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Evolution of spin phonon coupling by substituting Cd for Zn in the frustrated spinel $ZnCr_2Se_4$

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Frustration makes a tremendous amount of degenerate ground states which provides no energy scale of its own. Any perturbation has to be considered strong and fascinating phenomena may be emergent upon relieving of frustration. Here, we report the evolution of spin phonon coupling in the frustrated spinel system $Zn_{1-x}Cd_xCr_2Se_4$ ($0 \leq x \leq 1$) from magnetization, specific heat and thermal conductivity. Our results give clear evidences that the spin-orientated structural transitions decay rapidly as x going from 0 to 0.4 while the correlations between spin and lattice degrees of freedom for $0.6 \leq x \leq 1$ become weak and can be explained in terms of the traditional magnetostriction effect. In addition, for $0 \leq x \leq 0.4$ thermal carriers reveal strong scattering from spin fluctuations in the vicinity of T_N owing to strong frustration, in stark contrast with those for $0.6 \leq x \leq 1$ where traditional phonon-like heat conduction behaviors are observed. Moreover, it is shown that a moderate applied magnetic field can drive readily the fluctuations-scattered thermal conductivity toward traditional phonon-like one as observed in $CdCr_2Se_4$, reaching about 30% for $x = 0.4$ at 25 K in 1 T. Such strong field-sensitive effects may introduce new promising functionalities for potential applications. [http://dx.doi.org/10.1063/1.4943762]

I. INTRODUCTION

The coupling between spin and lattice degrees of freedom plays an important role in the strongly correlated system. It has been attracting considerable interest not only from a fundamental view but also due to potential applications.[1,2] In particular, for highly frustrated chromium-based spinels with the formula ACr_2X_4 (where A = Zn, Cd, Hg and X = Se, S, O) it is an essential ingredient since the Cr^{3+} ions in an octahedral crystal field is Jahn–Teller inactive, which results in a quenching of the orbit and charge degrees of freedom. As a result, the coupling provides a possible path to lift the ground state degeneracy due to frustration.[3] In addition, many novel phenomena such as negative thermal expansion,[4] large magnetostriction effect,[4] spin Jahn-Teller instabilities[5] *et al*. can be observed in the context of spin-lattice coupling. The observations challenge our understanding of traditional magnetism but in addition offer new functionalities since the observed spin orderings always couple intimately with the associated distortions of the lattice.[6] For example, using the large magnetostriction effect in $ZnCr_2Se_4$, researchers has accomplished successfully controls of the superconductivity in $FeTe_{0.5}Se_{0.5}$.[7]

$ZnCr_2Se_4$ is an insulating complex antiferromagnet with $T_N = 21$ K.[8–10] At room temperature, it crystallizes in a cubic normal spinel structure with space group Fd-3m (No. 227). Zn^{2+} ions occupy

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the tetrahedral sites forming diamond sublattice and all of the Cr^{3+} ions take up the octahedral sites revealing the so-called pyrochlore lattice. Upon cooling, a cubic to tetragonal ($I4_1$ amd, No. 141) structural transition occurs at T_N. The magnetic order is dominated by the nearest neighbor Cr-Se-Cr ferromagnetic (FM) and more distant Cr-Se-A-Se-Cr or Cr-Se-Se-Cr antiferromagnetic (AFM) super-exchange interactions.[11] Although a large positive Curie-Weiss temperature Θ_{CW} (85 K) is unraveled,[12] the complex antiferromagnetic ground state appears far below Θ_{CW}. This suggests that a fierce competition between FM and AFM superexchanges exists upon cooling, making it a typical bond frustrated compound.[4,12] Interesting, a multiferroic behavior was observed based on the complex spin configurations below T_N.[13] Since the FM and AFM super-exchange interactions depend highly on the separation of the Cr^{3+} ions, Cd doping on the Zn site can turn the AFM for $ZnCr_2Se_4$ into FM, as typically shown in $CdCr_2Se_4$.[14] Albeit being studied for more than several decades, however, reports on the magnetic phase diagram for the system $Zn_{1-x}Cd_xCr_2Se_4$ ($0 \leq x \leq 1$) are controversial due to the presence of strong frustration and the intimate correlation between spin and lattice.[14–18] In the present case, any perturbation has to be considered strong.[19] Variations of the spin or lattice triggered by temperature, field or pressure (both chemical and external applied) would receive a severe response, which in turn can reflect themselves on a re-established equilibrium state. Hence, a combined investigation both from the magnetic and lattice aspects may offer comprehensive understanding of the elusive spin orders since the spin and lattice degrees of freedom show an inherent correlation.

In the present paper, we explore the evolution of spin-phonon coupling in the series $Zn_{1-x}Cd_x Cr_2Se_4$ ($0 \leq x \leq 1$) from the temperature and field dependent magnetization, specific heat as well as thermal conductivity. Our data give clear evidences that the spin-orientated structural transitions appear for $0 \leq x \leq 0.4$ while the correlation between spin and phonon becomes very weak and is dominated by the traditional magnetostriction interaction. In addition, for $0 \leq x \leq 0.4$ thermal carriers reveal strong scattering from spin fluctuations above T_N owing to strong frustration, in stark contrast with those for $0.6 \leq x \leq 1$ where traditional phonon-like heat conduction behaviors are observed as displayed in $CdCr_2Se_4$. To the best of our knowledge,[20–22] this may be the first report that a moderate applied magnetic field can drive readily the fluctuations-scattered thermal conductivity back to traditional phonon-like one.

II. EXPERIMENTAL

A series of polycrystalline samples of $Zn_{1-x}Cd_xCr_2Se_4$ ($0 \leq x \leq 1$) were prepared by standard solid state reaction method. Details about the sample preparation can be found elsewhere.[12] Room temperature X-ray diffraction (XRD) pattern was obtained by using X-ray diffractometer (Rigaku TTRIII). The magnetic data was collected on a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The specific heat and thermal conductivity were measured on a Quantum Design Physical Property Measurement System (PPMS).

III. RESULTS AND DISCUSSION

The XRD data for $Zn_{1-x}Cd_xCr_2Se_4$ ($0 \leq x \leq 1$) is analyzed by the standard Rietveld technique via the *Rietica* program.[23] All peaks can be well indexed by the cubic spinel structure with space group Fd-3m and no alien peaks is observed, which evidences good quality of the samples. Figure 1 shows the magnetization M versus temperature T at applied magnetic fields of H = 100 Oe and 10 kOe under both the zero-field-cooled (ZFC) and field-cooled (FC) sequences. In Fig. 1(a) and 1(b), we can see that for $0 \leq x \leq 0.4$ (the Zn-rich side), the magnetic ground state is of antiferromagnetic (AFM) while it exhibits typical ferromagnetic (FM) behaviors for $0.6 \leq x \leq 1$ (the Cd-rich side). The AFM and FM transition temperature T_Ns and T_Cs are temperatures where sharp downturns occur and extreme points of first-order derivative of M-T, respectively. Note that for $x = 0.4$, M shows a remarkable increment already from about 50 K upon cooling similar to that of $HgCr_2S_4$ compound,[24] implying some FM correlations above T_N.

At H = 10 kOe, T_N is shifted to lower temperatures for $x = 0$ and $x = 0.2$ and T_C increases gradually as x going from 0.6 to 1 [see Fig. 1(c) and 1(d)]. A peculiar feature is observed for

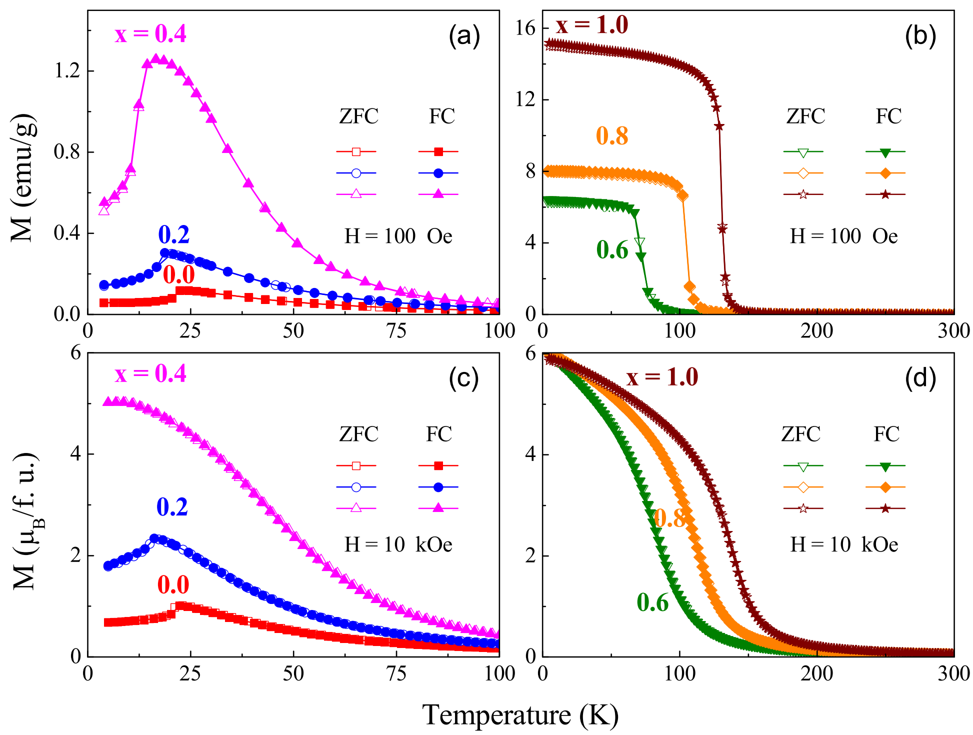

FIG. 1. Temperature dependence of magnetization (M) for $Zn_{1-x}Cd_xCr_2Se_4$ ($0 \le x \le 1$): (a) and (b) at 100 Oe; (c) and (d) at 10 kOe.

$x = 0.4$, where a complete suppression of the downturn behavior at low temperatures occurs. The field-related anomaly resembles that in $HgCr_2S_4$, where a meta-magnetic transition was observed.[24] The crossover of spin state from AFM to FM driven by such a low field (10 kOe) compared to that of the traditional Heisenberg antiferromagnets (10^3 kOe) indicates that AFM and FM exchange interactions are competing with each other and both are important in the determination of the ground state. The ground state for $x = 0.4$ at 10 kOe may be an essential FM spin alignment superimposed by the remnant of the AFM component since the magnetic moment (5 μ_B/f. u.) does not reach the saturated value (6 μ_B/f. u.). The details of T_Ns and T_Cs, the Curie-Weiss paramagnetic temperature as well as the lattice constants are all listed in TABLE I.

To see clearly the evolution of spin configuration with field, we performed magnetization as function of an applied field measurements. In Fig. 2(a), $M-H$ at 5 K manifests three anomalous points at H_{C1}, H_{C2} and H_{C3} with increasing the fields for $x = 0$.[25] The first relates to a re-orientation of the nonequivalent domains due to the tetragonal structural transition below T_N; the second hallmarks a field-induced structural transition from the low field tetragonal to high field cubic lattices;

TABLE I. Magnetic critical temperatures T_N and T_C, Curie-Weiss temperature Θ_{CW} and lattice constant a for $Zn_{1-x}Cd_xCr_2Se_4$ ($0 \le x \le 1$).

Composition	Néel temperature T_N (K) 100 Oe	Néel temperature T_N (K) 10 kOe	Curie temperature T_C (K) 100 Oe	Curie temperature T_C (K) 10 kOe	Curie-Weiss temperature Θ_{CW} (K)	Lattice constant a (Å)
$ZnCr_2Se_4$	21.5	20.5			85	10.495
$Zn_{0.8}Cd_{0.2}Cr_2Se_4$	20.5	17			107	10.544
$Zn_{0.6}Cd_{0.4}Cr_2Se_4$	15.5			43	122	10.595
$Zn_{0.4}Cd_{0.6}Cr_2Se_4$			71	83	151	10.644
$Zn_{0.2}Cd_{0.8}Cr_2Se_4$			105	112.5	167	10.700
$CdCr_2Se_4$			130	138	185	10.738

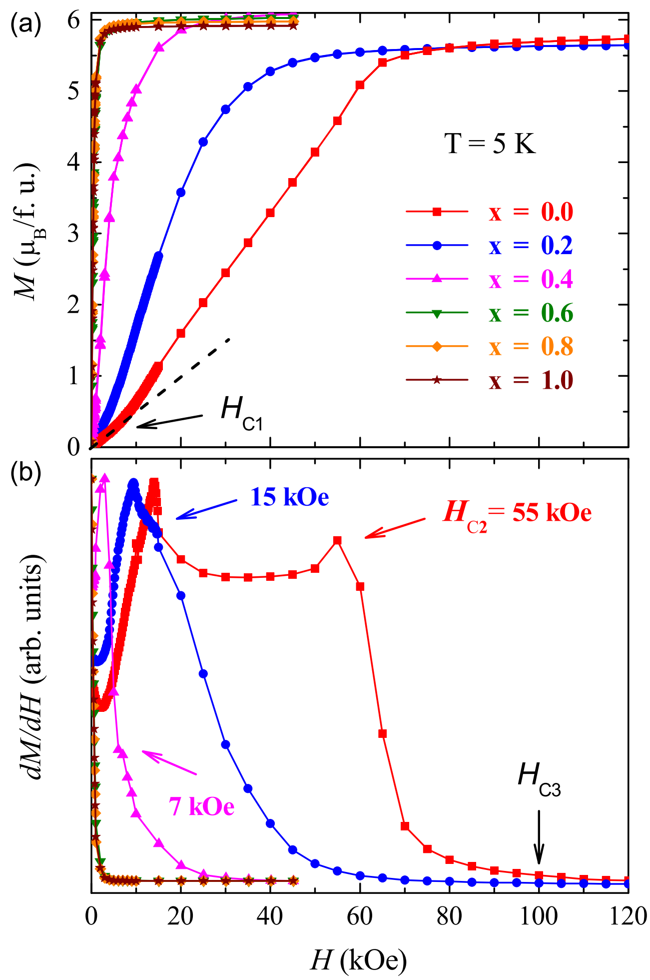

FIG. 2. (a) Magnetic field (H) dependent magnetization (M) at 5 K and (b) the derivative of M with respect to H for $Zn_{1-x}Cd_xCr_2Se_4$ ($0 \leq x \leq 1$).

the last signals a field above which a completely polarized spin state sets in. With increasing the Cd level, H_{C3} decreases rapidly from about 65 kOe at $x = 0$, 45 kOe at $x = 0.2$ to 20 kOe at $x = 0.4$ while it remains a very small constant value of 3.5 kOe for the Cd-rich side. At the same time, H_{C2} decreases drastically for the Zn-rich side and vanishes for the Cd-rich side, as displayed clearly in Fig. 2(b). As H_{C2} signals a magnetostructural transition originated from frustration for $ZnCr_2Se_4$,[25] the decrease of H_{C2} with x indicates a systematic weakening of spin-lattice coupling. It can be ascribed to the gradual release of frustration since the AFM interactions decreases markedly when replacing Zn by Cd, which can also be deduced from the rapid decrease of H_{C3} with x as indicated by arrows in Fig. 2(b). Again, here we find that at only about 20 kOe the magnetic ground state for $x = 0.4$ can be tune from AFM to FM, a novel property as also observed in $HgCr_2S_4$ spinel.[24]

The correlation and evolution of the spin and lattice degrees of freedom may also be traced from the specific heat data, as presented in the representative of C/T versus T in Fig. 3(a) and 3(b). On the one hand, a sharp peak appears at T_N for $x = 0$ signaling the transition of first order, which agrees well with the previous data.[4] For $x = 0.2$ the anomaly is observed to shift to 17 K and attenuate markedly. A very tiny broad peak centering at 12 K is discerned for $x = 0.4$, as displayed in the inset of Fig. 3(a). On the other hand, small cusps are observed at T_C for $x = 0.8$ and 1.0. Interestingly, for $x = 0.6$ only a big hump around T_C is exhibited as indicated by the dashed circle in Fig. 3(b). It is known that the magnetic ground state for $ZnCr_2Se_4$ is dictated by Cr-Se-Cr FM and Cr-Se-Zn-Se-Cr AFM super-exchange interactions.[11] Although the averaged net exchange interaction increases linearly with increasing the Cd level as can be inferred from TABLE I, fluctuations

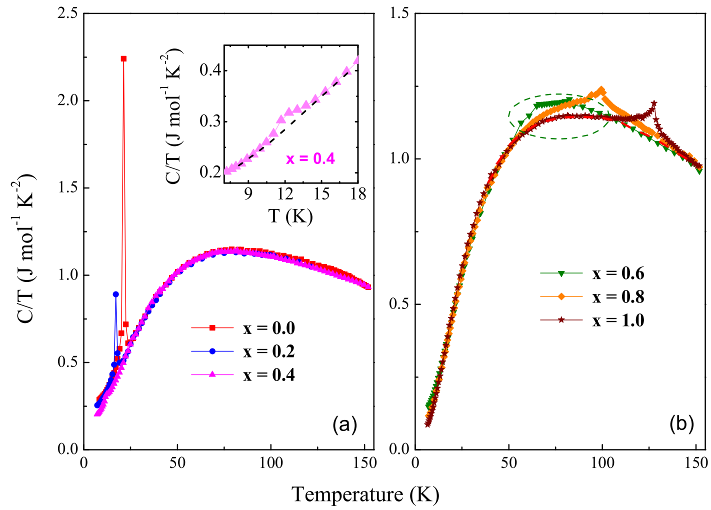

FIG. 3. Temperature dependence of the specific heat plotted as C/T vs T for $Zn_{1-x}Cd_xCr_2Se_4$ when (a) $0 \le x \le 0.4$ and (b) $0.6 \le x \le 1$. Inset: a polynomial fitting of the phonon specific heat for $x = 0.4$.

of sign and magnitude of exchanges may not be negligible especially for the intermediate region ($0.4 \le x \le 0.6$). In this sense, the net exchanges cannot strong enough to support any long-range magnetic order. As a result, the sluggish transitions for $x = 0.4$ and 0.6 in specific heat may be related to some short-range magnetic orders. Based on the procedure reported in Ref. 25, the change of magnetic entropy ΔS_m involved in the magnetic transition can be roughly estimated. Specifically, ΔS_m are 2.65, 0.85 and 0.28 J·mol^{-1} K^{-1} for the Zn-rich side while a constant value (2.7 J·mol^{-1} K^{-1}) is deduced for the Cd-rich side. These implies that considerable magnetic entropy has been released already at high temperatures and strong fluctuations exist.

Such strong spin fluctuations may influence significantly the transportation of thermal carriers.[26] Hence, we measured the thermal conductivity κ for $Zn_{1-x}Cd_xCr_2Se_4$ ($0 \le x \le 1$) as functions of temperature and magnetic field as shown in Fig. 4. In the absence of field, κ decreases

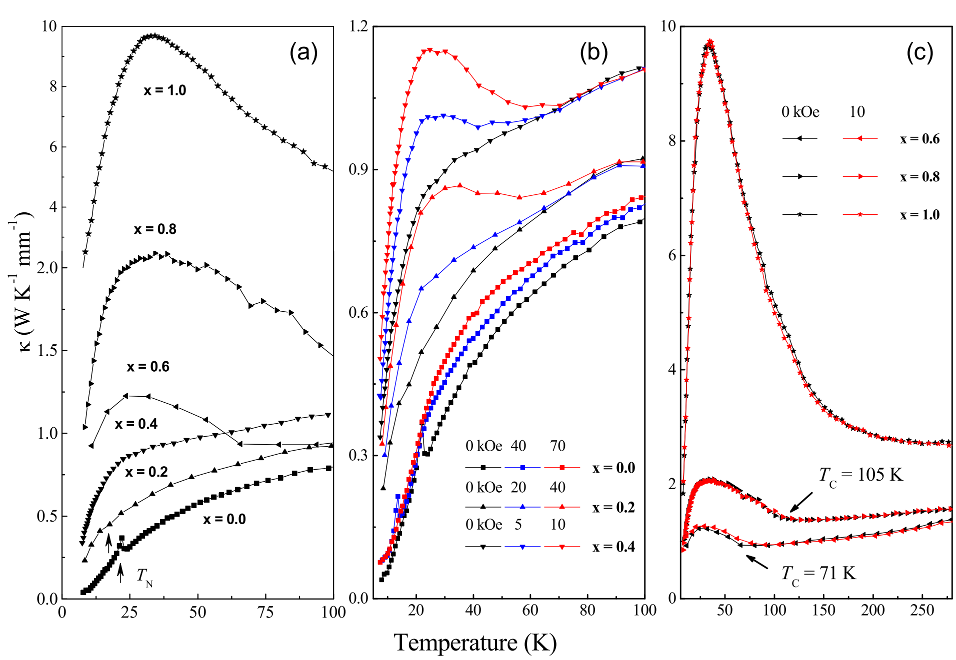

FIG. 4. Low temperature dependent thermal conductivity for $Zn_{1-x}Cd_xCr_2Se_4$ ($0 \le x \le 1$) at zero magnetic field (a) and at different applied magnetic fields (b) and (c).

monotonically with lowering temperature for $x = 0$. At T_N, it shows a cusp-like anomaly followed by a continuous decrease down to 7 K. The anomaly corresponds to the structural transition at T_N, in line with the specific data. For $x = 0.2$, the anomaly is tuned to about 18 K as presented in Fig. 4(a). For $x = 0.4$, κ decreases monotonically with lowering temperature till around 25 K, below which it decreases again but with a relatively larger slope. For the Cd-rich side, however, huge humps are observed at low temperatures, resembling the traditional pure phonon thermal conductivity with temperature.[27] In addition, kink-like anomalies are found at T_C for $x = 0.6$ and 0.8 [see Fig. 4(b)].

When applying a magnetic field, the cusp at T_N for $x = 0$ is shifted to about 13.5 K at 40 kOe and can even be suppressed completely at 70 kOe, as can be drawn from Fig. 4(b). In addition, κ increases gradually with field above T_N. The maximum rate of increase of κ is estimated to be 1.6 $W \cdot K^{-1}\ mm^{-1}\ Oe^{-1}$ at about 30 K. Most strikingly, for $x = 0.2$ and 0.4, applied magnetic fields can enhance the thermal conductivity drastically in addition to shifting the anomalies at T_N to lower temperatures. The maximum rate of increase for $x = 0.2$ and 0.4 at 30 K are 12.3 and 31.7 $W \cdot K^{-1}\ mm^{-1}\ Oe^{-1}$, respectively. To the best of our knowledge,[20–22] the present systems are the only reported compounds manifesting such a tremendous field-modulated thermal conductivity effect. As for the Cd-rich side, however, a field of 10 kOe gives no evident effect on the thermal conductivity as shown in Fig. 4(c).

The anomalies at T_N of κ for the Zn-rich side together with the kinks at T_C for the Cd-rich side imply intimate correlations between the spin and lattice degrees of freedom. As can be seen from Fig. 4(a), the traditional pure phonon thermal conductivity peak upon cooling disappears for the Zn-rich side, in stark contrast with that of the Cd-rich side where huge peaks are observed at low temperatures [see Fig. 4(c)]. As is discussed above, strong spin fluctuations exist above T_N. The fluctuations may scatter evidently the thermal carrier, phonon, giving rise to a continuous decrease of κ down to low temperatures. With increasing the Cd level, however, bond frustration is relieving rapidly and spin-phonon coupling decay correspondingly. Therefore, the magnitude of thermal conductivity increases gradually. At last, purely phonon-like thermal conductivity recovers and is dominated by traditional magnetostriction effect. As displayed in Fig. 3(b) and 4(c), only small cusps in specific heat and huge peaks at low temperature can be observed at T_C, typically observed in the FM $CdCr_2Se_4$. Besides, the features of thermal conductivity for $x = 0.2$ at 40 kOe and $x = 0.4$ at 10 kOe resemble extremly those of the Cd-rich side, namely, huge broad peaks at low temperatures. Looking back to the $M - H$ data, one may know that the spin states are almost FM for $x = 0.2$ at 40 kOe and $x = 0.4$ at 10 kOe. Under such circumstances, frustration and spin fluctuations are overcome by the applied fields. Thus it is reasonable that for $x = 0.2$ at 40 kOe and for $x = 0.4$ at 10 kOe thermal conductivities reveal peaks like in $CdCr_2Se_4$.

IV. CONCLUSIONS

In summary, we have investigated the correlation of spin and lattice for $Zn_{1-x}Cd_xCr_2Se_4$ ($0 \le x \le 1$). As increasing the Cd level x, frustration and spin fluctuations are relieving gradually as can be deduced from the $M - H$ and specific heat data. At the same time, spin-originated structural transitions disappears gradually while tiny correlation between spin and lattice dominated by the traditional magnetostriction effect is observed. For the Zn-rich side thermal carriers reveal strong scattering from spin fluctuations above T_N while traditional pure phonon thermal conducting behavior recovers for the Cd-rich side. In addition, we find that a moderate applied magnetic field can drive readily the fluctuations-scattered thermal conductivity for $x = 0.2$ and 0.4 back to its traditional behavior similar to that of $CdCr_2Se_4$, reaching about 30% at 25 K in 1 T for $x = 0.4$. Such a sensitive field-related effect may introduce a new kind of functionality for potential applications.

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