Chemical and physical pressure effects in the A-site spinel antiferromagnets CoM$_2$O$_4$ (M = Al, Co, and Rh)

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Abstract

Magnetic phase transitions under high pressure are reported for the diamond lattice antiferromagnet Co$_3$-$_x$Rh$_x$O$_4$ in the range of 0 \( x \) \( \leq \) 2.0, which is an isostructural \( S = 3/2 \) system for the well-known frustrated antiferromagnet CoAl$_2$O$_4$. In the Co$_3$-$_x$Rh$_x$O$_4$ system, magnetic and specific-heat measurements at ambient pressure revealed that a second-order antiferromagnetic transition occurred at the Néel temperature (\( T_N \)) which exhibits a nonmonotonic \( x \)-variation. The physical pressure variations of \( T_N \) were determined by ac-calorimetry under hydrostatic pressures up to \( p = 2.6 \) GPa for Co$_2$Rh$_x$O$_4$ and CoRh$_2$O$_4$. The rates of change of \( T_N \) with pressure (i.e., the pressure coefficients), 1.93 and 1.61 K GPa$^{-1}$, respectively, were comparable to those for CoAl$_2$O$_4$ and Co$_3$O$_4$, respectively. The pressure coefficients of magnetic ordering temperature for these A-site spinel compounds were considerably larger than those for other spinel and iron-garnet compounds which follow the empirical ‘10/3 law’. Simple analysis of the chemical and physical pressure coefficients of \( T_N \) revealed that \( T_N \) depended on both the lattice volume and the oxygen positional parameter \( u \).

1. Introduction

Investigation of pressure-induced phenomena has been a treasure chest for the discovery of novel physical and chemical phenomena and development of new functional materials. As a result of rapid developments in pressure generation and high-pressure measurement techniques in recent decades, many condensed matter researchers have been able to study materials in the presence of high magnetic external fields at very low temperatures and high pressures. In magnetic materials, for example, magnetovolume effects have been revealed by applying a magnetic field and external pressure. One can thereby manipulate magnetic and electronic states by applying pressure to induce magnetoelastic interactions, hybridization between localized and itinerant spins, and electronic interactions that depend on bond lengths and bond angles in exotic materials. Such materials include high-\( T_c \) layered structural superconductors as well as heavy fermion compounds and magnetic insulators situated in the vicinity of a magnetic phase boundary due to competitive interactions [1].

A so-called A-site spinel has a chemical composition AB$_2$X$_4$, where A, B, and X are a divalent magnetic cation, trivalent nonmagnetic cation, and chalcogen ion such as O$^{2-}$, S$^{2-}$, or Se$^{2-}$, respectively. In a spinel structure, as shown in figure 1(a), the A- and B-sites are tetrahedrally and octahedrally surrounded by the anion, respectively. Figure 1(b) visualizes that the spinel-type structure consists of the AX$_4$-tetrahedron and BX$_6$-octahedron. The X-ion is located at \( (u, u, u) \), where \( u \) is called the anion positional parameter or simply the \( u \)-parameter. Depending on the ratio of the ionic radii of cations located at the A- and B-sites, \( r(A)/r(B) \), the \( u \)-parameter deviates from an ideal value of 0.250 [2]. The anions are arranged in ideal cubic closest packing at \( u = 0.250 \). At \( u = 0.250 \), the B-site is surrounded by a regular X$_6$-octahedron, but the X$_6$-octahedron...
distorted when \( u \neq 0.250 \). In figure 1(c), the displacement of anion from the regular octahedral site is indicated by a red arrow for \( u > 0.250 \). The X-anions around the A-site remain in a regular tetrahedron even when \( u \) differs from 0.250. The A-site forms a diamond lattice that consists of two face-centered cubic (fcc) interpenetrating lattices shifted along the \([111]\) direction. Interestingly, a fcc antiferromagnetic lattice shows magnetic frustration, whereas a diamond lattice is magnetically bipartite. Although a nearest-neighbor interaction \( J_1 \) stabilizes an antiferromagnetic (Néel) state, frustration effects can be anticipated in a diamond magnet if a next nearest-neighbor interaction, \( J_2 \), is introduced [3]. This condition therefore leads to a highly degenerated magnetic state and hence to a large reduction of the long-range magnetic ordering temperature, \( T_m \).
As depicted schematically in figure 2 (right-hand side), it is indicated by a Monte-Carlo simulation [3] that the Néel state is destabilized rapidly with increasing $J_2/J_1$ and transforms to a spin-spiral state at $J_2/J_1 = 1/8$. Remarkably, the magnetic transition temperature of the cobalt aluminate CoAl$_2$O$_4$, which is a partially inverted A-site spinel oxide, is strongly suppressed to $T_m = 8.5$ K compared with the Weiss temperature $\theta = -95$ K [4–7]. It is revealed by neutron diffraction measurements [8, 9] that the magnetic state of CoAl$_2$O$_4$ is characterized to be in the Néel state but in the vicinity of the phase boundary at $J_2/J_1 = 1/8$. The recent discovery that the $T_m$ for CoAl$_2$O$_4$ increases with increasing pressure with a pressure coefficient $(1/T_m)(dT_m/dP)$ equal to 0.044 GPa$^{-1}$ [7] suggests that $T_m$ (i.e., the degree of frustration for the A-site cobalt spinel system) can be controlled by application of pressure. Both physical pressure and chemical pressure can control the magnetic frustration parameter $J_2/J_1$ (figure 2). The manipulation of $J_2/J_1$ by chemical pressure was hypothesized and investigated by Melot et al in CoAl$_{2-x}$Ga$_x$O$_4$ [10]. Due to the large inversion induced by the Ga-substitution, chemical pressure effects on magnetism seem to be dominated by inversion effects. Actually, the Ga$^{3+}$ ion is preferentially distributed randomly into both the A- and B-sites. Consequently, as shown schematically in figure 2 (left-hand side), the antiferromagnetic transition temperature is rapidly suppressed, and the spin-glass (SG) state is stabilized in CoAl$_{2-x}$Ga$_x$O$_4$ when $0 < x \leq 2$. In figure 2, $\eta$ denotes the degree of inversion. There is considerable expansion of the volume at the same time because of the difference of ionic radii between Al$^{3+}$ and Ga$^{3+}$. Suppression of the inversion is thus essential for an investigation of pressure effects on magnetism in magnetically frustrated A-site spinel antiferromagnets.

In this study, we used magnetic and specific heat measurements to determine the chemical and physical pressure effects on the $T_m$ of inversion-free spinel oxides, Co$_3$O$_4$, CoRh$_2$O$_4$, and their solid solution Co$_{3-x}$Rh$_x$O$_4$ with $0 < x < 2$. In these spinel magnet, the apparent realization of a stable antiferromagnetic state below $T_m$ indicates that magnetism is weakly frustrated where is at $J_2/J_1 \ll 1/8$ and $\eta = 0$ in figure 2. On the one hand, the physical pressure coefficients of $T_m dT_m/dP$, for Co$_3$Rh$_2$O$_4$ and CoRh$_2$O$_4$ are positive and comparable to the previously obtained values 0.39 and 2.16 K/GPa for CoAl$_2$O$_4$ [7] and Co$_3$O$_4$ ($T_m = 30$ K) [11], respectively. On the other hand, the chemical pressure effects on $T_m$ are much smaller than the physical pressure effects. We used the crystallographic parameters obtained from a Rietveld analysis of x-ray diffraction (XRD) patterns measured in a synchrotron facility to examine the correlation between crystallographic and magnetic states together with previously reported pressure effects in Co$_3$O$_4$ [11–13], CoAl$_2$O$_4$ [7], and other magnetic spinel compounds that follow the so-called 10/3 law [14]. It is plausible that not only the unit cell volume and also the $u$-parameter have an effect on $T_m$ significantly for Co$_{3-x}$Rh$_x$O$_4$. It seems to be essential to figure out the discrepancy between the physical and chemical pressure effects that during volume contractions by applying physical and chemical pressures, the $u$-parameter changes oppositely [13].

2. Experimental

A solid–solid reaction method was used to synthesize Co$_{3-x}$Rh$_x$O$_4$ polycrystalline samples for $x = 0.25, 0.5, 1.0, 1.5, 1.75$ and $2.0$ with the proper amounts of CoO (4N) and Rh$_2$O$_3$ (2N). The mixed powder was calcinated at $1050$ °C in O$_2$-gas flow for 12 h and cooled to room temperature at a rate of $42.5$ °C h$^{-1}$. We made powder XRD
measurements with a synchrotron x-ray source and crystal structure refinements with Rietveld analysis software, RIETAN-PF\cite{15}. Powder XRD measurements using synchrotron radiation ($\lambda = 0.65296$ Å) were conducted for $x = 0.5, 1.0 1.5$ and 2.0 on the BL15XU beam line at SPring-8 (Harima, Japan)\cite{16}. We could not obtain a single phase for $x = 0.25$ which exhibits a phase separation with Rh-poor and Rh-rich spinel phases.

Magnetization and specific heat at ambient pressure were measured with a Magnetic Properties Measurement System (MPMS-XL; Quantum Design) and Physical Properties Measurement System (PPMS; Quantum Design), respectively. Under high pressure, the magnetic transition temperature was measured via ac-calorimetry\cite{17} using a piston-cylinder type cell with a hybrid cylinder consisting of BeCu (outer layer) and NiCrAl (inner layer) alloys. The pressure at the sample position was calibrated using a manganin manometer installed in the sample space with Daphne 7373 (Idemitsu) as the pressure-transmitting medium.

3. Results and discussion

Figure 3 shows XRD profiles for $x = 0.5, 1.0, 1.5, \text{ and } 2.0$ in $\text{Co}_3-x\text{Rh}_x\text{O}_4$. The profiles indicate a single-phase spinel structure without any impurity phases in whole composition for $0.5 \leq x \leq 2.0$. The lattice constant closely followed expectations for Vegard’s law (figure 4(a)) as the Co$^{3+}$ cations in Co$_3$O$_4$ were replaced by Rh$^{3+}$ ions. The $u$-parameter decreased linearly as a function of $x$. Table 1 lists the refined crystallographic parameters. The relative change of $u(x)$ between $x = 0$ and 2.0, $\Delta u/u = (u(2.0) - u(0))/u(0)$, was somewhat smaller than the corresponding change observed in $\text{CoAl}_2-x\text{Ga}_x\text{O}_4 (0 \leq x \leq 2.0)$\cite{10}. This difference in $\Delta u/u$ may have been due to differences in the patterns of the $x$-variations of inversion $\eta(x)$ between these pseudo ternary compounds. In $\text{Co}_{3-x}\text{Rh}_x\text{O}_4$, the cation distribution is represented by the chemical formula $(\text{Co}_{1-\eta}\text{Rh}_\eta)[\text{Co}_{2-x-\eta}\text{Rh}_\eta\text{O}_4]$ where parentheses, square brackets, and $\eta$ indicate the A-site occupations, B-site occupations, and inversion, respectively. Normal and inverse spinel structures correspond to $\eta = 0$ and 1, respectively. At ambient pressure, the cobalt oxide Co$_3$O$_4$ is a normal spinel, i.e., the cation distribution $(\text{Co}^{3+})[\text{Co}^{2+}_2\text{O}_4]$ is established with high-spin ($S = 3/2$) and low-spin ($S = 0$) states for the A- and B-occupied cobalt ions, respectively. The ternary spinel oxide CoRh$_2$O$_4$ ($x = 2.0$) also seems to be a normal spinel. In $(\text{Co}^{2+})[\text{Rh}^{3+}_2\text{O}_4]$, the Co$^{3+}$ is in a high-spin ($S = 3/2$) state, and the Rh$^{3+}$ is in a low-spin ($S = 0$) state\cite{18,19}. 

![Figure 3. Powder XRD patterns for Co$_{3-x}$Rh$_x$O$_4$ with x-ray wavelength $\lambda = 0.6530$ Å.](image-url)
Figure 4. (a) Lattice constant and \( \mu \)-parameter and (b) A- and B-site occupancies for Co and Rh ions as a function of \( x \). Solid lines are guides for visualization.

Table 1. Crystallographic parameters and reliability factor obtained by Rietveld refinement for Co\(_{3-x}\)Rh\(_x\)O\(_4\).

| \( x \) | \( a (\text{Å}) \) | \( \mu \) | \( g_A(\text{Co}) \) | \( g_A(\text{Rh}) \) | \( g_B(\text{Co}) \) | \( g_B(\text{Rh}) \) | \( R_{wp} \) | References |
|-------|-------------|-----|-------------|-------------|-------------|-------------|-------------|---------|-----------|
| 0     | 8.0832(1)   | 0.2656(5) | 1            | —           | 1           | —           | —           | [21]    |
| 0.5   | 8.18775(0)  | 0.26323(5) | 0.9991(9)    | 0.0009(9)   | 0.7504(5)   | 0.2496(5)   | 3.26        | this work |
| 1.0   | 8.28973(1)  | 0.26247(4) | 0.99557(8)   | 0.0043(8)   | 0.5021(4)   | 0.4979(4)   | 2.30        | this work |
| 1.5   | 8.38908(2)  | 0.26122(4) | 1.00(1)      | 0.00(1)     | 0.250(5)    | 0.750(5)    | 2.69        | this work |
| 2.0   | 8.50068(1)  | 0.26087(4) | 1.00(1)      | 0.00(1)     | 0.000(5)    | 1.000(5)    | 2.73        | this work |
| 2.0\( ^b \) | 8.503(1)   | 0.2601(1)  | 1.00(1)      | 0.00(1)     | 0.05(5)     | 1.000(5)    | —           | [19]    |

\( ^a \) Nominal composition.

\( ^b \) Note that composition \( x \) was determined to be 1.90 by the Rietveld refinement of neutron diffraction data.

Figure 4(b) shows the A- and B-site occupancies of Co ions (\( g_A(\text{Co}) \) and \( g_B(\text{Co}) \), respectively) and Rh ions (\( g_A(\text{Rh}) \) and \( g_B(\text{Rh}) \), respectively) as a function of \( x \). As expected, the inversion \( \eta \) corresponding to \( g_A(\text{Rh}) \) was less than 0.01 for \( 0 < x \leq 2.0 \). This inversion was much smaller than that of the boundary between the antiferromagnetic (AF) and SG phases (\( \eta_c \approx 0.08 \)) in CoAl\(_2\)O\(_4\) [6].

The cation distribution of \( \eta < \eta_c \) established in Co\(_{3-x}\)Rh\(_x\)O\(_4\) was reflected in the temperature dependence of the magnetic susceptibility \( \chi_{\text{mod}}(T) \), which is typical of antiferromagnetism (figure 5). In the paramagnetic temperature region, susceptibility closely follows a modified Curie-Weiss law \( \chi(T) = C/(T-\theta) + \chi_0 \), where \( C \), \( \theta \), and \( \chi_0 \) are the Curie constant, Weiss temperature, and temperature-independent component, respectively, although \( \chi(T) \) was not depicted at paramagnetic temperature region. The effective moments \( p_{\text{eff}} \) extracted from
increased in the vicinity of CoRh₂O₄ and d₀.39 K for the pressure coefficient and its magnetic state seems to be a Néel state in the vicinity of the phase boundary at
Hereafter, the temperature associated with these anomalies of d were comparable to the analogous coefficient of the magnetic transition temperature
values obtained by least-squares. For x = 2.0, these paramagnetic parameters were consistent with previously reported values [5, 19]. Values of the frustration factor, defined as f = −θ / T_N, were 3.5 [5], 2.1, and 1.2 for x = 0, 1.0, and 2.0, respectively. The temperature derivative of \( \chi_B / \chi \) exhibited a sharp anomaly (figure 6(a)) that has previously been reported [7, 20]. A lambda-type anomaly in the specific heat C(T), consistent with a 2nd-order magnetic phase transition, was apparent at x = 1.0 and 2.0 (figure 6(b)). The transition points apparent as the maximum value of d\( \chi_B / \chi \) and inflection point of C(T) corresponded well within an experimental error. Hereafter, the temperature associated with these anomalies of d\( \chi_B / \chi \) and C(T) are denoted as T_N. The transition temperature T_N(x) decreased with decreasing x, reached a shallow minimum at x ≈ 1.5, and increased in the vicinity of CoRh₂O₄ (figure 6(c)). The magnetic phase diagrams of Co₃₋ₓRhₓO₄ and Co[Al₁₋ₓCoₓ]₃O₄ (0 ≤ y ≤ 1) [21] were quite different. The composition-temperature (y-T) phase diagram for the latter system is complicated and has steep phase boundaries, whereas in the paramagnetic state the susceptibility \( \chi(T) = C / (T−θ) \) is nearly independent of y. In particular, the Curie constant C and Weiss temperature θ are nearly constant with respect to y.

Figures 7(a) and (b) show the temperature dependence of the ac-specific heat at various pressures for x = 1.0 and 2.0, respectively. In both samples, the transition point increases linearly with respect to pressure up to the maximum experimental pressure \( p = 2.6 \) GPa (figure 7(c)). The linear pressure coefficients d\( T_N / dp \) obtained by a least-squares fitting were 1.94 ± 0.09 and 2.05 ± 0.06 K/GPa for x = 1.0 and 2.0, respectively. These values were comparable to the analogous coefficient of 2.2 K/GPa for Co₁₃O₄ [11] and much larger than the value of 0.39 K/GPa for CoAl₂O₄ [7]. Table 2 lists T_N determined by specific heat and magnetization at ambient pressure and d\( T_N / dp \) with bulk modulus B₀ for Co₃₋ₓRhₓO₄ and related magnetic spinel compounds. The empirical law for the pressure coefficient of the magnetic transition temperature T_m has been called the ‘10/3 law’ and is expressed as d\( \ln T_m / \ln V = −10/3 \) or d\( T_m / dp = (10/3)κ T_m \) where T_m = T_N or T_C (Curie point for ferromagnets), and V and κ are the volume and compressibility, respectively [1, 14, 22, 23]. In transition metal chalcogenide and oxide spinel compounds, the pressure coefficient closely follows the 10/3 law [14, 22, 23]. The empirical law can be derived if one considers the kinetic part of the superexchange interaction \( J = AT^2 / U \) where A, t, and U are a constant, the transfer integral, and the correlation interaction, respectively. Note that t corresponds to a band width W, which is known to be proportional to \( V^{-2/3} \) [24]. In remarkable contrast, the A-site cobalt spinel compounds exhibit larger values of the logarithmic coefficient defined as \( \gamma_V = −(\ln T_m / \ln V) \) (figure 8(a) and (b)). In CoAl₂O₄, magnetic ordering is suppressed by magnetic frustration, and its magnetic state seems to be a Néel state in the vicinity of the phase boundary at \( J_s / J = 1/8 \). This situation causes the value of \( \gamma_V \) to be large for CoAl₂O₄. In contrast to the case of CoAl₂O₄, the magnetic state of
Co$_{3-x}$Rh$_x$O$_4$ is a rather stable Néel state far from the phase boundary at $J_2/J_1 = 1/8$ (see figure 2). However, the $\gamma_V$ is considerably larger for Co$_{3-x}$Rh$_x$O$_4$ than for CoAl$_2$O$_4$. Indeed, as shown in figure 8(c), $\gamma_V$ decreased monotonically with increasing $f$ for the A-site cobalt spinel oxides examined in this work. We need to stress a question that arises immediately: why is there a negative correlation between the logarithmic volume coefficient $\gamma_V$ and the frustration factor $f$ in A-site cobalt spinel magnets? To obtain some insight into the cause of this remarkable finding, we determined whether $T_N$ depended on not only the volume but also another crystallographic variable of a cubic spinel compound, the $u$-parameter.

From the discrepancy between the chemical and physical pressure effects on magnetism and crystallographic parameters, one can estimate the volume- and $u$-parameter contributions to $dT_N(p, x)/dp$ in Co$_{3-x}$Rh$_x$O$_4$ as...
It is apparent from Figure 8(b) that $\gamma V$ is rather smaller when it is determined via chemical pressure for $\text{Co}_3-x\text{Rh}_x\text{O}_4$ than via physical pressure for $\text{Co}_3\text{O}_4$, $\text{Co}_2\text{RhO}_4$, and $\text{CoRh}_2\text{O}_4$. From the initial slope of $T_N(x)$ at $x \leq 0.5$, we estimated $dT_N/dp$ to be $0.56$ K GPa$^{-1}$, which is much smaller than the value determined via physical pressure, $2.2$ K/GPa at $x = 0$ [11], but it is consistent with the value obtained from the empirical 10/3 law, $10T_N/3B_0 = 0.52$ K/GPa. Here we used $\kappa \approx 1/B_0$. To calculate the pressure coefficient, we used the bulk modulus $B_0 = 190$ GPa for the cubic spinel phase of $\text{Co}_3\text{O}_4$ [12]. As can be seen in figure 9(a), the $\kappa$-parameters

Figure 7. Temperature variation of ac-specific heat signal at various pressures for (a) $\text{CoRh}_2\text{O}_4$ and (b) $\text{Co}_2\text{RhO}_4$. (c) The $x$-dependence of the magnetic transition temperature for $\text{Co}_3-x\text{Rh}_x\text{O}_4$. Dashed lines represent the linear least-squares fits assuming the pressure dependence to be linear: $T_N(p) = T_N(0) + (dT_N/dp)p$. 

follows.
with the exception of CoAl$_2$O$_4$, the A-site spinel magnets examined in this work were characterized by spin (and $u$) generally move closer together toward the A-site cation along the $\langle 111 \rangle$ direction. Consequently, the B-site octahedral volume increases. In the case of Co$_{1-x}$Rh$_x$O$_4$, there is a decrease of $u$ with respect to $x$; while both the B-site octahedral volume ($V_{oct}$) and the A-site tetrahedral volume ($V_{tet}$) increase, the ratio $V_{oct}/V_{tet}$ increases (figure 8(b)).

In the case of the physical pressure–induced crystallographic variations of Co$_3$O$_4$, $u$ decreases only slightly with increasing pressure [12, 13]. For one of the end numbers, CoRh$_2$O$_4$, $u$ decreases to seem with increasing pressure, because one can estimate $\Delta \{V_{oct}(\text{Rh}^{3+})/V_{tet}(\text{Co}^{3+})\}/\Delta p \propto [1 - B_0(\text{CoO})/B_0(\text{Rh}_2\text{O}_3)] > 0$ where the bulk moduli at the A- and B-site polyhedrons are assumed to be $B_0(\text{Rh}_2\text{O}_3) = 233$ GPa [25] and $B_0(\text{CoO}) = 179$ GPa [26] for corundum–type rhodium sesquioxide $\alpha$-Rh$_2$O$_3$ and NaCl-type cobalt monoxide CoO, respectively. Actually, the magnetic interactions between the A-site spins $J_1$ and $J_2$ are mediated via bonding of $A(\text{Co}^{3+})$–O–B(\text{Co}^{3+} or Rh$^{3+}$)–O–A(\text{Co}^{3+})$. Because the bond angles $A$–O–B and $O$–B–$O$ are the coupling angles for $J_1$ and $J_2$, the interactions depend on $u$. Note that bond angles depend solely on $u$ [2]. It is plausible, therefore, that $T_N$ is a function of volume and the $u$ parameter, and the derivative of $T_N$ can therefore be expressed as

$$
\frac{dT_N}{T_N} = \left( \frac{\partial \ln T_N}{\partial \ln V} \right)_u \frac{dV}{V} + \left( \frac{\partial \ln T_N}{\partial u} \right)_V \frac{du}{u}
$$

for Co$_{1-x}$Rh$_x$O$_4$. We assume that the logarithmic volume and $u$-parameter coefficients $\alpha = -(\partial \ln T_N/\partial \ln V)_u$ and $\beta = -(\partial \ln T_N/\partial u)_V$ are constants with respect to $p$ and $x$ in the vicinity of $p = 0$ and $x = 0$ for Co$_{1-x}$Rh$_x$O$_4$.

We used previously reported values of $dT_N/\partial p$ (2.2 K GPa$^{-1}$), $dV/\partial p$ (–2.0 Å$^3$ GPa$^{-1}$), and $du/\partial p$ (–5.1 $\times$ 10$^{-5}$ GPa$^{-1}$) along with values of $dT_N/\partial x$ (–9.1 K), $dV/\partial x$ (41 Å$^3$), and $du/\partial x$ (–0.0024) obtained in this work to estimate the volume and $u$-parameter coefficients $\alpha = 9.8$ and $\beta = 70$, respectively, for Co$_3$O$_4$. See appendix to know how the value of $dT_N/\partial x$ was estimated for Co$_{1-x}$Rh$_x$O$_4$. On the assumption that $du/\partial p$ was independent of $x$ for Co$_{1-x}$Rh$_x$O$_4$, we also estimated $\alpha$ and $\beta$ at $x = 1.0$ and 2.0 (figure 10). The rapid increment of the ratio $\beta/\alpha$ at $x > 1.0$ was responsible for the nonmonotonic variation of $T_N(x)$, i.e., $T_N(x)$ reached a minimum at $x \approx 1.5$ and increased with increasing $x$ at $x \approx 2.0$. At $x = 1.5$, where $\beta/\alpha = 12$, there was a crossover from a volume-dominant to a $u$-parameter-dominant region. This simple analysis revealed that the discrepancy between the apparent volume dependences of $T_N$ under chemical and physical pressures and the nonmonotonic variations of $T_N$ with $x$ were due to $\beta$ having a value effectively comparable to that of $\alpha$ and the opposite tendency in the $x$- and $p$-variations of the $u$-parameter. The significant increase of $\beta$ with increasing $x$ apparent in Co$_{1-x}$Rh$_x$O$_4$ may be responsible for the negative correlation between $\gamma_V$ and $f = -\theta/T_N$ (figure 8(c)), whereas $\alpha(x)$ is nearly constant.

In CoAl$_2$O$_4$, magnetic frustration can be the dominant factor that suppresses the magnetic long-range order. With the exception of CoAl$_2$O$_4$, the A-site spinel magnets examined in this work were characterized by spin states that exhibited an antiferromagnetic order below $T_N$ and relatively weak frustration scaled by frustration factors $f$ that equal 3.5 and 1.2 for $x = 0$ and 2.0 [5, 19], respectively. Thermomagnetic and neutron diffraction measurements [19] revealed that CoRh$_2$O$_4$ was a canonical, nonfrustrated antiferromagnet with $J_1 = 0.62$ meV. In Co$_3$O$_4$, Ikedo et al [27] have found that incommensurate antiferromagnetic ordering develops below $T_N$ ~ 30 K and have pointed out that spin and/or charge fluctuation of Co$^{3+}$ at the B-site may be responsible for the inhomogeneous spin structure. We could not detect any macroscopic signals for the examined samples which suggest magnetic transformation from the incommensurate to the Néel states. It is therefore still unclear whether the magnetically ordered spin state in Co$_3$O$_4$ is a stable Néel state and far from the phase boundary at

### Table 2. Magnetic transition temperature at ambient pressure ($T_N$) defined as the inflection point in $G\langle T \rangle$ and the peak temperature in $dG\langle T \rangle/dT$, its pressure coefficient ($dT_N/\partial p$), and bulk modulus ($B_0$) for the A-site spinel compounds.

| $x$  | $T_N(C)$ (K) | $V_{oct}(\partial V/\partial T)$ (K) | $dV/\partial p$ (K GPa$^{-1}$) | $B_0$ (GPa) | References |
|------|--------------|-------------------------------------|-------------------------------|------------|------------|
| 0    | 30.4$^a$     | 29.5(3)                            | 2.16                          | 190 [12]   | [11, 27]   |
| 0.5  | 25.5(5)      | —                                   | —                             | 190$^b$    | this work  |
| 1.0  | 24.0(5)      | 1.94                                | (190)$^b$                     | this work  |
| 1.5  | 23.5(3)      | —                                   | —                             | this work  |
| 1.75 | 24.0(2)      | —                                   | —                             | this work  |
| 2.0  | 25.0(3)      | 2.05                                | (190)$^b$                     | this work  |
| CoAl$_2$O$_4$ | 8.5(4)       | 9.0(2)                             | 0.39                          | 197$^c$    | [7]        |

$^a$ Determined by $\mu$-SR measurement [11].

$^b$ The value of bulk modulus in parentheses was assumed.

$^c$ From reference [30].
\( J_2 / J_1 = 1/8 \). Nevertheless, it is worth noting again that the nearest neighbor and next nearest neighbor interactions can depend on not only \( V \) but also \( u \). In other words, the bond lengths and the bond angles in the
Figure 9. (a) Lattice constant as a function of \( u \)-parameter for \( \text{Co}_{3-x}\text{Rh}_x\text{O}_4 \) and \( \text{Co}_3\text{O}_4 \) at ambient pressure \([12]\) and under high pressure \([13]\). (b) The \( u \)-parameter dependences of the volume ratios for the tetrahedron \( \text{AO}_4 \) and the octahedron \( \text{BO}_6 \) with respect to volume of the unit cell \( V = a^3 \).

Figure 10. \( x \)-variations of logarithmic volume and \( u \)-parameter coefficients of \( T_N \) for \( \text{Co}_{3-x}\text{Rh}_x\text{O}_4 \) estimated by assuming \( T_N = T_N(V, \alpha) \) to be a function both of \( V \) and \( \alpha \) and \( du/dV = \text{constant with respect to } x \).
respective A–O–B–O–A bonds connecting magnetic sites in the inter and intra fcc sublattice are a function of V and u. Further investigation is needed to confirm whether the spin system approaches the phase boundary and exhibits a magnetic phase transition from Néel to spin-spiral states [3] in CoAl2O4 under negative chemical pressure, although the chemical and physical pressure effects on Jz/J1 in A-site spinel compounds are not necessarily similar. Probably, CoAl2−xRhxO4 seems to be appropriate system because Rh3+ cation occupies preferably in the B-site [6].

It can be speculated that the disorder caused by random occupation of the cations into the B-site (denoted as the B-site disorder) results in crystallographic local distortions, and, consequently, distributions of bond lengths and angles can be anticipated to realize in the range 0 < x < 2.0 except the end numbers of x = 0 and 2.0. Indeed, the quadratic approximation of T_{N}(x) obtained in appendix can be expressed as

\[ T_{N}(x) = T_{N}(0) + (K_{2} + 2K_{3})x - K_{4}x^{2}, \]

where \( K_{4} = x(2-x) \) is a measure of the B-site disorder (figure 6(c)). It is naively interpreted that the second linear the third quadratic terms with respect to x are related to the volume and disorder effects, respectively. Consequently, the distributions of magnetic interactions between Co2+ ions due to the B-site disorder are possibly detected as broadenings and/or smearing out of the transition anomalies in specific heat and magnetic susceptibility. Expectedly, the distribution of the magnetic transition is detected by a sharpness of thermodynamic anomaly at the transition as a concave feature with respect to x. As can be seen in figures 6(a) and (b), any broadenings of the transition anomalies in specific heat and susceptibility are not obviously observed. Also, the transition peak height of d \( \chi / dT \), which can be a measure of the degree of the special distribution of T_{N}, increases monotonically with increasing x (figure 6(a)). That is, the disorder effect on the transition at T_{N} is not detected macroscopically. Nevertheless, it cannot be ruled out completely that the concave feature of T_{N}(x) is related to the B-site disorder.

Finally, let us comment on the fact that the pressure coefficients for the A-site cobalt spinel compounds were larger than predicted by the 10/3 law adhered to empirically in other spinel magnets. A plausible scenario is that charge transformation (charge and spin redistribution) is induced by application of pressure prior to the valence transition in CoAl2O4 that occurs at a \( p_{c} \) of ~17 GPa [13]. At the critical pressure, the charge configuration changes from the normal spinel (Co3+)\([Co^{3+}Co^{3+}]\)O4 to the inverse spinel (Co3+)\([Co^{3+}Co^{3+}]\)O4. The u-parameter signals the charge reconfiguration as relatively large decrement (figure 9(a)) and, consequently, increment of the local polyhedral volume ratio \( V_{oct}/V_{tet} \) (figure 9(b)). Based on the fact that the ambient pressure states were confirmed to be the high spin (S = 3/2) and low spin (S = 0) states at the A- and B-sites, respectively, one can deduce that the magnetic state at \( p > p_{c} \) was S = 2 for the A-site and S = 1/2 (Co3+) and 0 (Co3+) for the B-site [13]. It is still unclear whether the high-pressure phase is maintained in the cubic spinel structure in the same way that the ambient pressure phase is maintained in Co3O4 [12, 13]. It is therefore worthwhile to ask whether Co3−xRhxO4 is also likely to exhibit a pressure-induced valence and/or structural transition that is probably coupled with spin and orbital degrees of freedom. When CoRh2O4 is in the u-dominant region, drastic structural and/or electronic state changes are expected to occur because of the strong trivalent preference for the Rh ion in the octahedral coordination. Those changes might include reduction of the coordination number at the Rh-site and insulator–metal transition. The inverse spinel compound MnCo2O4 is one of the exceptional examples that shows a negative pressure derivative dlnT_{C}/dp = −0.0187(3) GPa−1 [28]. It should be noted that because MnCo2O4 has the same ionic configuration with the high-pressure inverse spinel phase of CoO4, charge transfer between the A- and B-site cations might occur even at ambient pressure, a phenomenon that has been observed in the inverse spinel Co3O4 under high pressure [12, 13]. This situation is similar to the negative chemical pressure effect in Co3−xRhxO4 at \( x \approx 2.0 \) (figure 6(c)).

In summary, we investigated the chemical and physical pressure dependence of the antiferromagnetic transition temperature T_{N} for the weakly frustrated A-site spinel compounds Co3−xRhxO4 (0 < x < 2.0). The crystallographic parameters and cation configuration were determined precisely by the Rietveld refinement of XRD profiles measured using a synchrotron x-ray diffractometer. The samples for 0 < x < 2.0 were confirmed to be normal spinels, that is, the inversion (the A-site occupant of Rh ion) was negligibly small. The physical pressure coefficient of T_{N} was positive and considerably larger than the empirical value for magnetic chalcogenides predicted from the 10/3 law, while T_{N}(x) varied nonmonotonically under chemical pressure. This difference may have been due to the logarithmic coefficients being larger with respect to the u-parameter than with respect to volume. Application of physical and chemical pressures in these experiments have produced results that have enhanced the basic knowledge needed to understand magnetism and manipulation of the magnetic state in strongly frustrated antiferromagnetic A-site spinel compounds such as CoAl2O4.

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Appendix

Estimation of $dT_N/dx$

Plausibly, the $x$-variation of $T_N$ for Co$_3$-Rh$_x$O$_4$ shows a parabolic with respect to $x$. Figure 6(c) shows that the result of least squares method reproduces the $T_N(x)$ curve quite sufficiently within the experimental error and gives fitting parameters $K_0 = 29.4(2)$, $K_1 = -9.1(4)$ and $K_2 = 3.4(2)$ for a quadratic function $T_N(x) = K_0 + K_1x + K_2x^2$. From the obtained parabolic function, we estimated the value of $dT_N/dx$ in the range of $0 \leq x \leq 2.0$ as a function of $x$.

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