# Pressure Tuning of Magnetism and Drastic Increment of Thermal Conductivity under Applied Magnetic Field in $HgCr_2S_4$ *

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*$HgCr_2S_4$ is a typical compound manifesting competing ferromagnetic (FM) and antiferromagnetic (AFM) exchanges as well as strong spin–lattice coupling. Here we study these effects by intentionally choosing a combination of magnetization under external hydrostatic pressure and thermal conductivity at various magnetic fields. Upon applying pressure up to 10 kbar at 1 kOe, while the magnitude of magnetization reduces progressively, the AFM ordering temperature $T_N$ enhances concomitantly at a rate of about 1.5 K/kbar. Strikingly, at 10 kOe the field polarized FM state is found to be driven readily back to an AFM one even at only 5 kbar. In addition, the thermal conductivity exhibits drastic increments at various fields in the temperature range with strong spin fluctuations, reaching about 30% at 50 kOe. Consequently, the results give new experimental evidence of spin–lattice coupling. Apart from the colossal magnetocapacitance and colossal magnetoresistance reported previously, the findings here may enable new promising functionalities for potential applications.*

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In the family of chromium-based spinels with the formula $ACr_2X_4$ (here $A$=Zn, Cd, Hg and $X$=Se, S, O), magnetic $Cr^{3+}$ ions form a corner-sharing tetrahedral network named as pyrochlore lattice. This lattice is known to be a highly frustrated system and therefore constitutes a prototype system for studying spin frustration.[1,2] However, its role in stabilizing a magnetic ground state is far from being well understood, and many frustration-related phenomena have been reported. For example, in oxides, direct antiferromagnetic (AFM) exchange interactions dominate and strong geometric frustration is involved. The magnetic transitions are accompanied by structural distortions which have been treated as a spin-driven Jahn–Teller effect.[3,4] The sulfides and selenides, with larger lattice constants, are dominated by 90° Cr-$X$-Cr ferromagnetic (FM) and more neighboring Cr-$X$-$A$-$X$-Cr or Cr-$X$-$X$-Cr AFM superexchanges.[5] Bond frustration-related phonon splitting has been observed.[6,7] Since $Cr^{3+}$ ions show a half-filled $t_{2g}$ shell and a quenching of the charge and orbit, spin-lattice coupling may be one of the most important factors that stand behind these exotic physics.[8–12]

$HgCr_2S_4$ reveals a large positive Curie–Weiss temperature $\Theta_{CW} = 142$ K,[5] while exhibiting a complex AFM order at a critical temperature $T_N \ll \Theta_{CW}$,[13] implying strong competition of FM and AFM exchanges. Although no phonon splitting has been detected at $T_N$, polar modes under field reveal shifts exactly correlated with the magnetization.[14] Interestingly, colossal magnetocapacitance (CMC) and colossal magnetoresistance (CMR) of $HgCr_2S_4$ are found in the temperature range with strong FM fluctuations,[15] similar to those of FM $CdCr_2S_4$.[16] To date however, it is still under debate whether the CMC and CMR effects observed in both compounds are inherent or not.[17,18]

Pressure can alter the lattice parameter by direct compression of the lattice and thus is a powerful tool for studying phase transition. In $HgCr_2S_4$, given the strong spin-lattice coupling, spin fluctuations and competing FM and AFM exchanges,[19] pressure-related studies should be of great benefit to the understanding of the complex magnetic behavior.

In this Letter, motivated by the presence of spin-lattice coupling in $HgCr_2S_4$, we intend to probe it from magnetization via varying external pressure and thermal conductivity by changing the magnetic field. We find that pressure can drive readily a field-polarized FM state back to an AFM one. Moreover, we observe a remarkable enhancement of thermal conductivity under field. Consequently, our results supply new evidence for competing FM and AFM exchanges as well as strong correlation between the spin and lattice.

The polycrystalline sample of $HgCr_2S_4$ was prepared by the standard solid state reaction method. High purity (99.9%) binary mercury sulfide and el-

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ementary Cr and S powders were mixed according to the stoichiometric ratio. The mixture was then sealed in an evacuated quartz tube and heated slowly to 800℃ in seven days. The procedure is repeated several times to avoid possible nonreacted raw materials. Finally, the production was annealed at 800℃ in an atmosphere of sulfur excess.

The x-ray diffraction (XRD) pattern at room temperature was obtained by using an x-ray diffractometer Rigaku TTRIII. The thermal conductivity measurement was carried out on a physical property measurement system (PPMS, Quantum Design). Magnetization measurements were performed with a commercial SQUID magnetometer MPMS-XL (Quantum Design) and the application of hydrostatic pressure by using silicone oil as the pressure medium was performed in an Easylab Mcell 10 pressure cell.

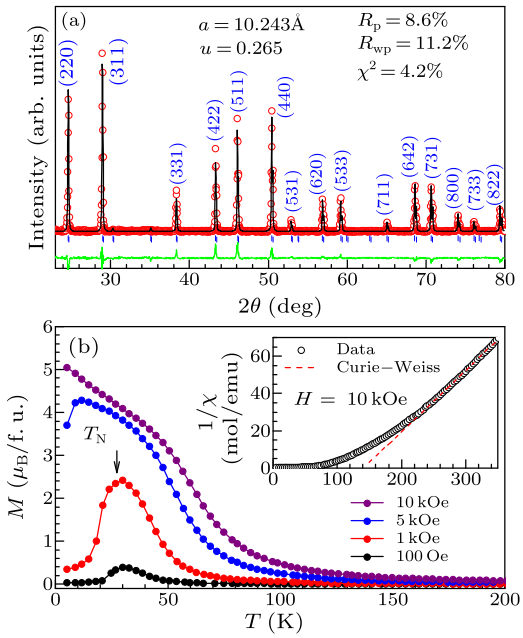


**Fig. 1.** (Color online) (a) XRD pattern of polycrystalline $HgCr_2S_4$. The Rietica program[20] is used to fit the profile. (b) Temperature dependence of magnetization at different fields from 100 Oe to 10 kOe. Inset: the inverse susceptibility for $HgCr_2S_4$ at 10 kOe. The red dashed line is a fitting by using the Curie–Weiss behavior.

The XRD pattern of $HgCr_2S_4$ was analyzed by the standard Rietiveld method using the Rietica program,[20] as displayed in Fig. 1(a). All the observed peaks can be well indexed by the cubic spinel structure with space group $Fd\bar{3}m$ (No. 227) and the fitting yields a lattice constant of 10.243(2) Å and sulfur positional parameter $u = 0.265$, similar to the previous reports.[19]

Figure 1(b) exhibits the temperature dependence of magnetization ($M$) measured at several applied magnetic fields up to 10 kOe. At 100 Oe, with lowering the temperature, $M$ first shows a steep increase at $T_C = 60$ K, indicative of strong ferromagnetic correlations and then reaches a maximum at $T_N = 30$ K followed by an abrupt decline entering an AFM magnetic state.[13] Upon enhancing the magnetic field, $T_N$ is observed to shift to lower temperatures at a rate of about 4 K/kOe. At 10 kOe, a field polarized FM state sets in. It should be noted that in addition to a remarkable increment of the magnitude of $M$, the applied field turns the critical temperature $T_C$ up rapidly, where FM fluctuations are observed initially upon cooling.[19] The temperature dependence of the inverse susceptibility in the inset of Fig. 1(b) reveals a large positive Curie–Weiss temperature 140 K and an effective magnetic moment almost to 3.87 $\mu_B$, in agreement with the spin-only value of $Cr^{3+}$ ions in an octahedral crystal field.

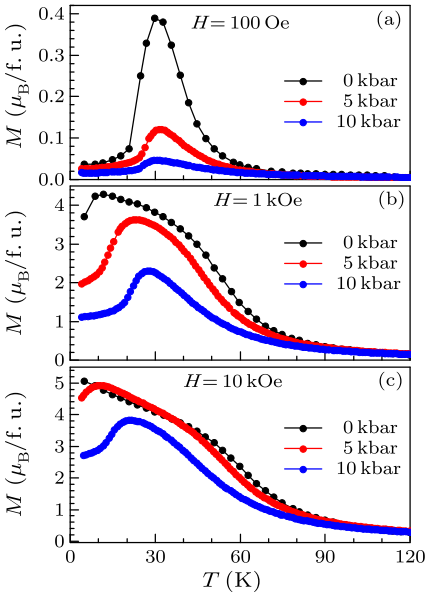


**Fig. 2.** (Color online) Temperature dependence of magnetization under applied hydrostatic pressure at (a) 100 Oe, (b) 1 kOe and (c) 10 kOe.

Figure 2 presents the effect of hydrostatic pressure on the temperature-dependent magnetization of the spinel $HgCr_2S_4$. In a field of 100 Oe, an application of external pressure suppresses the magnitude of $M$ drastically as displayed in Fig. 2(a). With the increasing field to 1 kOe in Fig. 2(b), in addition to progressive decreases of the magnitude of $M$, $T_N$ shifts to higher temperatures evidently at a rate of 1.5 K/kbar. Most importantly, a pressure of 5 kbar can drive the field of 10 kOe polarized FM state back into an AFM one with $T_N = 10$ K as observed in Fig. 2(c). With further increasing the pressure at 10 kOe, $T_N$ is observed to shift to a temperature as high as 21 K. From the above results we can find that the applied pressure acts oppositely as field. While the external magnetic field favors the FM exchange, the pressure may favor the AFM one. The magnitude of $M$ is remarkably suppressed when increasing the pressure, especially in the vicinity of $T_N$, indicating enhancement of spin

fluctuations. In addition, the extreme sensitivities of the magnitude of $M$ as well as $T_N$ in response to applied pressure and field evidence strong competition between the FM and AFM exchanges and spin-lattice coupling due to strong frustration. To the best of our knowledge, this is the first compound among the chromium spinels that manifests itself such a strong cross control of magnetism by varying applied pressure and field.

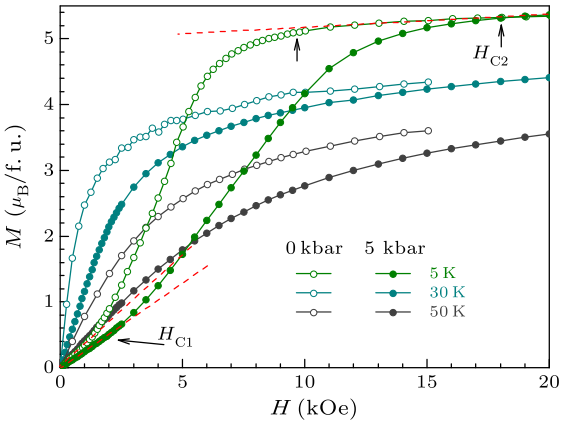


**Fig. 3.** (Color online) Magnetic field dependence of magnetization under applied hydrostatic pressure at selected temperatures of 5, 30 and 50 K. The definitions of the two critical fields are indicated.

To see more clearly the effect of pressure on magnetism, we further measured the isotherm curves $M$–$H$ at three selected temperatures 5, 30 and 50 K as presented in Fig. 3. In the absence of pressure at 5 K, $M$ first grows linearly up to a critical field $H_{c1} = 1$ kOe, increases again with a larger slope and finally saturates at a critical field of $H_{c2} = 10$ kOe. As reported previously,[5] $H_{c1}$ signals a metamagnetic transition from a complex AFM to field polarized FM-like state. At 30 and 50 K, typical soft FM magnetization behaviors[5] are observed and $M$ saturates beyond $H_{c2}$ with considerable moments remaining, evidencing strong FM correlations even above $T_N$, in accordance with the above $M$–$T$ data. On the other hand, when applying an external pressure of 5 kbar, at 5 K the two critical magnetic fields in $M$–$H$, $H_{c1}$ and $H_{c2}$, shift simultaneously to higher fields of about 2 and 17 kOe, respectively. In addition, at 30 and 50 K, the fields of $H_{c2}$ that require fulfilling a complete polarized FM state increase significantly. Such strong pressure effects on magnetism reflect the pressure favoring the AFM state as well as strong spin–lattice coupling.

The strong spin–lattice coupling can also be manifested in the following temperature-dependent thermal conductivity $\kappa$ measurement. As displayed in Fig. 4, $\kappa$ decreases smoothly with temperature in the absence of magnetic field. Upon further cooling below about 60 K, $\kappa$ increases slightly and experiences a maximum at about 25 K followed by a sharp decrease down to the lowest temperature. An applied field of 1 kOe shows no evident effect on $\kappa$. At 5 kOe, however, $\kappa$ increases evidently, especially below $T_C$ where strong spin fluctuations appear. For a system with strong spin fluctuations and spin–lattice coupling, thermal carriers can be scattered by both phonons and spinons, as evidenced in $ZnCr_2Se_4$.[21] The applied field inhibits spin fluctuations and thus reduces the scattering from spinons to thermal carriers, resulting in the drastic increment of $\kappa$. With the field increasing up to 50 kOe, $\kappa$ increases continuously, reaching about 30% at 30 K. Interestingly, the applied field turns the critical temperature $T_C$, where spin fluctuations can be initially observed in $M$–$T$ (60 K at 100 Oe), toward higher temperatures violently (80 K at 10 kOe, 110 K at 50 kOe).

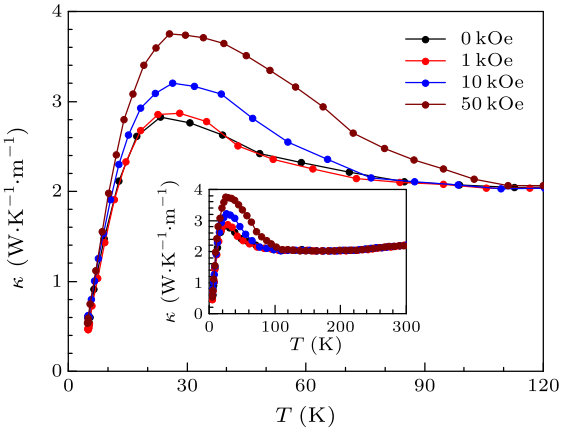


**Fig. 4.** (Color online) Low temperature-dependent thermal conductivity at various magnetic fields up to 50 kOe. The inset shows a complete view of thermal conductivity from 5 K to 300 K.

In summary, we have investigated the spin-lattice coupling in polycrystalline $HgCr_2S_4$. By applying pressure up to 10 kbar at 1 kOe, $T_N$ can be readily tuned to higher temperatures and at 10 kOe the field polarized FM state is observed to drive back to an AFM one. In addition, the temperature-dependent thermal conductivity shows a dramatic increment in the temperature range with strong spin fluctuations. These effects reflect competing FM and AFM exchanges and spin–lattice coupling due to the strong bond frustration. The successful controls of magnetism by pressure and thermal conductivity by field may provide new promising functionalities for potential applications.

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