

Thermal study of the interplay between spin and lattice in CoCr_2O_4 and CdCr_2O_4

Suguru Kitani,¹ Makoto Tachibana,² Naoya Taira,¹ and Hitoshi Kawaji¹

¹*Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan*

²*National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan*

(Received 13 March 2012; published 4 February 2013)

The interplay between spin and lattice degrees of freedom in the spinels CoCr_2O_4 and CdCr_2O_4 has been investigated by heat capacity and thermal expansion measurements. In CoCr_2O_4 , sharp anomalies are observed at the magnetic phase transition temperatures of 13, 26, and 93 K. A large pressure dependence of the transition temperature at 13 K, which is calculated from the heat capacity and thermal expansion, indicates strong spin-lattice coupling in the incommensurate phase. This result provides the possibility of the reduction of lattice symmetry from cubic at the phase transition. In CdCr_2O_4 , negative thermal expansion due to spin-lattice coupling emerges in temperature from 140 to 45 K, which is followed by strong positive thermal expansion at lower temperature. The magnetostructural transition at 7.8 K is observed as a large anomaly with an indication for a large pressure dependence of the transition temperature. The unusual thermal expansion suggests the importance of other perturbations besides exchange interactions between Cr ions for the formation of the spin clusters. Our results demonstrate that thermal measurements can help to further understand the frustrated systems with strong spin-lattice coupling.

DOI: [10.1103/PhysRevB.87.064402](https://doi.org/10.1103/PhysRevB.87.064402)

PACS number(s): 75.47.Lx, 75.40.Cx, 65.40.De, 75.80.+q

I. INTRODUCTION

Frustrated systems have been intensively studied because of the presence of various kinds of novel physical properties. A strong competition between magnetic exchange interactions leads to a macroscopically degenerated ground state, which may result in a spin-liquid state down to the lowest temperature.^{1,2} However, a weak perturbation can lift the macroscopic degeneracy with relieving the frustration, and consequently some kind of ordered state is generally formed in the ground state. In relieving the frustration, the interplay between spin and lattice degrees of freedom, i.e., spin-lattice coupling, plays an important role in systems without orbital degrees of freedom. A typical example is known as a spin-driven Jahn-Teller effect,^{3,4} which reduces the frustration by distorting the lattice. In addition, the spin-lattice coupling often induces unusual dielectric properties such as a magnetocapacitance effect.⁵

Magnetic spinels with the general formula AB_2X_4 often show exotic physical properties, for example, molecular spin excitations,⁶ spin-orbital liquid,⁷ and heavy-fermion behavior.⁸ In this study we focus on the cubic spinel oxides CoCr_2O_4 and CdCr_2O_4 without the orbital degrees of freedom, in which the tetrahedral A site is occupied by the magnetic ion Co^{2+} ($e^4 t_2^3$) or nonmagnetic ion Cd^{2+} ($e^4 t_2^6$), and the octahedral B site by the magnetic ion Cr^{3+} ($t_{2g}^3 e_g^0$). The dominant exchange interaction is an antiferromagnetic nearest neighbor interaction between Cr^{3+} ions due to the direct overlap of t_{2g} orbitals. Additional nearest neighbor interactions between Co^{2+} ions, and between Co^{2+} and Cr^{3+} ions, are also important in CoCr_2O_4 . For these compounds we do not need to deal with complex problems of the orbital degrees of freedom, and characteristic features on thermal properties of CoCr_2O_4 and CdCr_2O_4 should be correlated with the distinct effects of the spin-lattice coupling.

CoCr_2O_4 is known as a multiferroic material with spontaneous magnetization and magnetically induced ferroelectricity in a conical spin state.⁹ Already in 1962, the ground-state spin

structure of spinels was theoretically analyzed by Lyons *et al.* using the Heisenberg model with the two exchange interactions J_{AB} and J_{BB} .¹⁰ According to the theory, any magnetic ground state of CoCr_2O_4 should be unstable^{11,12} due to the strong competition between J_{AB} and J_{BB} . Indeed, a complex sequence of magnetic transitions is observed.⁹ A ferrimagnetic transition from the paramagnetic state occurs at $T_C = 93$ K. With further decrease in temperature, a conical spin state with an incommensurate wave vector $\mathbf{Q} \sim (0.63, 0.63, 0)$ is formed at $T_S = 26$ K, which is accompanied by spontaneous electric polarization. Finally, a lock-in transition occurs at $T_L \sim 13$ K with a slight change in \mathbf{Q} . The magnetically induced ferroelectricity below T_S can be explained by the inverse Dzyaloshinskii-Moriya¹³ or spin-current,¹⁴ where a spiral spin configuration induces an electric polarization. However, considerably different behaviors have been reported for the conical spin state.^{11,12,15–17}

CdCr_2O_4 is a strongly frustrated Heisenberg antiferromagnet due to the geometric frustration of the corner-sharing tetrahedral network of Cr^{3+} ions. Because of the strong frustration, the paramagnetic phase remains well below the Curie-Weiss temperature $|\Theta_{CW}| = 70$ K. In addition, a spin-liquid-like state with the low-energy excitations of antiferromagnetic hexagonal spin cluster has been observed in the paramagnetic phase.¹⁸ At $T_N = 7.8$ K, CdCr_2O_4 undergoes a magnetostructural transition from a cubic paramagnetic phase to a tetragonal antiferromagnetic phase, which is elongated in the c axis to relieve the frustration. Neutron scattering studies^{18,19} reveal that the magnetic structure of the antiferromagnetic state has an incommensurate wave vector $\mathbf{Q} \sim (0, 0.09, 1)$. This long-range spiral ordering has been attributed to weak Dzyaloshinskii-Moriya interactions.²⁰ Furthermore, distinctive infrared spectra have been observed in which a phonon mode corresponding to the modulation of the Cr-Cr distance shows softening below 130 K and splitting at T_N .^{21–23} These phonon behaviors were explained as a result of the spin-lattice coupling.

In the present study we studied the interplay between spin and lattice degrees of freedom in CoCr_2O_4 and CdCr_2O_4 using heat capacity and thermal expansion measurements. Considering the strong spin-lattice coupling in these compounds, detailed thermal expansion data provide not only insights into lattice properties but also deeper understanding of spin properties. However, both compounds have been investigated extensively through x-ray and neutron scattering experiments, and detailed thermal expansion data have not been reported. For these compounds, the thermal measurements will be especially valuable in clarifying the following points: (1) For CoCr_2O_4 , the degree of distortion of the lattice through the conical spin transition and lock-in transition. (2) For CdCr_2O_4 , the behavior of the lattice in the paramagnetic phase, and how the lattice changes through the magnetostructural transition.

II. EXPERIMENT

Single crystals of CoCr_2O_4 were grown by a chemical vapor transport technique with CrCl_3 as the transport agent. Single crystals of CdCr_2O_4 were synthesized by a flux method using PbO as the flux.²⁴ To estimate the lattice heat capacity of CdCr_2O_4 , single crystals of ZnGa_2O_4 were also prepared by a flux method using PbO and B_2O_3 as the flux.²⁵ We verified by the magnetization measurements that the phase transition temperatures of CoCr_2O_4 and CdCr_2O_4 are in good agreement with the previous reports.^{9,22}

Heat capacity was measured by the relaxation technique using a Quantum Design physical property measurement system (PPMS) for the temperature range from 2 to 300 K. In each measurement, the temperature rise ΔT was 2% of the base temperature for the range from 2 to 50 K, 3% for the range from 50 to 150 K, and 3 K above 150 K. For evaluating the critical exponent α of the conical spin transition in CoCr_2O_4 , the temperature rise $\Delta T = 0.05$ K was used to measure the heat capacity around the phase transition temperature.

Thermal expansion measurements were carried out with a capacitance dilatometer constructed from silver.^{26–28} The measurements were performed on the same samples used in the heat capacity measurements with the direction along the cubic $\langle 111 \rangle$ and the length of 1.05 and 1.10 mm for CoCr_2O_4 and CdCr_2O_4 , respectively. Thermal expansivity data $\Delta L/L_0$ ($\Delta L = L - L_0$; L_0 refers to the value at 293 K) were taken on heating direction with a rate of 1 K/min between 2 and 300 K. The thermal expansion coefficient $\alpha = L_0^{-1}(d\Delta L/dT)$ was obtained by smoothing the $\Delta L/L_0$ data with a Savitzky-Golay filter²⁹ and then differentiating. The results were compared with those of point-by-point differentiation, and we confirmed that the sharp features of the transitions were fully retained through the smoothing. The accuracy of the heat capacity and thermal expansion coefficient is estimated from measurements on a copper reference sample, and it is better than 1%.

III. RESULTS AND DISCUSSION

A. CoCr_2O_4

The heat capacity C_p of CoCr_2O_4 is presented in Fig. 1, which shows good agreement with the results of previous studies.⁹ The ferrimagnetic transition at $T_C = 93$ K is found as a λ -like peak. The most striking feature is a very sharp peak

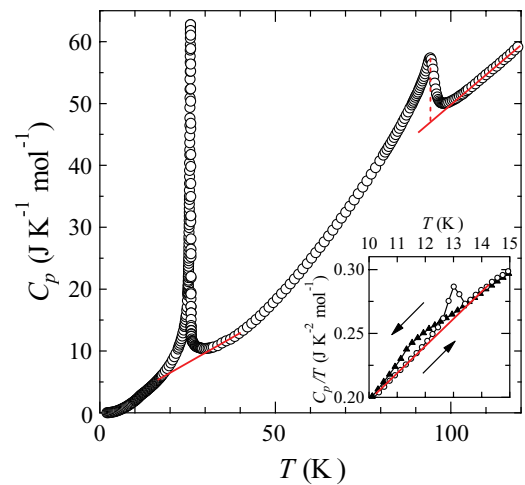


FIG. 1. (Color online) Heat capacity C_p of CoCr_2O_4 . The inset shows C_p/T of the vicinity of the lock-in transition $T_L = 13$ K. The red lines are used to obtain the jumps and the excess contributions in C_p .

at $T_S = 26$ K due to a transition to the conical spin state.^{9,17} The extremely sharp peak may indicate the first-order nature of this transition. The lock-in transition at $T_L \sim 13$ K shows a small change in C_p , and there is a thermal hysteresis as seen in the inset of Fig. 1, suggesting a first-order transition. It should be noted that there is a possibility of the underestimation of the latent heat for a first-order transition by the relaxation method. To exclude the possibility, we carried out heat capacity measurements with different thermal pulses. In each measurement there is no anomaly in the relaxation curve. The obtained heat capacity data shows little difference except for the peak temperature and heat capacity values just around the transition temperature at T_S and T_L . The transition entropies estimated from these data are the same within 10%.

It is interesting that thermal hysteresis could not be observed for the conical spin transition at T_S . In addition, we found second-order characteristics in the thermal expansion measurements discussed later, as the other experiments show a second-order-like change at the conical spin transition.^{9,16} If the conical spin transition is actually a second-order transition, the critical behavior of the heat capacity near the transition can be written by the commonly used function $C^\pm = (A^\pm/\alpha)|t|^{-\alpha} + B + Et$, where $t = (T - T_S)/T_S$ is the reduced temperature and the superscript + (–) corresponds to $t > 0$ ($t < 0$). However, any fitting parameters could not describe the critical behavior using the same critical exponent α for $t > 0$ and $t < 0$, because of the sharp rise on the high temperature side $t > 0$. Without the consideration of the regular contribution $B + Et$, the least-square fit between $3 \times 10^{-3} < |t| < 8 \times 10^{-3}$ leads to the critical exponents $\alpha^+ = 1.23$ and $\alpha^- = 0.57$. These critical exponents are extremely larger than the conventional universality classes having $\alpha = -0.133$ or -0.015 for standard XY or Heisenberg models.³⁰ It is known that the system having the chiral degrees of freedom shows relatively large critical exponents $\alpha = 0.34$ and 0.24 for the chiral XY and Heisenberg universality classes,³¹ though these values are also much smaller than the present results. A extremely large value was reported for

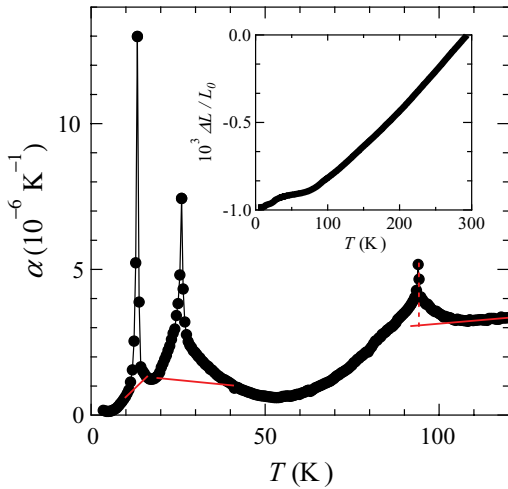


FIG. 2. (Color online) Thermal expansion coefficient α of CoCr_2O_4 below 120 K. The lines are the baselines used to obtain the jumps and the excess contributions in α . The inset shows the linear thermal expansivity $\Delta L/L_0$ in the entire region.

$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ showing $\alpha = 0.93$,³² which is characterized by a strong charge-lattice-spin coupling. It may suggest the possibility that in CoCr_2O_4 spin degrees of freedom couple to not only lattice but other degrees of freedom.

Figure 2 shows the thermal expansion coefficient α of CoCr_2O_4 , which is obtained from the high-resolution linear thermal expansivity $\Delta L/L_0$ data shown in the inset. At T_C , α shows a λ -like peak as in C_p . The λ shape of the peak is due to short-range fluctuations, which is typical for a second-order transition. With further decrease in temperature, an upturn begins below 50 K, and large peaks are found at T_S and T_L . In contrast to the results of C_p , the lock-in transition at T_L exhibits a large peak representing significant lattice distortion.

The upturn below 50 K is considered to be related to the development of spiral short-range order observed in inelastic neutron scattering experiments.¹² The spiral short-range order characterizes the conical spin structure below 26 K, which suggests that the growth of the short-range order should relate to the conical spin transition at 26 K. The spiral short-range order apparently grows below 50 K. Accordingly, some sign of the conical spin transition could appear up to 50 K. Indeed, Lawes *et al.* reported anomalous dielectric behavior around 50 K,³³ which was attributed to the development of the spiral short-range order. That is because dielectric properties could be affected by the spiral spin structure breaking spatial inversion symmetry. The spiral spin structure also induces with strong spin-lattice coupling through inverse Dzyaloshinsky-Moriya interaction. Thus, it is natural to consider that the upturn of the thermal expansion coefficient below 50 K correlates to the development of the spiral short-range order. This indicates that the effects of the conical spin transition is over a wide temperature range. Furthermore, the shape of the transition peak seems to be a second-order transition rather than a first-order transition.

The pressure dependence of each transition temperature in CoCr_2O_4 was calculated using the baselines shown in Figs. 1 and 2. For the second-order ferrimagnetic transition at T_C , the pressure dependence of the transition temperature dT_C/dp

can be evaluated from the Ehrenfest relation $dT_C/dp = \Delta\beta V_m T_C / \Delta C_p$, where $V_m = 4.4 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ is the molar volume,³⁴ $\Delta\beta = 3\Delta\alpha$ is the jump in volume thermal expansion coefficient at T_C , and ΔC_p is the jump in C_p at T_C . The result $dT_C/dp = 2.6 \text{ K/GPa}$, estimated from $\Delta C_p = 10.5 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta\alpha = 2.2 \times 10^{-6} \text{ K}^{-1}$, is in good agreement with 2.5 K/GPa obtained from the magnetic induction method measured between 0 and 1.15 GPa.³⁵

For the transition to the conical spin state at T_S , dT_S/dp can be calculated from the Clausius-Clapeyron relation $dT_S/dp = \Delta V / \Delta S$ with assuming the first-order transition, where ΔV and ΔS denote the change in volume and entropy at the transition. We obtain $\Delta V = 3.1 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ and $\Delta S = 5.0 \text{ J K}^{-1} \text{ mol}^{-1}$ from the integration of the anomalies $\Delta V = V_m \int 3\Delta\alpha(T) dT$ and $\Delta S = \int [\Delta C_p(T) / T] dT$, which results in $dT_S/dp = 0.62 \text{ K/GPa}$. The baselines for the transition at T_S are estimated by drawing a line between 18 and 40 K, considered as clearly appearing as the effect of the transition on C_p and α data, which is a method generally used for estimating a baseline of a first-order transition. Although the baselines for the transition at T_S seem a little arbitrary, the validity can be supported from the following reasons. Below 40 K, the correlation length of the short-range order apparently increases with decreasing error bar.¹² In addition, the minimum value in C_p/T is approximately 40 K. On the other hand, the correlation length below the conical spin transition temperature 26 K increases with decreasing temperature, and almost saturates at about 15 K. Moreover, the α data between $T_L < T < T_S$ show a minimum value at 18 K. In the case of the second-order transition, the dT_S/dp can be evaluated from the Ehrenfest relation. Taking the same baseline in the case of the first order, we obtained $\Delta C_p = 52.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta\alpha = 6.31 \times 10^{-6} \text{ K}^{-1}$, which leads to $dT_S/dp = 0.40 \text{ K/GPa}$. Both values are quantitatively equivalent with each other obtained by assuming first order and second order.

For the first-order lock-in transition at T_L , dT_L/dp was calculated to be $dT_L/dp = 80 \text{ K/GPa}$ using the Clausius-Clapeyron relation with $\Delta V = 1.3 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ and $\Delta S = 1.7 \times 10^{-2} \text{ J K}^{-1} \text{ mol}^{-1}$. There is no published data for the pressure dependence of T_S and T_L .

The positive values for all of the pressure dependence of the transition temperature in CoCr_2O_4 indicate that low-temperature phases prefer a smaller volume. The small values of dT_C/dp and dT_S/dp indicate a weak influence of volume change to the phase stability. On the other hand, the large value of dT_L/dp implies that the incommensurate (IC) phase between $T_L < T < T_S$ is highly sensitive for pressure. Thus, a small difference in atomic distances due to a slightly different sample quality may be the origin of confusion in reports such as various spin structures below T_S ^{11,12,15-17} and the different behavior of the multiferroic property at the lock-in transition.^{9,17} Interestingly, T_L is hardly varied by applying magnetic field,³⁴ i.e., small dT_L/dH . The combination of two Clausius-Clapeyron relations with large dT_L/dp and small dT_L/dH leads to a large value of $\Delta V / \Delta M$ at the lock-in transition.

An IC phase is often found in systems with strong competition between exchange interactions as seen in CoCr_2O_4 .^{11,12,15-17} An IC phase due to strong magnetic com-

petition is also observed in multiferroic compounds RMn_2O_5 ($R = \text{Ho, Dy, Tb}$)³⁶ and $MnWO_4$,³⁷ which have strong spin-lattice coupling. With decreasing temperature from the IC phase, a lock-in transition is generally found. In RMn_2O_5 and $MnWO_4$, the linear expansion anomalies at the lock-in transition are highly anisotropic^{36,37}; the axis with the change of a magnetic modulation shows a large expansion anomaly, and the other axis shows a relatively small expansion anomaly. These behaviors have been attributed to the strong spin-lattice coupling. From this point of view, the thermal expansion at the lock-in transition in CoCr_2O_4 should correspond to the magnetic modulation characterized by a wave vector $\mathbf{Q} \sim (q, q, 0)$ ⁹ since the large value of dT_L/dp indicates that the spin couples considerably to the lattice. However, CoCr_2O_4 is believed to remain cubic in its ground state.^{9,16,38} Our result may imply the possibility of the reduction of lattice symmetry from cubic at the lock-in transition. This idea is supported by the observation of a small signature of mode splittings in the infrared spectra.³⁸

B. CdCr_2O_4

The C_p of CdCr_2O_4 is presented in Fig. 3, which shows a very sharp peak due to the magnetostructural transition at $T_N = 7.8$ K. The result agrees with the previous experiments,²² except for a sharper peak. The dashed line in Fig. 3 denotes the estimated lattice heat capacity. We determined the lattice heat capacity from the C_p of ZnGa_2O_4 with its temperature axis scaled by 1.075 to overlap with the C_p of CdCr_2O_4 above 150 K. The calculated magnetic entropy of $24.0 \text{ J K}^{-1} \text{ mol}^{-1}$ is in good agreement with the theoretical value $2R \ln 4 = 23.1 \text{ J K}^{-1} \text{ mol}^{-1}$. The large contribution of the magnetic heat capacity above T_N shows that spin fluctuations exist up to approximately 150 K. Since the magnetostructural transition is first order, the relaxation method could underestimate the latent heat at the transition. We confirmed the validity of the present result by comparing the transition entropy with the result of the adiabatic method.³⁹

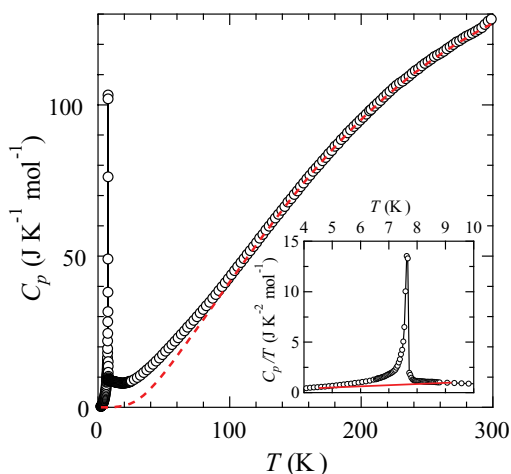


FIG. 3. (Color online) Heat capacity C_p of CdCr_2O_4 . The dashed line shows the lattice heat capacity calculated by scaling C_p of ZnGa_2O_4 . The inset shows C_p/T in the vicinity of the magnetostructural transition at $T_N = 7.8$ K. The line is used to obtain the excess contribution.

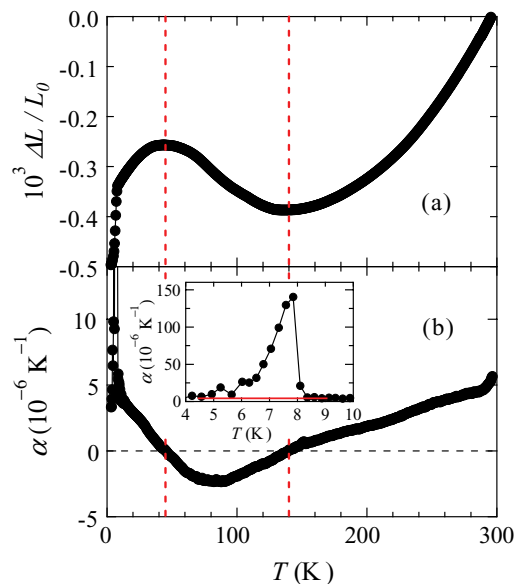


FIG. 4. (Color online) (a) The temperature dependence of the linear thermal expansivity $\Delta L/L_0$ of CdCr_2O_4 . Negative thermal expansion is seen in the temperature range from 140 to 45 K. (b) The thermal expansion coefficient α of CdCr_2O_4 . The inset in the lower frame shows α of the vicinity of the magnetostructural transition at $T_N = 7.8$ K, where the line is used to calculate the excess contribution.

Figures 4(a) and 4(b) show the $\Delta L/L_0$ and the α of CdCr_2O_4 , respectively. With decreasing temperature from room temperature, $\Delta L/L_0$ first decreases and then increases below 140 K, which results in a broad minimum around 140 K. Such behavior, called negative thermal expansion (NTE), is occasionally observed in frustrated materials.^{28,40} With further decreasing temperature, positive thermal expansion returns at 45 K. At T_N we can see a large jump in $\Delta L/L_0$ and an extremely sharp peak in α showing a large lattice distortion.

Before discussing the peculiar thermal expansion behavior, we launch into the pressure dependence of the magnetostructural transition temperature dT_N/dp . The dT_N/dp is calculated from the Clausius-Clapeyron relation. Taking the baselines as shown in the insets of Figs. 3 and 4, we obtain $\Delta V = 2.2 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}$ and $\Delta S = 3.2 \text{ J K}^{-1} \text{ mol}^{-1}$, which lead to $dT_N/dp = 6.9 \text{ K/GPa}$. On the other hand, the result of the susceptibility measurements under pressure shows $dT_N/dp \sim 0.7 \text{ K/GPa}$,⁴¹ which is about a tenth of the present result.

The validity of our result is confirmed from the following discussion. ΔV can be also estimated from the change of the lattice constant. In the cubic phase at $10 \text{ K} > T_N$, the reported lattice constant is 8.58882 \AA .^{18,42} In the tetragonal phase at $6 \text{ K} < T_N$, no lattice constants have been reported, but Kim *et al.*⁴² have reported the nearest neighbor Cr-Cr distances of 3.034 and 3.040 \AA for the ab plane and along the c axis, respectively. Assuming that the fractional coordinates of atoms are scarcely changed across the transition,⁴³ ΔV is estimated to be $\sim 3 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}$, which is close to the our measurements ($\Delta V = 2.2 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}$). On the other hand, ΔS cannot be 10 times larger than the estimated value because of the limitation of the total entropy change for

the transition. These indicate that the discrepancy between the present result and that of Ref. 41 is intrinsic.

The dT_N/dp of CdCr_2O_4 derived from thermodynamic relations corresponds to the value at zero magnetic field and ambient pressure, in contrast the susceptibility measurements in Ref. 41 were carried out under 1 T and at high pressures. Indeed, a complex change of dT_N/dp depending on the magnetic field and pressure is observed in ZnCr_2O_4 ,⁴⁴ which has strong spin-lattice coupling and undergoes a similar magnetostructural transition as in CdCr_2O_4 . In particular, T_N of ZnCr_2O_4 is strongly affected by magnetic field at low pressures. The difference in T_N between ambient pressure and 0.35 GPa increases several times with increasing magnetic field from 0 to 1 T. Thus, a similar effect of the magnetic field on T_N is expected in CdCr_2O_4 at low pressures.

However, the magnetic field effect shows the opposite tendency between CdCr_2O_4 and ZnCr_2O_4 ; with increasing the magnetic field, the dT_N/dp of CdCr_2O_4 is reduced, while the dT_N/dp of ZnCr_2O_4 is increased. The difference may be related to the opposite tetragonal distortion of CdCr_2O_4 with the elongated c axis¹⁸ compared to ZnCr_2O_4 with the contracted c axis⁴⁵ at T_N . Further research on the detailed effects of the magnetic field and pressure could help to clarify the reason of the opposite tetragonal distortion.

Now we discuss the peculiar thermal expansion behavior. The onset temperature of the NTE coincides with the onset of the magnetic contribution in the C_p . Furthermore, the infrared spectra show softening of the phonon mode corresponding to the modulation of the Cr-Cr distance below the same temperature.²¹⁻²³ These behaviors have been attributed to the spin-lattice coupling,⁴⁶ and this is also supported by *ab initio* calculation.⁴⁷ Thus, the NTE in CdCr_2O_4 should be related to the spin-lattice coupling. However, positive thermal expansion returns at 45 K. This behavior is in contrast to NTE observed in other spinel compounds with strong spin-lattice coupling that continues down to the lowest temperature or at least down to the transition temperature.^{28,40} Moreover, this positive thermal expansion has large positive value of $\alpha \sim 4.5 \times 10^{-6} \text{ K}^{-1}$ at 10 K, which is close to the value of $\alpha \sim 5.0 \times 10^{-6} \text{ K}^{-1}$ at room temperature. It indicates that the NTE may be correlated with a unique property in CdCr_2O_4 . Thus, our results suggest that other perturbations should be taken into account for future theory of the formation mechanism of the spin cluster.

For CdCr_2O_4 , the formation of antiferromagnetic hexagonal Cr cluster has been reported.¹⁸ The growth of the hexagonal Cr clusters with decreasing temperature is expected

to enhance the antiferromagnetic interaction and contract the bond distance within the hexagonal Cr cluster, which would induce positive thermal expansion. Then, the results of the thermal expansion measurements can be interpreted as the effect of the hexagonal Cr cluster overwhelming the effect of the NTE below 45 K. This idea provides a key to clarifying the formation mechanism of the hexagonal Cr clusters. Since the phonon mode related to the NTE continues to soften below 45 K,²¹⁻²³ other perturbations may significantly affect the Cr ions in the hexagonal Cr cluster. Recently, Conlon and Chalker⁴⁸ have suggested that further neighbor interactions beside an antiferromagnetic nearest neighbor interaction are important for the formation of spin cluster. However, because the NTE expands the distance between the Cr ions, exchange interactions between the Cr ions may be weakened with the decrease in temperature. It indicates that other perturbations (e.g., quantum fluctuations) are also intimately deeply related to the formation of the hexagonal Cr clusters. Thus, this result suggests that other perturbations should be taken into account for future theory of the formation mechanism of the spin cluster.

IV. SUMMARY

We have investigated the interplay between spin and lattice degrees of freedom in CoCr_2O_4 and CdCr_2O_4 using thermal expansion and heat capacity measurements. The large pressure dependence of the lock-in transition in CoCr_2O_4 indicates that the spins are strongly coupled to the lattice in the incommensurate phase. Since the strong spin-lattice coupling can induce anisotropic expansion along the magnetic modulation vector, there may be lattice distortion below the lock-in transition. The unusual thermal expansion behavior in CdCr_2O_4 suggests that other perturbations besides exchange interactions between Cr ions are needed to form spin clusters. The derived pressure dependence of the magnetostructural transition temperature indicates that the magnetic field and pressure induce an opposite effect from ZnCr_2O_4 with similar properties to CdCr_2O_4 . These results demonstrate that thermal measurements are valuable for understanding the spin-lattice coupling in frustrated systems.

ACKNOWLEDGMENTS

The authors would like to thank K. Mizushima for useful discussions, and M. Rotter and H. Müller for advice on the thermal expansion measurements.

¹J. S. Gardner, S. R. Dunsiger, B. D. Gaulin, M. J. P. Gingras, J. E. Greedan, R. F. Kiefl, M. D. Lumsden, W. A. MacFarlane, N. P. Raju, J. E. Sonier, I. Swainson, and Z. Tun, *Phys. Rev. Lett.* **82**, 1012 (1999).

²M. Matsuda, M. Azuma, M. Tokunaga, Y. Shimakawa, and N. Kumada, *Phys. Rev. Lett.* **105**, 187201 (2010).

³Y. Yamashita and K. Ueda, *Phys. Rev. Lett.* **85**, 4960 (2000).

⁴O. Tchernyshyov, R. Moessner, and S. L. Sondhi, *Phys. Rev. Lett.* **88**, 067203 (2002).

⁵T. Kimura, S. Kawamoto, I. Yamada, M. Azuma, M. Takano, and Y. Tokura, *Phys. Rev. B* **67**, 180401(R) (2003).

⁶K. Tomiyasu, H. Suzuki, M. Toki, S. Itoh, M. Matsuura, N. Aso, and K. Yamada, *Phys. Rev. Lett.* **101**, 177401 (2008).

⁷V. Fritsch, J. Hemberger, N. Büttgen, E.-W. Scheidt, H.-A. K. von Nidda, A. Loidl, and V. Tsurkan, *Phys. Rev. Lett.* **92**, 116401 (2004).

- ⁸S. Kondo, D. C. Johnston, C. A. Swenson, F. Borsa, A. V. Mahajan, L. L. Miller, T. Gu, A. I. Goldman, M. B. Maple, D. A. Gajewski, E. J. Freeman, N. R. Dilley, R. P. Dickey, J. Merrin, K. Kojima, G. M. Luke, Y. J. Uemura, O. Chmaissem, and J. D. Jorgensen, *Phys. Rev. Lett.* **78**, 3729 (1997).
- ⁹Y. Yamasaki, S. Miyasaka, Y. Kaneko, J.-P. He, T. Arima, and Y. Tokura, *Phys. Rev. Lett.* **96**, 207204 (2006).
- ¹⁰D. H. Lyons, T. A. Kaplan, K. Dwight, and N. Menyuk, *Phys. Rev.* **126**, 540 (1962).
- ¹¹N. Menyuk, K. Dwight, and A. Wold, *J. Phys. (Paris)* **25**, 528 (1964).
- ¹²K. Tomiyasu, J. Fukunaga, and H. Suzuki, *Phys. Rev. B* **70**, 214434 (2004).
- ¹³I. A. Sergienko and E. Dagotto, *Phys. Rev. B* **73**, 094434 (2006).
- ¹⁴H. Katsura, N. Nagaosa, and A. V. Balatsky, *Phys. Rev. Lett.* **95**, 057205 (2005).
- ¹⁵S. Funahashi, Y. Morii, and H. R. Child, *J. Appl. Phys.* **61**, 4114 (1987).
- ¹⁶L. J. Chang, D. J. Huang, W.-H. Li, S.-W. Cheong, W. Ratcliff II, and J. W. Lynn, *J. Phys.: Condens. Matter* **21**, 456008 (2009).
- ¹⁷Y. J. Choi, J. Okamoto, D. J. Huang, K. S. Chao, C. T. C. H. J. Lin, M. van Veenendaal, T. A. Kaplan, and S.-W. Cheong, *Phys. Rev. Lett.* **102**, 067601 (2009).
- ¹⁸J.-H. Chung, M. Matsuda, S.-H. Lee, K. Kakurai, H. Ueda, T. J. Sato, H. Takagi, K.-P. Hong, and S. Park, *Phys. Rev. Lett.* **95**, 247204 (2005).
- ¹⁹M. Matsuda, M. Takeda, M. Nakamura, K. Kakurai, A. Oosawa, E. Lelièvre-Berna, J.-H. Chung, H. Ueda, H. Takagi, and S.-H. Lee, *Phys. Rev. B* **75**, 104415 (2007).
- ²⁰G.-W. Chern, C. J. Fennie, and O. Tchernyshyov, *Phys. Rev. B* **74**, 060405(R) (2006).
- ²¹R. V. Aguilar, A. B. Sushkov, Y. J. Choi, S.-W. Cheong, and H. D. Drew, *Phys. Rev. B* **77**, 092412 (2008).
- ²²C. Kant, J. Deisenhofer, T. Rudolf, F. Mayr, F. Schrettle, A. Loidl, V. Gnezdilov, D. Wulferding, P. Lemmens, and V. Tsurkan, *Phys. Rev. B* **80**, 214417 (2009).
- ²³T. Rudolf, C. Kant, F. Mayr, J. Hemberger, V. Tsurkan, and A. Loidl, *New J. Phys.* **9**, 76 (2007).
- ²⁴H. A. Dabkowska, *J. Cryst. Growth* **54**, 607 (1981).
- ²⁵Z. Yan and H. Takei, *J. Cryst. Growth* **171**, 131 (1997).
- ²⁶M. Rotter, H. Müller, E. Gratz, M. Doerr, and M. Loewenhaupt, *Rev. Sci. Instrum.* **69**, 2742 (1998).
- ²⁷M. Tachibana, N. Taira, H. Kawaji, and E. Takayama-Muromachi, *Phys. Rev. B* **82**, 054108 (2010).
- ²⁸M. Tachibana, N. Taira, and H. Kawaji, *Solid Stat. Commun.* **151**, 1776 (2011).
- ²⁹A. Savitzky and M. J. E. Golay, *Anal. Chem.* **36**, 1627 (1964).
- ³⁰A. Pelissetto and E. Vicari, *Phys. Rep.* **368**, 549 (2002).
- ³¹H. Kawamura, *J. Phys.: Condens. Matter* **10**, 4707 (1998).
- ³²J. A. Souza, Y.-K. Yu, J. J. Neumeier, H. Terashita, and R. F. Jardim, *Phys. Rev. Lett.* **94**, 207209 (2005).
- ³³G. Lawes, B. Melot, K. Page, C. Ederer, M. A. Hayward, T. Proffen, and R. Seshadri, *Phys. Rev. B* **74**, 024413 (2006).
- ³⁴N. Mufti, A. A. Nugroho, G. R. Blake, and T. T. M. Palstra, *J. Phys.: Condens. Matter.* **22**, 075902 (2010).
- ³⁵T. Kanomata, T. Tsuda, H. Yasui, and T. Kaneko, *Phys. Lett. A* **134**, 196 (1988).
- ³⁶C. R. dela Cruz, F. Yen, B. Lorenz, M. M. Gospodinov, C. W. Chu, W. Ratcliff, J. W. Lynn, S. Park, and S.-W. Cheong, *Phys. Rev. B* **73**, 100406(R) (2006).
- ³⁷R. P. Chaudhury, F. Yen, C. R. dela Cruz, B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, *Physica B* **403**, 1428 (2008).
- ³⁸S. Bordács, D. Varjas, I. Kézsmárki, G. Mihály, L. Baldassarre, A. Abouelsayed, C. A. Kuntscher, K. Ohgushi, and Y. Tokura, *Phys. Rev. Lett.* **103**, 077205 (2009).
- ³⁹K. Mizushima, H. Kawaji, and T. Atake (unpublished).
- ⁴⁰J. Hemberger, H.-A. K. von Nidda, V. Tsurkan, and A. Loidl, *Phys. Rev. Lett.* **98**, 147203 (2007).
- ⁴¹H. Ueda and Y. Ueda, *Phys. Rev. B* **77**, 224411 (2008).
- ⁴²J.-H. Kim, M. Matsuda, H. Ueda, Y. Ueda, J.-H. Chung, S. Tsutsui, A. Q. R. Baron, and S.-H. Lee, *J. Phys. Soc. Jpn.* **80**, 073603 (2011).
- ⁴³S.-H. Lee, H. Takagi, D. Louca, M. Matsuda, H. U. S. Ji, Y. Ueda, T. Katsufuji, J.-H. Chung, S. Park, S.-W. Cheong, and C. Broholm, *J. Phys. Soc. Jpn.* **79**, 011004 (2010).
- ⁴⁴Y. Jo, J.-G. Park, H. C. Kim, W. Ratcliff II, and S.-W. Cheong, *Phys. Rev. B* **72**, 184421 (2005).
- ⁴⁵S.-H. Lee, C. Broholm, T. H. Kim, W. Ratcliff II, and S.-W. Cheong, *Phys. Rev. Lett.* **84**, 3718 (2000).
- ⁴⁶A. B. Sushkov, O. Tchernyshyov, W. Ratcliff II, S. W. Cheong, and H. D. Drew, *Phys. Rev. Lett.* **94**, 137202 (2005).
- ⁴⁷C. J. Fennie and K. M. Rabe, *Phys. Rev. Lett.* **96**, 205505 (2006).
- ⁴⁸P. H. Conlon and J. T. Chalker, *Phys. Rev. B* **81**, 224413 (2010).