are listed in Table I. The respective lattice parameters are provided in Tables S1 and S2 [46].

In order to understand the origin behind these pressure-induced structural transitions, we have performed DFT calculations on MnCr$_2$O$_4$ assuming a paramagnetic (PM) cubic structure and two different tetragonal AFM configurations, one with Mn spin-up and parallel to each Mn cation and Cr spin-down aligned parallel to each Cr cation but antiparallel to the Mn ones (similar to the experimental observation at ambient pressure [51]), and one with all Mn$^{2+}$ in spin-up states, and half of Cr$^{3+}$ in the same plane on the $c$ axis with spin-up states, the other half spin-down as in CoCr$_2$O$_4$ [45] called AFM-MnCr

TABLE I. Elastic parameters (volume $V_T$, bulk modulus $B_T$, and the pressure derivative of bulk modulus $B'_T$) for the various phases of MnCr$_2$O$_4$ and NiCr$_2$O$_4$, as obtained by Birch-Murnaghan equations of state [49,50]. Each parameter is evaluated at the transition pressure point $P_T$. N/A: not available.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$P_T$ (GPa)</th>
<th>$V_T/Z$ (Å$^3$)</th>
<th>$B_T$ (GPa)</th>
<th>$B'_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCr$_2$O$_4$</td>
<td>Exp.</td>
<td>10$^{-4}$</td>
<td>75.2 (exp.)</td>
<td>212(5)</td>
</tr>
<tr>
<td>$Fd\bar{3}m$</td>
<td>DFT (ParaM)</td>
<td>79.4</td>
<td>164.6</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>Exp. [53]</td>
<td>75.5</td>
<td>180</td>
<td>N/A</td>
</tr>
<tr>
<td>MnCr$_2$O$_4$</td>
<td>Exp.</td>
<td>8.3</td>
<td>72.5 (exp.)</td>
<td>230(6)</td>
</tr>
<tr>
<td>HP1</td>
<td>DFT (AFM-MnCr)</td>
<td>72.8</td>
<td>164.1</td>
<td>4.5</td>
</tr>
<tr>
<td>MnCr$_2$O$_4$</td>
<td>Exp.</td>
<td>21.1</td>
<td>69.3 (exp.)</td>
<td>231(3)</td>
</tr>
<tr>
<td>HP2</td>
<td>DFT (AFM-Cr)</td>
<td>30.5</td>
<td>69.5</td>
<td>164.3</td>
</tr>
<tr>
<td>NiCr$_2$O$_4$</td>
<td>Exp.</td>
<td>10$^{-4}$</td>
<td>71.9 (exp.)</td>
<td>183(1)</td>
</tr>
<tr>
<td>$I4_1/amd$</td>
<td>DFT (ParaM)</td>
<td>73.9</td>
<td>165.3</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>DFT (AFM)</td>
<td>75.5</td>
<td>166.5</td>
<td>3.6</td>
</tr>
<tr>
<td>NiCr$_2$O$_4$</td>
<td>Exp.</td>
<td>19.4</td>
<td>64 (exp.)</td>
<td>182(6)</td>
</tr>
<tr>
<td>$P4_2_1_2$</td>
<td>DFT (ParaM)</td>
<td>28.0</td>
<td>62.5</td>
<td>154.7</td>
</tr>
<tr>
<td></td>
<td>DFT (AFM)</td>
<td>32.0</td>
<td>61.2</td>
<td>146.0</td>
</tr>
</tbody>
</table>
FIG. 3. Calculated enthalpies of the cubic paramagnetic (black), the tetragonal AFM1 (AFM-MnCr, blue), and tetragonal AFM2 (AFM-Cr, red) phases as a function of pressure. Inset: the enthalpy difference between the tetragonal AFM1 and AFM2 phases and the cubic phase with respect to pressure. Enthalpy $H$ is defined as $H(P) = E + PV$, and a lower value of $H$ indicates the phase stability. The cubic→AFM-MnCr transition is calculated at 17 GPa (experimental value is 8.3 GPa). The AFM-MnCr→AFM-Cr transition is expected to take place at 30.5 GPa (extrapolated in Fig. S2 in Supporting Material [46], the experimental value is 21.1 GPa).

and AFM-Cr, respectively (Tables S2 and S3 [46]). From our calculations, we could find that the cubic→AFM-MnCr and the AFM-MnCr→AFM-Cr transitions take place at 17 and 30.5 GPa, respectively (Fig. 3 and Fig. S2 [46]). Even though the experimental and calculated transition pressures exhibit discrepancies in their values, owing partially to the fact that DFT calculations are performed at 0 K and not at room temperature as the experiments, as well as the overestimation of the lattice parameters within the GGA used here (see, e.g., Ref. [52]), we are confident that we have captured the main features of the observed MnCr$_2$O$_4$ pressure-induced structural transitions, i.e., that both structural transitions are accompanied/triggered by changes in the magnetic properties of MnCr$_2$O$_4$. We will return back to this point later.

Despite the aforementioned transition pressure discrepancies, the calculated lattice parameters, $c/a$ axial ratios, and the $P$-$V$ data for the various phases of MnCr$_2$O$_4$ are qualitatively very similar to their experimental counterparts [Figs. 2(b) and 2(c)]. We can immediately observe that the DFT-calculated values lie always higher than their experimental counterparts, attributed to the tendency of the GGA approximation used here to overestimate the unit-cell volumes and, concomitantly, underestimate the bulk moduli [52].

B. Compression of Jahn-Teller active tetragonal NiCr$_2$O$_4$

Turning now to the high-pressure structural behavior of NiCr$_2$O$_4$, selected XRD patterns at various pressures are shown in Fig. 2(b). At ambient conditions, NiCr$_2$O$_4$ adopts a tetragonal $I4_1/amd$ structure ($Z = 4$), a direct subgroup of the $Fd\bar{3}m$ phase [54], given the Ni$^{2+}$ Jahn-Teller active ions [55]. Compression leads to changes in the XRD patterns starting at 19.4 GPa, with the most notable difference being the vanishing of the intense Bragg peak at 10.4° [Fig. 4(a)]. Therefore, it is obvious that NiCr$_2$O$_4$ has undergone a structural transition at 19.4 GPa. Indexing of the high-pressure NiCr$_2$O$_4$ modification led to another tetragonal structure with SG $P4_2_2_1_2$ ($Z = 8$) [Fig. 4(b)]. The $I4_1/amd \rightarrow P4_2_2_1_2$ transition does not involve any cationic coordination increase for either Ni$^{2+}$ or Cr$^{3+}$ (SG $P4_2_2_1_2$ is a subgroup of SG $I4_1/amd$). Even though such phase has been observed as a low-temperature modification of MgTi$_2$O$_4$ [56], this is one of the rare reports of a Cr-bearing spinel adopting this particular tetragonal structure.

The high quality of the XRD patterns allowed for Rietveld refinements of the NiCr$_2$O$_4$ diffractograms. The respective lattice parameters and atomic coordinates are provided in Table S4 [46]. Here we show the tetragonal $c/a$ axial ratio and the $P$-$V$ data for the two NiCr$_2$O$_4$ phases (Fig. 5). As we can observe in Fig. 5(a), the tetragonal $c/a$ axial ratio increases upon compression, indicating the enhancement of the Jahn-Teller polyhedral distortion in the NiCr$_2$O$_4$ $I4_1/amd$ ambient-pressure structure. We note here that the $I4_1/amd$ symmetry dictates one single Ni–O bond distance in the NiO$_4$ tetrahedra, and two Cr–O bond distances in the CrO$_6$ octahedra (two apical bonds along the long $c$ axis, and two equatorial bonds parallel to the tetragonal $ab$ plane) comprising the tetragonal spinel phase. Thus, the increase of the $c/a$ ratio directly implies the elongation of the CrO$_6$ octahedra along the $c$ axis, i.e., the apical Cr–O bonds are increasing at the expense of the equatorial ones, in excellent agreement with our refined Cr-O data (Table S4 [46]). Nevertheless, the overall Jahn-Teller distortion in the starting NiCr$_2$O$_4$ $I4_1/amd$ phase is small and is virtually eliminated upon compression, as revealed by the pressure-induced evolution of the Jahn-Teller distortion parameter $\sigma_{JT}$, as in the case of CuWO$_4$ [57,58] (Fig. S3 [46]).

Upon passing into the high-pressure $P4_2_2_2_2$ phase, we can observe that the $c/a$ ratio decreases by ~2% due to the abrupt reduction of the $c$ axis (Fig. 5(a) and Table S4 [46]), resulting also in a ~3% volume change at the $I4_1/amd \rightarrow P4_2_2_2_2$ transition point [Fig. 5(b)], thus classifying the transition as of first order. We can also notice that the pressure-induced $c/a$ trend reverses in the $P4_2_2_2_2$ phase, i.e., the equatorial Cr–O bonds expand at the expense of the apical ones. The latter observation indicates that (a) the Jahn-Teller distortion caused by the Ni$^{2+}$ ions persists also in the high-pressure phase, contrary to the general trend of eliminating the Jahn-Teller effect upon sufficient compression [59], and (b) the overall polyhedral distortion in the high-pressure $P4_2_2_2_2$ modification is opposite to the starting $I4_1/amd$ one. Plotting of the Jahn-Teller distortion parameter $\sigma_{JT}$ shows that the Jahn-Teller distortion increases one order of magnitude in the $P4_2_2_2_2$ phase at the transition point (Fig. S3 [46]). Further compression enhances the CrO$_6$ polyhedral distortion, whereas a downturn in the pressure slope of $\sigma_{JT}$ is detected close to 36–40 GPa. Extrapolation of the respective data indicates the complete Jahn-Teller suppression at ~120 GPa. Given the discussion that follows below, we tend to attribute the enhancement of the Jahn-Teller distortion upon the $I4_1/amd \rightarrow P4_2_2_2_2$ transition not as the driving force behind the observed structural change, as e.g. in the case of CuWO$_4$ [57,58], but rather as a byproduct of the magnetic changes accompanying the structural modification.
FIG. 4. (a) Selected XRD patterns of NiCr$_2$O$_4$ at various pressures ($T = 300$ K, $\lambda = 0.4340$ Å). The various phases are distinguished by black ($I4_1/amd$) and red ($P4_32_12$) colors. (b) Examples of Rietveld refinements of NiCr$_2$O$_4$ XRD patterns at 6.9 GPa (top) and at 36.1 GPa (bottom). Dots stand for the measured spectra, the red solid lines represent the best refinements, and their difference is drawn as blue lines. Vertical ticks mark the respective Bragg-peak positions.

In Fig. 5(b) we plot the experimental and calculated $P$-$V$ data for both phases. We can immediately observe that the DFT-calculated values always lie higher than their experimental counterparts, attributed to the tendency of the GGA approximation used here to overestimate the unit-cell volumes and, concomitantly, underestimate the bulk moduli [52]. Interestingly, we note that the experimental bulk modulus of the high-pressure $P4_32_12$ phase is similar to the bulk modulus value of the starting $I4_1/amd$ structure, implying a smaller bulk modulus for $P4_32_12$, i.e., the high-pressure phase of NiCr$_2$O$_4$ appears to be softer than the ambient-pressure structure; this is more evident in our DFT calculations (Table I). Even though such effect is quite unusual in high-pressure studies, a possible cause might be underlying electronic effects due to changes in the nature of interionic bonding after the $I4_1/amd \rightarrow P4_32_12$ transition (e.g., the Cr-O distances expand by $\sim 6\%$, whereas the Ni–O bond lengths shorten by $\sim 8\%$ at the transition point), as in the case of CrN [60].

Our DFT calculations in the case of NiCr$_2$O$_4$ were performed assuming a PM and AFM $I4_1/amd$ structures, as well as a PM and an AFM high-pressure $P4_32_12$ phase (Table S5 [46]). Evaluation of the respective enthalpies indicates that the AFM $I4_1/amd$ structure adopts the PM $P4_32_12$ phase close to 25 GPa (Fig. 6), in good agreement with the experimental value, whereas the PM $I4_1/amd$ phase transforms into the PM $P4_32_12$ phase close to 35 GPa (the AFM $P4_32_12$ phase is adopted in both cases 5 GPa higher than the PM one; Fig. 6 and Fig. S3 [46]). However, from the reasons reported earlier regarding the temperature effect, as well as the overestimation of the volume within the GGA approximation, it appears that the calculated transition pressure depends also on the choice of the exact magnetic configuration. The latter enlightens the inconsistencies in the experimental and calculated transition pressures in the case of MnCr$_2$O$_4$, as we discuss in more detail in the next section.

C. Pressure-induced structural transition and magnetic exchange in Cr spinels

Having established the transition pressures ($P_{Tr}$) for both MnCr$_2$O$_4$ and NiCr$_2$O$_4$ spinels, we turn now to some common aspects of the (first) pressure-induced structural transition in the Cr-spinel series. Comparison of the available literature reveals that for sulfide and selenide Cr spinels, the cubic $\rightarrow$ tetragonal transition is always accompanied by a volume decrease of 4–5% at the transition point [19–23,61]. In addition, DFT calculations have identified concomitant magnetic changes accompanying these structural transitions, i.e., from the starting FM states toward AFM ones [20–22]. Taken together, we were able to identify a linear relationship between the $P_{Tr}$ of Cr-bearing spinel sulfides and selenides and the $K_{nnn}/J_{nn}$ ratio of next-nearest-neighbor $K_{nnn}$ to nearest-neighbor $J_{nn}$ magnetic exchange interactions [19,20].

Given, however, that the $K_{nnn}$ interactions are not relevant for Cr-oxide spinels bearing magnetic $A^{2+}$ cations [2,4,18], does a similar relation between $P_{Tr}$ and magnetic exchange...
interactions hold for these materials? For this purpose, we have calculated the relevant magnetic exchange parameters $J_{AA}$, $J_{BB}$, and $J_{AB}$ for the whole spinel series with magnetic $A^{2+}$ cations ($A^{2+} = \text{Mn-Cu}$) at ambient pressure, the most important magnetic parameters in these compounds [4,18]. All of these data, alongside relevant literature values [4,18,62,63], are listed in Table S8 [46]. We note that $J_{AA}$ represents the interactions between $A^{2+}$ cations, $J_{AB}$ denotes the magnetic exchange between $A^{2+}$ and $Cr^{3+}$, and $J_{BB}$ stands for $Cr^{3+}$-$Cr^{3+}$ interactions.

In Fig. 7 we plot the calculated $J_{BB}$ exchange parameter as a function of $P_{Tr}$ for all the relevant spinels. We can immediately observe a linear dependence of the two parameters with the exception of CuCr$_2$O$_4$, which undergoes an isostuctural transition at $P_{Tr} = 25$ GPa, most likely resulting from pressure-induced orbital reorientation [24]. We note also that the calculated magnetic exchange interactions of CuCr$_2$O$_4$ are much larger compared to the rest of the spinels (Table S8 [46]), possibly accounting for the absence of any structural transition up to 50 GPa [24]. On the other hand, CoCr$_2$O$_4$ undergoes a structural distortion at about 16 GPa, attributed to magnetic frustration [45]. Moreover, FeCr$_2$O$_4$ has been studied interactions hold for these materials? For this purpose, we have calculated the relevant magnetic exchange parameters $J_{AA}$, $J_{BB}$, and $J_{AB}$ for the whole spinel series with magnetic $A^{2+}$ cations ($A^{2+} = \text{Mn-Cu}$) at ambient pressure, the most important magnetic parameters in these compounds [4,18]. All of these data, alongside relevant literature values [4,18,62,63], are listed in Table S8 [46]. We note that $J_{AA}$ represents the interactions between $A^{2+}$ cations, $J_{AB}$ denotes the magnetic exchange between $A^{2+}$ and $Cr^{3+}$, and $J_{BB}$ stands for $Cr^{3+}$-$Cr^{3+}$ interactions.

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FIG. 6. Calculated enthalpies of the $I4_1/ amd$ (AFM, blue), the $P4_12_12_2$-AFM (black), and the $P4_12_12_2$ ParaM (red) NiCr$_2$O$_4$ phases as a function of pressure. Inset: the enthalpy difference between the $P4_12_12_2$ (AFM and paraM) and $I4_1/ amd$ (AFM) phases with respect to pressure. Enthalpy $H$ is defined as $H(P) = E + PV$, and a phase is stable if it has a lower value of $H$. The $I4_1/ amd$-AFM $\rightarrow$ $P4_12_12_2$-ParaM transition takes place at 25 GPa, whereas the $I4_1/ amd$-AFM $\rightarrow$ $P4_12_12_2$-AFM transition is estimated at 30 GPa.

FIG. 5. Plot of the (a) $c/a$ axial ratio and (b) volume per f.u. as a function pressure for the two modifications of NiCr$_2$O$_4$ (error bars lie within the symbols). The closed and open symbols correspond to experimental and DFT data, respectively. The vertical dashed lines through the symbols indicate the fitted Birch-Murnaghan equations of state [49,50]. Nomenclature of the symbols is as follows: Black circles and red squares correspond to the PM $I4_1/amd$ and $P4_12_12_2$ phases of NiCr$_2$O$_4$, respectively. The black and red (X) symbols stand for the corresponding AFM $I4_1/amd$ and $P4_12_12_2$ phases of NiCr$_2$O$_4$, respectively, as obtained from DFT calculations. The obtained elastic parameters are listed in Table I. The respective lattice parameters are provided in Tables S4 and S5 [46]. The overall deformation of the NiCr$_2$O$_4$ polyhedra is also drawn for clarity in panel (a).
up to 93 GPa [64,65]. These studies established an $Fd\bar{3}m \rightarrow I4_1/mmd$ structural transition close to 12 GPa in FeCr$_2$O$_4$ due to Jahn-Teller effects. Further compression leads to Fe$^{2+}$-Cr intercationic site exchange and a high-spin to low-spin state transition of divalent Fe [64]. We should also note here that the $P_{Tc}$ of several ternary $AB_2X_4$ compounds was shown to depend on the cationic radii ratio of the respective constituent ions [66,67]; such relationship, however, does not seem to hold for Cr-bearing spinels (see Fig. 10 in Ref. [20]).

From our plot (Fig. 7) it becomes immediately evident that the structural distortions/transitions observed in the Cr-spinel series are closely interrelated to magnetic rather than steric or Jahn-Teller effects. Considering our aforementioned results on spinel sulfides and selenides with nonmagnetic $A^{2+}$ cations, we can generally state at this point that the structural transitions in Cr-based spinels are intimately connected with the Cr-Cr magnetic exchange interactions.

In order to link our suggestion with the theory developed by Lyons, Kaplan, Dwight, and Menyuk (LKDM) for these systems [2], the magnetic ground state and/or the magnetic frustration of a cubic-spinel compound can be described by the parameter $u$:

$$u = \frac{4J_{BB}S_B}{3J_{AB}S_A},$$

where $S_A$ and $S_B$ denote the spin magnitude of the $A$ and $B$ cations in the $AB_2X_4$ spinel phase [68]. It is clear that the parameter $u$ represents the relative strength between the two different nearest-neighbor interactions $J_{BB}$ and $J_{AB}$. According to LKDM, the numerical value of $u$ describes the magnetic ground state of the spinel, with $u \leq 8/9$ denoting a collinear AFM Néel state (e.g., all $A$-site spins parallel to each other and antiparallel to the $B$-site spins), $8/9 < u < 1.298$ a ferrimagnetic spiral configuration, whereas for $u > 1.298$ the latter ferrimagnetic configuration becomes unstable, resulting in an unstable spiral state. Therefore, it becomes clear that the larger the magnitude of $u$, the more magnetically unstable the respective spinel becomes. Given that the $J_{BB}$ coupling constant displays a larger enhancement under pressure compared to $J_{AB}$ (Fig. 8; see also Table I in Ref. [45]), we can reasonably anticipate the enhancement of the magnetic instability in these systems under compression. Consequently, it appears that this built-up pressure-induced magnetic instability is partially relieved by structural transitions in these materials, leading possibly also to the realization of new magnetic ground states [20,45,64].

Indeed, our DFT calculations have revealed that the structural transitions may be accompanied by magnetic ones in both MnCr$_2$O$_4$ and NiCr$_2$O$_4$ spinels. Regarding the former, we mentioned earlier the discrepancies between the experimental and calculated $P_{Tc}$ for the observed structural transitions. Considering the sensitivity of the calculated enthalpy on the choice of the exact magnetic configuration (see the NiCr$_2$O$_4$ discussion earlier), one possible explanation behind the $P_{Tc}$ discrepancies might be that the selected tetragonal AFM-MnCr and AFM-Cr states might not be the most suitable candidates for describing the MnCr$_2$O$_4$ magnetic configurations in the respective high-pressure tetragonal structures. More complex magnetic ground states with tetragonal symmetries might be needed for this purpose, a task which lies beyond the scope of the present paper.

Finally, we consider it interesting to compare the present results on Cr spinels with the recent high-pressure studies conducted on the $A^{2+}V_2O_4$ spinels ($A^{2+} = Mg, Mn, Fe, Co, Zn, Cd$) [11,53]. Compared to the Cr$^{3+}$-bearing oxospinels with localized $3d_{t_{2g}}$ electrons (Cr$^{3+}$: $S = 3/2$) and large electronic band gaps, the V$^{3+}$-bearing spinels (V$^{3+}$: $3d^{2}$; $S = 1$) are closer to a localized-itinerant transition under compression [11,69]. Interestingly, such an electronic transition was speculated to take place at a critical intermetallic separation distance $R_c$ between the Cr$^{3+}$-Cr$^{3+}$ ($R_c = 2.84\ \text{Å}$) and the V$^{3+}$-V$^{3+}$ ($R_c = 2.97\ \text{Å}$) cations [5,70]. For the V$^{3+}$ spinels, however, the proposed $R_c$ appears to be overestimated [53]. This appears to be the case also for the Cr-bearing oxospinels, as, e.g., the intermetallic Cr$^{3+}$-Cr$^{3+}$ distance in CoCr$_2$O$_4$ reaches $R_c = 2.84\ \text{Å}$ close to 30 GPa, but without any indication of a metallic transition [45]. Moreover, the high-pressure $P_{4i212}$ modification of NiCr$_2$O$_4$ exhibits an intermetallic Cr$^{3+}$-Cr$^{3+}$ distance of 2.6 Å close to 50 GPa, again with no indication...
of metallization (at least visually). Hence, the concept of a critical intermetallic separation distance leading to localized-to-itinerant transitions in transition-metal compounds should be revisited.

IV. CONCLUSIONS

In summary, we have investigated the high-pressure structural behavior of the MnCr$_2$O$_4$ and NiCr$_2$O$_4$ spinels at room temperature. In both cases, we have unraveled pressure-induced structural transitions into tetragonal modifications. In the case of MnCr$_2$O$_4$, the structural transitions did not result in sizable volume changes at the respective transition points. On the other hand, NiCr$_2$O$_4$ undergoes a first-order $I4_1/amd \rightarrow P4_2_1_2$ transition with a reversal of the $c/a$ axial ratio slope, indicating opposite Jahn-Teller effects in the two structures.

Considering the present results, as well as the available literature, we have shown that the Cr-oxide spinels with magnetic $A^+$ cations ($A^+ = \text{Mn, Fe, Co, Ni, Cu}$) follow a similar trend as their chalcogenide counterparts with nonmagnetic $A^{2+}$ ions, i.e., the transition pressure is proportional to the magnitude of the Cr-Cr magnetic exchange interactions active in these compounds. Therefore, we have reached the conclusion that knowing the Cr-Cr magnetic exchange interactions alone suffices to account for the high-pressure behavior of these systems. It would be interesting to search for analogous interrelations of magnetic and structural properties in relevant material families.

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See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.97.184435 for the complete set of experimental and calculated structural parameters, as well as the list of magnetic data used for our DFT calculations. An overview table for all relevant spinels is also supplied for convenience.


