Magnetic-Competition-Induced Colossal Magnetoresistance in n-Type $HgCr_2Se_4$ under High Pressure

J. P. Sun,[1,2] Y. Y. Jiao,[1,3] C. J. Yi,[1,2] S. E. Dissanayake,[4,5] M. Matsuda,[4] Y. Uwatoko,[6] Y. G. Shi,[1,2,7] Y. Q. Li,[1,2,7] Z. Fang,[1,2,7] and J.-G. Cheng[1,2,7,*]

[1]*Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
[2]*School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190, China*
[3]*Faculty of Science, Wuhan University of Science and Technology, Wuhan, Hubei 430065, China*
[4]*Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[5]*Department of Physics, Duke University, Durham, North Carolina 27708, USA*
[6]*Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*
[7]*Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, China*

(Received 25 March 2019; published 22 July 2019)

The n-type $HgCr_2Se_4$ exhibits a sharp semiconductor-to-metal transition (SMT) in resistivity accompanying the ferromagnetic order at $T_C = 106$ K. Here, we investigate the effects of pressure and magnetic field on the concomitant SMT and ferromagnetic order by measuring resistivity, dc and ac magnetic susceptibility, as well as single-crystal neutron diffraction under various pressures up to 8 GPa and magnetic fields up to 8 T. Our results demonstrate that the ferromagnetic metallic ground state of n-type $HgCr_2Se_4$ is destabilized and gradually replaced by an antiferromagnetic, most likely a spiral magnetic, and insulating ground state upon the application of high pressure. On the other hand, the application of external magnetic fields can restore the ferromagnetic metallic state again at high pressures, resulting in a colossal magnetoresistance (CMR) as high as $\sim 3 \times 10^{11}\%$ under 5 T and 2 K at 4 GPa. The present study demonstrates that n-type $HgCr_2Se_4$ is located at a peculiar critical point where the balance of competition between ferromagnetic and antiferromagnetic interactions can be easily tipped by external stimuli, providing a new platform for achieving CMR in a single-valent system.

DOI: 10.1103/PhysRevLett.123.047201

The chromium chalcogenide spinels $CdCr_2S_4$, $CdCr_2Se_4$, and $HgCr_2Se_4$ are well-known ferromagnetic semiconductors that have been studied for several decades [1–4]. Many anomalous physical properties such as colossal magnetoresistance (CMR) [5,6], anomalous Hall effect [5], and the redshift of optical absorption edge [7] have been observed in these compounds due to the intimated correlation between the charge and spin degrees of freedom.

Recently, $HgCr_2Se_4$ has received renewed interest because first-principles calculations have predicated a novel Chern semimetal state and quantized anomalous Hall effect [8]. In the earlier reports, $HgCr_2Se_4$ was found to exhibit semiconducting behavior with a ferromagnetic (FM) transition at $T_C = 106$–120 K [3,4,9], which can be tuned by hole or electron doping [10]. Its saturated magnetic moment 5.64 μ_B/f.u. is close to the expected high-spin Cr^{3+} ion [3,4]. Following the theoretical prediction, some of us synthesized high quality n-type $HgCr_2Se_4$ single crystals, for which the FM order at $T_C = 106$ K is accompanied with a sharp semiconductor to metal transition (SMT) with eight orders of drop in resistivity [11,12]. Under magnetic field, the FM transition moves to higher temperatures, leading to a CMR $\sim 6 \times 10^6\%$ at 8 T and 107 K [12,13]. The observed CMR in single-valent $HgCr_2Se_4$ has a different origin from the mixed-valent manganese perovskites, in which the double-exchange mechanism is dominant [14]. Andreev reflection spectroscopy measurements provide direct evidence that n-type $HgCr_2Se_4$ is a half-metal below T_C with spin polarizations as high as 97% [12]. Since the interesting properties of $HgCr_2Se_4$ occur around or below $T_C = 106$ K, it is desirable to enhance T_C to higher temperatures from the viewpoint of practical applications.

High pressure (HP), as an effective and clean knob, can be employed to precisely tune the crystal structure, electronic, and magnetic properties of materials. A comprehensive HP study on $HgCr_2Se_4$ is still lacking. An earlier HP study on $HgCr_2Se_4$ showed that its room-temperature resistivity decreases by 1 order of magnitude in the pressure range 0.5–1.5 GPa, followed by another weak anomaly at around 6 GPa [15]. The dramatic drop of resistivity was explained as a pressure-induced SMT [15]. However, the metallic state was not verified by the temperature dependence of resistivity under pressure. A recent theoretical calculation seems to support the pressure-induced SMT, but the predicted critical pressure of 11.4 GPa is an order

of magnitude higher [16]. Efthimiopoulos *et al.* found two successive structural transformations in $HgCr_2Se_4$ under HP; i.e., the cubic Fd-$3m$ phase first transforms to a tetragonal $I4_1/amd$ phase at about 15 GPa and then to a structurally disordered or partial amorphous phase above 21 GPa [17]. It was speculated that the Fd-$3m$ to $I4_1/amd$ transformation is accompanied with an insulator to metal transition because the Raman signal disappears after the structural transition [17]. Therefore, all existing experimental and theoretical studies indicated the possible occurrence of pressure-induced SMT in $HgCr_2Se_4$, which has not been verified so far.

Here we performed a comprehensive HP study on n-type $HgCr_2Se_4$ single crystals by measuring its magnetotransport, dc and ac magnetic susceptibility, as well as neutron diffraction under various pressures up to 8 GPa. The studied sample has a FM transition $T_C = 106$ K and saturation moment $M_s \sim 5.5\ \mu_B$ at ambient pressure. Details about crystal growth, experimental methods, and magnetic characterizations at ambient pressure are given in the Supplemental Material [18]. Surprisingly, we found the FM metallic ground state of n-type $HgCr_2Se_4$ is destabilized and gradually replaced by an antiferromagnetic (AFM), most likely a spiral magnetic, and insulating state upon the application of HP, which is counterintuitive and in striking contrast to all previous studies [15–17]. On the other hand, magnetic fields can restore the FM metallic state again at high pressures, resulting in a CMR as high as $\sim 3 \times 10^{11}\%$ under 5 T and 2 K at 4 GPa. Our study demonstrates that $HgCr_2Se_4$ situates at a critical point where the competition between FM and AFM exchange interactions can be easily tuned by pressure and magnetic field. Because of the strong coupling between the spin and charge degrees of freedom, n-type $HgCr_2Se_4$ thus represents a unique example that the magnetic phase competition can induce a significant CMR in a single-valent system.

Figure 1 displays the temperature dependence of resistivity $\rho(T)$ for n-type $HgCr_2Se_4$ at 0 and 8 T under various pressures up to 7 GPa. $\rho(T)$ under 8 T was recorded upon warming up after zero-field-cooled (ZFC) from room temperature. At ambient pressure, its $\rho(T)$ at 0 T displays a sharp SMT manifested by about eight orders drop below $T_C = 106$ K, Fig. 1(a). Here, we define T_C as the interception between two straight lines below and above. The SMT in $\rho(T)$ at 8 T moves to higher temperature ~ 200 K, resulting in a CMR $\sim 10^6\%$ around T_C, in agreement with previous studies [12,13]. When increasing pressure to 1 GPa, the sharp drop is still very clear, but the FM order has been lowered to ~ 90 K, Fig. 1(b). Meanwhile, a weak upturn appears in $\rho(T)$ below $T_{min} \sim 10$ K. Similarly, the SMT at 1 GPa also shifts to higher temperature ~ 150 K under 8 T. Upon further increasing pressure to 2 GPa, the concomitant FM order and the SMT were suppressed to ~ 70 K. Surprisingly, the low-temperature upturn is strongly enhanced; i.e., the resistivity increases by three

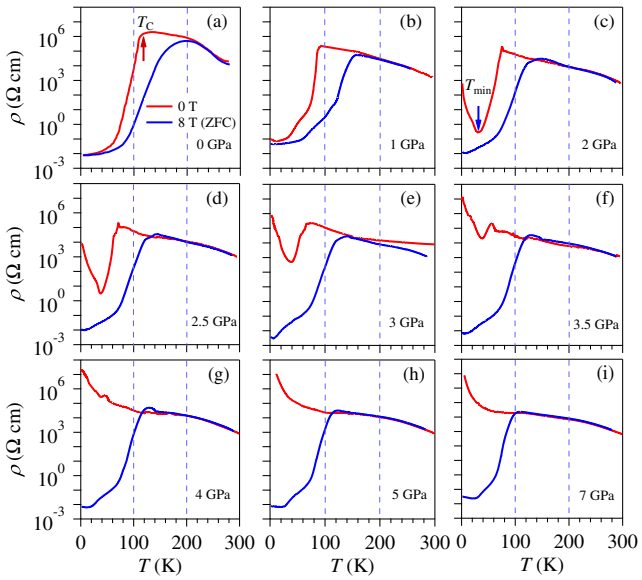

FIG. 1. (a)–(i) Temperature dependence of resistivity $\rho(T)$ of $HgCr_2Se_4$ at 0 and 8 T under various pressures up to 7 GPa.

orders of magnitude below T_{min}, which has also been enhanced to ~ 30 K. The opposite pressure dependencies of T_C and T_{min} result in a reduction of the metalliclike region in between T_C and T_{min}. Again, the 8 T magnetic field restores the metallic state, Fig. 1(c). At $P \geq 2.5$ GPa, T_{min} does not change too much, but the metalliclike region at $T_{min} < T < T_C$ shrinks quickly and almost vanishes at $P > 3.5$ GPa, when the semiconducting behavior retains to the lowest temperature. Such a pressure-induced metal to insulator transition in n-type $HgCr_2Se_4$ is quite unexpected and is in striking contrast with all previous studies mentioned above [15–17]. Interestingly, we found that the application of magnetic field can change the situation dramatically. As shown in Figs. 1(d)–1(i), the resistivity at 8 T exhibits sharp SMT as observed at lower pressures. Our results thus indicate that HP destabilizes the FM metallic ground state, whereas the magnetic field can restore it.

Before we proceed to investigate the underlying mechanism for such an intriguing phenomenon, we first evaluate the detailed effect of the magnetic field on resistivity or MR under each pressure. Figure 2 shows the representative $\rho(T)$ and MR under different magnetic fields at 2, 3, 4, and 7 GPa. Similarly, the data under magnetic field were collected in the ZFC mode. Here we define MR as $100\% \times [\rho_{xx,0} - \rho_{xx}(H)]/\rho_{xx}(H)$. For $P = 2$ GPa, the upturn below $T_{min} \sim 30$ K can be easily suppressed by a moderate magnetic field < 0.5 T, above which the metallic state persists down to the lowest temperature. Here, we can clearly see that T_{min} is progressively suppressed by magnetic field, and the MR increases from $10^2\%$ to $10^6\%$ upon cooling below T_{min}. With increasing pressure to 3 GPa, the resistivity value at T_{min} is 3 orders of magnitude higher than that at 2 GPa, illustrating that pressure further stabilizes the

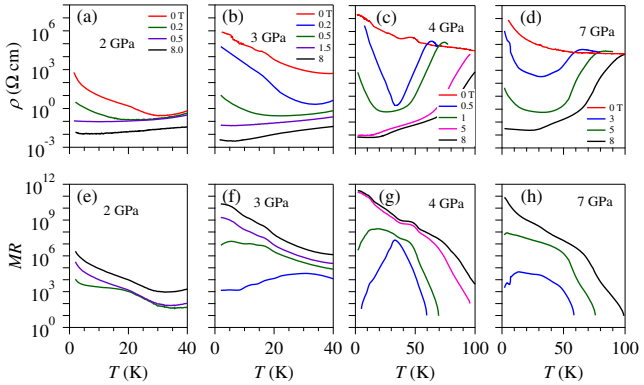

FIG. 2. Temperature dependence of resistivity $\rho(T)$ and MR ratio at different magnetic fields (ZFC) under various represented pressures: (a) 2, (b) 3, (c) 4, and (d) 7 GPa. In (a)–(d) and (e)–(h), the resistivity $\rho(T)$ and MR have the same coordinate range as in (a) and (e).

insulating state. Accordingly, the magnetic field to restore the metallic state also increases quickly with pressure, and a metallic state cannot be fully recovered up to 8 T at 7 GPa. As seen in Figs. 2(g) and 2(h), a CMR as high as $\sim 10^{11}\%$ can be achieved under 5 T and 2 K at 4 GPa or under 8 T and 2 K at 7 GPa. Such a MR $\sim 10^{11}\%$ is close to the largest CMR value in the perovskite manganites [19]. These results further demonstrate that pressure and magnetic field play opposite roles in controlling the electronic ground state of this system.

Because the electrical transport properties of half-metallic $HgCr_2Se_4$ are governed by the magnetic state [8,12], it is instructive to determine how the magnetic ground state evolves under pressure. For this purpose, we first measured dc and ac magnetic susceptibility under HP. Figure 3(a) shows the dc magnetization $\chi(T)$ for $HgCr_2Se_4$ up to 0.88 GPa measured in ZFC mode under 100 Oe [18]. As can be seen, the FM transition temperature is gradually lowered with increasing pressure, but the FM order remains robust at 2 K up to ~ 0.9 GPa.

Figure 3(b) displays the ac magnetic susceptibility $\chi'(T)$ to further track the evolution of the magnetic ground state under higher pressures [20]. We can see that the FM T_C was continuously reduced to ~ 70 K at 2.5 GPa, consistent with the resistivity data shown in Fig. 1(d). The nearly parallel shift down of T_C illustrates that the FM exchange interactions are weakened by pressure. On the other hand, a clear drop develops below ~ 10 K in $\chi'(T)$ under 1 GPa, and it becomes more pronounced and moves to higher temperatures with pressure. We noticed a kink anomaly around 8 K in the $\chi'(T)$ of 1.5 GPa, whose origin is not clear [21]. The sharp drop of $\chi'(T)$ appears at ~ 35 K under 2.5 GPa. Similar behavior was also observed in MnP [22], in which the transition from FM to a double helical state induces a sharp drop of $\chi'(T)$ as observed here. The drop of $\chi'(T)$ thus suggests that the FM ground state might transform to an AFM or helimagnetic state under pressure. Thus we define T_N as shown in Fig. 3(b). Since the drop in $\chi'(T)$ takes place at nearly the same temperature as $T_{\min}$ in resistivity, Fig. 1, the upturn should be attributed to the development of the AFM state. Above 2.5 GPa, the plateau in $\chi'(T)$ disappears completely and there left only a single peak anomaly, which stays nearly at the same temperature ~ 40 K but its magnitude decreases gradually with pressure. The broad maximum in $\chi'(T)$ of $HgCr_2Se_4$ at $P \geq 3$ GPa is very similar to that observed in $HgCr_2S_4$ at ambient pressure, corresponding to the development of noncollinear AFM or spiral magnetic order at $T_N = 22$ K [23]. The presence of spiral rather than FM order in $HgCr_2S_4$ has been attributed to the enhanced further-neighbor AFM interactions relative to the nearest-neighbor FM interaction [23]. These observations thus indicate that the FM ground state of $HgCr_2Se_4$ is most likely replaced gradually by a noncollinear AFM or spiral state similar to $HgCr_2S_4$.

To verify the pressure-induced spiral magnetic ground state, we perform single-crystal neutron diffraction

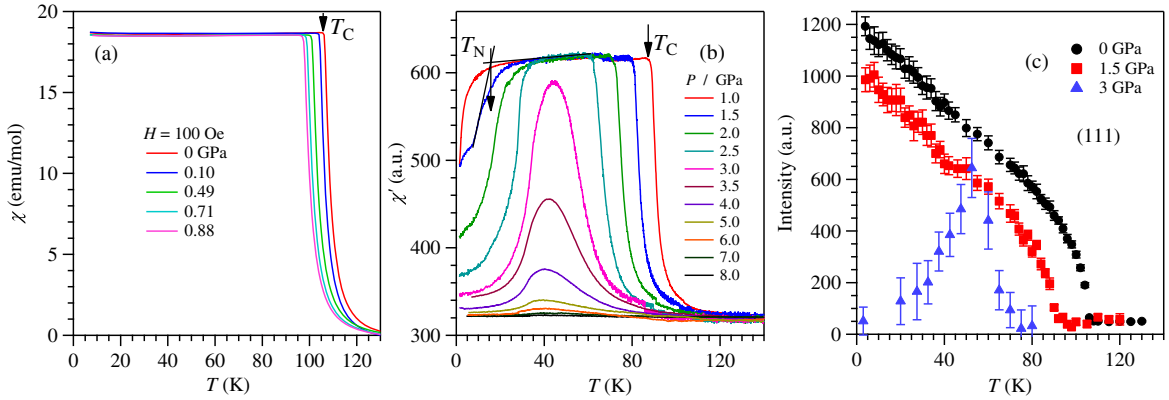

FIG. 3. (a),(b) Temperature dependence of dc and ac susceptibility of $HgCr_2Se_4$ under high pressures. The ferromagnetic transition temperatures T_C and the antiferromagnetic transition temperatures T_N are marked by arrows. (c) Temperature dependence of the integrated intensities of the (111) Bragg peak observed by neutron diffraction at 0, 1.5, and 3.0 GPa. The intensities between different pressures are normalized using the (111) nuclear Bragg peak intensities above T_C.

measurements under HP. Figure 3(c) shows the temperature dependencies of (111) Bragg peak intensity at 0, 1.5, and 3 GPa. The weak signal at high temperatures above T_C represents the nuclear contribution, and the magnetic contribution develops below T_C. Because the intensity of the magnetic Bragg peak should be proportional to the square of the ordered moment, the observation of nonsaturated (111) intensity below T_C at 0 and 1.5 GPa is an unusual behavior. It might suggest an unconventional FM ordering process that involves a strong magnetoelastic coupling, as evidenced by the deviation from the Debye-Gruneisen theory for the lattice constant below T_C [13]. Although the $\chi'(T)$ at 1.5 GPa shows a small decrease below ~ 20 K, there is no anomaly observed with neutron diffraction. Nonetheless, a weak diplike anomaly is visible around 40 K, which might be associated with the partial development of spiral AFM order that reduces the neutron intensity as that at 3 GPa shown below. With increasing pressures, the FM ordering T_C decreases, and the decrease of the (111) intensity corresponds to the reduction of the FM moment. At 3.0 GPa, the FM component, which developed below ~ 70 K, decreases sharply below ~ 50 K. This behavior is consistent with the $\chi'(T)$ data shown in Fig. 3(b). We also searched for additional magnetic peaks around (111) in the range of (HHL) with $0.8 \leq H \leq 1.2$ and $0.8 \leq L \leq 1.2$ below 50 K. However, no noticeable magnetic signal was observed. Although our present HP neutron diffraction experiments did not provide direct evidence for the spiral magnetic order, the sharp drop of (111) intensity at 3 GPa unambiguously demonstrated the destruction of FM order by pressure, and are consistent with either disordered state or an incommensurate spiral-type AFM state with short periodicity.

The stabilization of spiral magnetic order in $HgCr_2Se_4$ under HP is further supported by the comparison with $HgCr_2S_4$. As shown in Fig. 1, our $\rho(T)$ data at $1 < P < 3.5$ GPa share some similarities with metamagnetic $HgCr_2S_4$, which forms a spiral magnetic order below $T_N \sim 22$ K and can be easily converted into an FM state above ~ 1 T [23,24]. For $HgCr_2S_4$, its resistivity first changes from a semiconductor to metallicle state at ~ 80 K due to the presence of strong FM correlations, and then restores to a reentrant insulating behavior below 25 K when spiral magnetic order sets in. The upturn at low temperature changes back to metallic behavior under moderate magnetic field [24]. Thus, this comparison not only leads a strong support for the spiral order in $HgCr_2Se_4$ under pressure, but also highlights a very similar role of physical pressure as the chemical pressure realized via replacing Se with smaller S [25,26].

Based on the obtained T_C^{ρ}, $T_{\min}^{\rho}$ from resistivity and $T_C^{\chi'}$, $T_N^{\chi'}$ from magnetic susceptibility, we construct the temperature-pressure phase diagram of $HgCr_2Se_4$ as shown in Fig. 4. The evolution of the magnetic phase transitions can be visualized more vividly in a contour plot of $\chi'(T)$

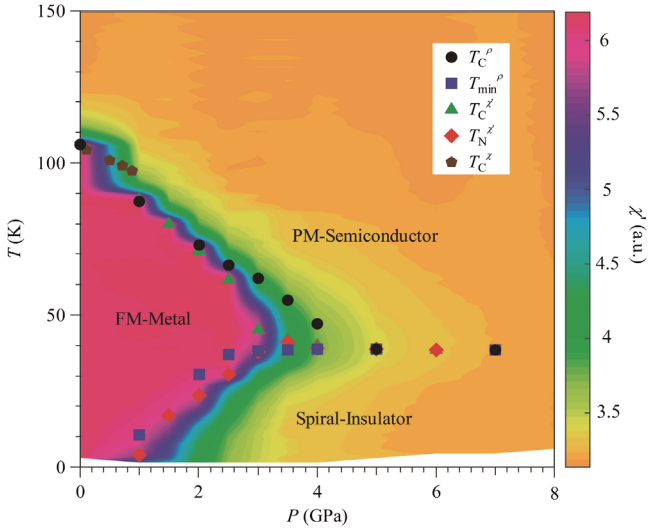

FIG. 4. Temperature-pressure phase diagram of n-type $HgCr_2Se_4$. The ferromagnetic ordering temperatures (T_C, black filled circle, green triangle, and brown pentagon), the upturn in resistivity ($T_{\min}$, blue square), and the spiral magnetic ordering temperatures (T_N, red rhombus) as a function of hydrostatic pressure.

superimposed in the phase diagram. It shows explicitly the gradual suppression of the FM order followed by the emergence and subsequent growth of new AFM, most likely a spiral magnetic order. From the phase diagram, we can also see that the FM and spiral magnetic order are merged at ~ 4 GPa, and the phase boundary between paramagnetic (PM) semiconducting and spiral insulating regions cannot be distinguished at higher pressures. Moreover, the phase diagram also highlights the fact that at ambient pressure $HgCr_2Se_4$ should be located close to a critical point where the spiral magnetic state strongly competes with the FM ground state.

Our present HP study provides direct evidence that can link the development of insulating behavior in n-type $HgCr_2Se_4$ with pressure destabilization of the FM ground state. According to a recent theoretical study on the chromium spinels [27], $HgCr_2Se_4$ is located inside the FM region at ambient pressure due to the presence of dominant nearest-neighbor (NN) FM interaction J_1, negligible second NN FM $J_2 \sim 0.0014 J_1$, and sizable third NN AFM $J_3 \sim -0.109 J_1$. In the phase diagram of $J_3/|J_1|$ vs $J_2/|J_1|$, $HgCr_2Se_4$ is close to the boundary between the FM and spiral state and the enhancement of either J_2 or J_3 relative to J_1 can drive it closer or into the spiral magnetic state. In the present case, the reduction of Cr-Cr distances under pressure that can effectively enhance both J_2 and J_3 should thus favor the spiral magnetic order. Actually, analyses of low-temperature specific heat have suggested the presence of AFM contributions inside the FM ground state at ambient pressure [11]. Apparently, the application of HP effectively tips the balance of competition between NN FM and third NN AFM interactions and should eventually

stabilize a spiral magnetic ground state. Because the chemical potential of half-metallic $HgCr_2Se_4$ is very small, a deviation from perfect ferromagnetism or even the stabilization of spiral magnetic order under pressure would reduce the *s-d* exchange splitting and destroy the metallic state by opening a gap between the Hg-6*s* and Se-4*p* bands [8,12].

In summary, our HP measurements highlight that *n*-type $HgCr_2Se_4$ is a very unique single-valent FM metallic system which involves strong coupling between lattice, electronic, and magnetic degrees of freedom. Pressure and magnetic field can tip the balance between FM and AFM interactions in $HgCr_2Se_4$ in an opposite way. HP suppresses the FM order by enhancing the AFM exchange couplings, and gradually stabilizes the spiral magnetic and insulating ground state. On the other hand, the magnetic field can easily modify the magnetic interactions to switch the ground state back to the FM metallic state. Through switching between different magnetic ground states, a CMR as high as $\sim 10^{11}\%$ can be achieved due to the strong coupling between the charge and spin degrees of freedom. Our present work thus provides a means for realizing a novel state where the CMR can be obtained via switching between two distinct electronic ground states in a single-valent system. By utilizing chemical substitutions, if we can push the FM transition to room temperature, this feature can be used to harvest applicable spin electronic devices, such as spin valve or the memory storage devices.

We thank Prof. Jianshi Zhou from University of Texas at Austin for the encouragement and the enlightening discussions. This work is supported by the National Key R&D Program of China (Grants No. 2018YFA0305700 and No. 2017YFA0302901), the National Natural Science Foundation of China (Grants No. 11888101, No. 11574377, No. 11834016, No. 11874400, No. 61425015, No. 11774399), the Strategic Priority Research Program and Key Research Program of Frontier Sciences of the Chinese Academy of Sciences (Grants No. XDB25000000, No. XDB07020100, and No. QYZDB-SSW-SLH013), and Beijing Natural Science Foundation (Z180008). A portion of this research used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. Y. Y. J. and J. P. S. acknowledge support from the China Postdoctoral Science Foundation and the Postdoctoral Innovative Talent program.

*jgcheng@iphy.ac.cn

[1] N. Menyuk, K. Dwight, and J. Arnott, Ferromagnetism in $CdCr_2Se_4$ and $CdCr_2S_4$, J. Appl. Phys. **37**, 1387 (1966).

[2] S. B. Berger and H. L. Pinch, Ferromagnetic resonance of single crystals of $CdCr_2Se_4$ and $CdCr_2S_4$, J. Appl. Phys. **38**, 949 (1967).

[3] P. K. Baltzer, H. W. Lehmann, and M. Robbins, Insulating Ferromagnetic Spinels, Phys. Rev. Lett. **15**, 493 (1965).

[4] P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, Exchange interactions in ferromagnetic chromium chalcogenide syinels, Phys. Rev. **151**, 367 (1966).

[5] N. I. Solin and N. M. Chebotaev, Magnetoresistance and hall effect of the magnetic semiconductor $HgCr_2Se_4$ in strong magnetic fields, Phys. Solid State **39**, 754 (1997).

[6] N. I. Solin, V. V. Ustinov, and S. V. Naumov, Colossal magnetoresistance of the inhomogeneous ferromagnetic semiconductor $HgCr_2Se_4$, Phys. Solid State **50**, 901 (2008).

[7] T. Arai, M. Wakaki, S. Onari, K. Kudo, T. Satoh, and T. Tsushima, Magnetoabsorption in single-crystal $HgCr_2Se_4$, J. Phys. Soc. Jpn. **34**, 68 (1973).

[8] G. Xu, H. M. Weng, Z. J. Wang, X. Dai, and Z. Fang, Chern Semimetal and the Quantized Anomalous Hall Effect in $HgCr_2Se_4$, Phys. Rev. Lett. **107**, 186806 (2011).

[9] L. Goldstein, P. Gibart, and A. Selmi, Transport properties of the ferromagnetic semiconductor $HgCr_2Se_4$, J. Appl. Phys. **49**, 1474 (1978).

[10] K. Minematsu, K. Miyatani, and T. Takahashi, Magnetic and electrical properties of impurity doped $HgCr_2Se_4$, J. Phys. Soc. Jpn. **31**, 123 (1971).

[11] W. D. Wang, A. Li, T. Dong, M. Li, X. L. Fu, S. S. Miao, P. Zheng, P. Wang, Y. G. Shi, J. L. Luo, and N. L. Wang, Anomalous behavior of low temperature specific heat in $HgCr_2Se_4$, J. Low Temp. Phys. **171**, 127 (2013).

[12] T. Guan, C. J. Lin, C. L. Yang, Y. G. Shi, C. Ren, Y. Q. Li, H. M. Weng, X. Dai, Z. Fang, S. S. Yan, and P. Xiong, Evidence for Half-Metallicity in *n*-Type $HgCr_2Se_4$, Phys. Rev. Lett. **115**, 087002 (2015).

[13] C. J. Lin, C. J. Yi, Y. G. Shi, L. Zhang, G. M. Zhang, J. Muller, and Y. Q. Li, Spin correlations and colossal magnetoresistance in $HgCr_2Se_4$, Phys. Rev. B **94**, 224404 (2016).

[14] C. Zener, Interaction between the d-shells in the transition metals. ii. Ferromagnetic compounds of manganese with perovskite structure, Phys. Rev. **82**, 403 (1951).

[15] P. Kistaiah, K. S. Murthy, and K. V. K. Rao, High pressure electrical resistivity of $HgCr_2Se_4$, J. Less-Common Met. **98**, L13 (1984).

[16] S. D. Guo and B. G. Liu, Density-functional-theory investigation of pressure induced semiconductormetal transitions in the ferromagnetic semiconductor $HgCr_2Se_4$, J. Phys. Condens. Matter **24**, 045502 (2012).

[17] I. Efthimiopoulos, A. Yaresko, V. Tsurkan, J. Deisenhofer, A. Loidl, C. Park, and Y. J. Wang, Pressurizing the $HgCr_2Se_4$ spinel at room temperature, Appl. Phys. Lett. **104**, 011911 (2014).

[18] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.123.047201 which includes crystal growth, experimental methods, and magnetic characterizations at ambient pressure.

[19] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Giant Negative Magnetoresistance in Perovskite-like $La_{2/3}Ba_{1/3}MnO_x$ Ferromagnetic Films, Phys. Rev. Lett. **71**, 2331 (1993).

[20] J.-G. Cheng, K. Matsubayashi, S. Nagasaki, A. Hisada, T. Hirayama, M. Hedo, H. Kagi, and Y. Uwatoko,

Integrated-fin gasket for palm cubic-anvil high pressure apparatus, Rev. Sci. Instrum. **85**, 093907 (2014).

[21] It can either be an artifact caused by a change of cooling rate during this measurement or arise from the pressure inhomogeneity that induces a distribution of antiferromagnetic transition temperatures.

[22] J. G. Cheng, K. Matsubayashi, W. Wu, J. P. Sun, F. K. Lin, J. L. Luo, and Y. Uwatoko, Pressure Induced Superconductivity on the Border of Magnetic Order in MnP, Phys. Rev. Lett. **114**, 117001 (2015).

[23] V. Tsurkan, J. Hemberger, A. Krimmel, H.-A. Krug von Nidda, P. Lunkenheimer, S. Weber, V. Zestrea, and A. Loidl, Experimental evidence for competition between antiferromagnetic and ferromagnetic correlations in $HgCr_2S_4$, Phys. Rev. B **73**, 224442 (2006).

[24] S. Weber, P. Lunkenheimer, R. Fichtl, J. Hemberger, V. Tsurkan, and A. Loidl, Colossal Magnetocapacitance and Colossal Magnetoresistance in $HgCr_2S_4$, Phys. Rev. Lett. **96**, 157202 (2006).

[25] H. Ueda and Y. Ueda, Pressure-enhanced direct exchange coupling observed in chromium spinels, Phys. Rev. B **77**, 224411 (2008).

[26] I. Efthimiopoulos, Z. T. Y. Liu, M. Kucway, S. V. Khare, P. Sarin, V. Tsurkan, A. Loidl, and Y. Wang, Pressure-induced phase transitions in the $CdCr_2S_4$ spinel, Phys. Rev. B **94**, 174106 (2016).

[27] Y. V. Tymoshenko, Y. A. Onykiienko, T. Muller, R. Thomale, S. Rachel, A. S. Cameron, P. Y. Portnichenko, D. V. Efremov, V. Tsurkan, D. L. Abernathy, J. Ollivier, A. Schneidewind, A. Piovano, V. Felea, A. Loidl, and D. S. Inosov, Pseudo-Goldstone Magnons in the Frustrated $S = 3/2$ Heisenberg Helimagnet $ZnCr_2S_4$ with a Pyrochlore Magnetic Sublattice, Phys. Rev. X **7**, 041049 (2017).