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CrAlGe: An itinerant ferromagnet with strong tunability by heat treatment

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We present a comprehensive investigation on CrAlGe and realize that it is an itinerant ferromagnet with strong tunability of the Curie temperature T_C and the spontaneous moment μ_0 depending on annealing heat treatment. While the value of T_C was previously reported to be 80 K with $\mu_0 \approx 0.41\mu_B$, in this work the two quantities attain values as high as 170 K and $0.66\mu_B$, respectively. Heat treatment does not cause changes of the lattice parameters and symmetry, but results in a slight narrowing of the Bragg peaks. The strong tunability of the itinerant ferromagnetism indicates significantly tunable hybridization between the Cr 3d electrons and the conduction bands, in agreement with the dominant Cr–Al/Ge bonds of this compound. Further tuning along the same line towards even stronger or weaker itinerant ferromagnetism promises an interesting follow-up to clarify the localized-itinerant duality of the 3d electrons in this compound.

Keywords: itinerant ferromagnet, localized-itinerant duality, heat treatment, hybridization

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Cooperative magnetism of itinerant d electrons is at the heart of modern condensed matter physics and closely related to a variety of emergent quantum phenomena such as unconventional superconductivity,[1] Mott metal–insulator transition,[2] and non-Fermi liquid.[3] In many of such systems, significant hybridization between the narrow d bands and extended conduction bands gives rise to strongly correlated electron behaviors with generally competing localized and itinerant electronic states. In spite of intensive investigations in the past decades, a satisfactory description of the magnetic phase transitions therein, which are frequently intertwined with some kind of quantum phenomena like unconventional superconductivity, still remains challenging.[4]

In this work, we focus on the ferromagnetic metal CrAlGe that crystallizes in the orthorhombic $TiSi_2$-type structure with space group $Fddd$ (No. 70). Previous studies on this compound show that the Curie temperature $T_C = 80$ K and the spontaneous moment $\mu_0 = 0.41\mu_B$ (Refs. [5–7]). The crystal structure of CrAlGe is characterized by a random occupation of Al and Ge at the 16f Wyckoff site, whereas Cr occupies the 8a site independently.[5] The projected ab plane consists of Al/Ge polyhedrons, of which Cr atoms are located at the center.[7] Random occupation of the nonmagnetic atoms Al and Ge appears to be crucial to the cooperative magnetism in this compound. For example, complex ferromagnetic cluster state was found to develop in CrAlGe subsequent to the ferromagnetic transition, and was ascribed to the Al/Ge disorder that results in competing magnetic interactions derived from Cr–Al and Cr–Ge bonds.[7] By contrast, the values of the Curie temperature and the spontaneous moment are substantially higher in MnAlGe, with $T_C = 503$ K and $\mu_0 = 1.7\mu_B$ (Ref. [8]). The latter compound crystallizes in a related structure of tetragonal Cu_2Sb-type and no chemical disorder takes place.

By studying the structural, magnetic, transport, and thermodynamic properties of CrAlGe, we show that the values of T_C and μ_0 in this compound are highly tunable with annealing heat treatment. This tunability indicates an important effect of the degree of crystallinity and/or the atomic disorder on the itinerant ferromagnetism. Interestingly, a good correlation of the strongly varied spontaneous moments μ_0 (between $0.41\mu_B$ and $0.66\mu_B$) and T_C (between 80 K and 170 K) is observed, suggestive of a localized-itinerant duality of the pertinent 3d bands and an intrinsic cooperative ferromagnetism following the Rhodes–Wohlfarth curve for ferromagnetic metals,[9] which relates the ordered moment to T_C. Compared to the chemical substitution studies that have also revealed varied values of T_C and μ_0,[10] annealing heat treatment of certain sample may yield much more reliable information on the ferromagnetic ordering and the associated spin fluctuations. The strong tunability will be discussed based on the disordered but dominant Cr–Al/Ge bond that forms the basis of the hybridiza-

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tion between Cr 3d and conduction bands.

The ploycrystalline CrAlGe samples were prepared by directly arc-melting stoichiometric Cr, Al, and Ge elements. Because considerable secondary phases were observed in the x-ray diffraction of the as-cast sample (Fig. 1(a)), annealing heat treatment in vacuum was carefully carried out to improve the sample quality. Prior to that, differential thermal analysis (DTA) was performed, which shows that CrAlGe melts at about 890 °C, see Fig. 1(b). We therefore choose four slightly lower temperatures of 700 °C, 750 °C, 800 °C, and 850 °C to anneal the sample for 24 h. In the following, we denote these samples by S700, S750, S800, and S850, respectively. The powder x-ray diffraction was measured by using a Rigaku SmartLab diffractometer. The dc magnetic susceptibility and magnetization measurements were carried out in an MPMS-SQUID (Quantum Design) magnetometer. The electrical resistivity was measured by a standard four-probe method, the specific heat by a thermal-relaxation method, and the seebeck effect by using one heater and two thermometers in a PPMS (Quantum Design).

The x-ray diffraction patterns recorded at room temperature for the four annealed samples, as well as the as-cast one are shown in Fig. 1(a). These results are in general in agreement with the data of previous reports.[5–7] While traces of secondary phases, mainly of unreacted Ge, can be discerned for S700 and S850, the samples S750 and S800 are single phase within the resolution limit of the current x-ray diffraction data. The lattice parameters obtained from the x-ray diffraction data for S800 are $a = 0.4750$ nm, $b = 0.8224$ nm, and $c = 0.8695$ nm, which are practically identical for all the samples. The considerably different magnetic properties of these compounds (to be shown below) prompt us to have a close inspection of the Bragg peaks with different annealing temperatures. As shown in Fig. 1(c) for the (131) reflections, one can discern that they are slightly different in broadness, which increases gradually in the order of S800, S750, S700 and S850. Assuming that the powders used for x-ray diffraction here are similar in size and shape for all the samples, the slightly different widths of the Bragg peaks indicate naively different degrees of local fluctuation of the lattice parameters. As will be shown below, the width of Bragg peaks can be roughly correlated with T_C, i.e., the samples with narrower Bragg peaks tend to have higher values of T_C. The reason why the samples S700 and S850 show broader Bragg peaks can be easily inferred from the DTA analysis (Fig. 1(b)). Probably, 700 °C is too low to allow for an enough thermal relaxation of the Al and Ge atoms, whereas 850 °C is too close to the melting point.

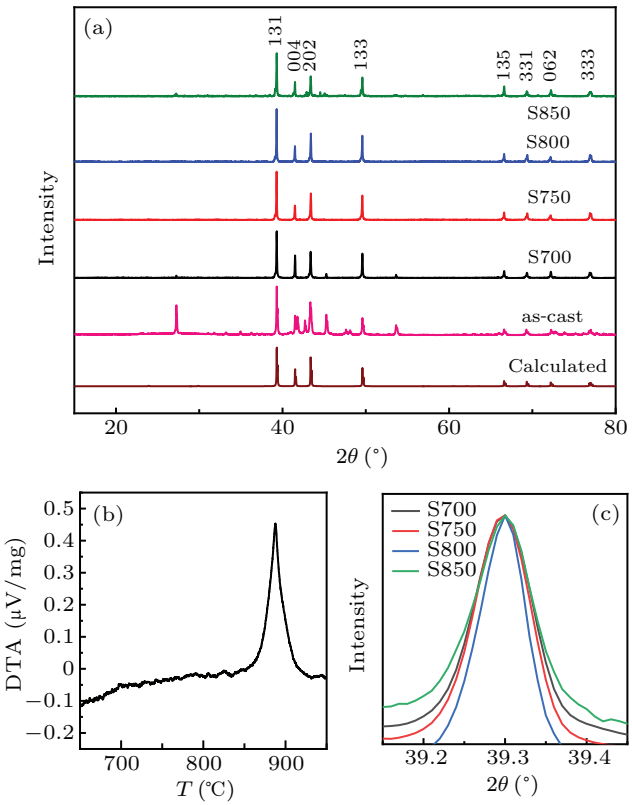


Fig. 1. (a) Powder x-ray diffraction patterns of the samples annealed at different temperatures, as compared to that of the as-cast sample. Calculated Bragg peaks are also shown for comparison. (b) The DTA thermogram of the as-cast CrAlGe sample. (c) Closeup of the (131) reflections, where slightly varied widths indicative of different crystallinities or Al/Ge disorders are observed.

Table 1. Magnetic and transport parameters characterizing the itinerant ferromagnetism in CrAlGe of different annealing heat treatments. The sample used in the previous work[5] was annealed at 800 °C. It, however, shows considerably different strengths of ferromagnetism to our S800 sample. The reason remains to be clarified.

T_{ann} (°C)	T_C (K)	*RRR*	A (μΩ·cm·K^{-2})	ρ_0 (μΩ·cm)	μ_0 (μ_B)	μ_s (μ_B)	μ_{eff} (μ_B)	μ_{eff}/μ_s	θ_p (K)
700	140	3.1	1.60×10^{-2}	111	0.52	0.54	1.74	3.22	156
750	160	4.0	1.69×10^{-2}	146	0.63	0.65	1.87	2.88	171
800	170	4.3	1.53×10^{-2}	156	0.66	0.68	1.89	2.78	179
850	147	3.2	1.65×10^{-2}	158	0.61	0.64	1.90	2.97	158
800 (Ref. [5])	80	–	–	–	0.41	0.45	1.89	4.20	95

In Fig. 2 we show the magnetic susceptibility $\chi(T)$ (inset) and the corresponding $\chi^{-1}(T)$ (main panel) for all the annealed samples. The applied external field was 1 T. Abrupt upturn in $\chi(T)$ indicating ferromagnetic transition is observed at much higher temperatures compared to the previously reported one (see below for the procedure to locate T_C). The values of T_C, which are tabulated in Table 1, vary significantly from 80 K (Ref. [5]) to 170 K of the sample S800. A bifurcation of the field-cooled and zero-field-cooled $\chi(T)$ in small fields (< 200 Oe) has been reported before and ascribed to the

onset of ferromagnetic cluster glass state.[7] Similar behaviors have also been observed in our samples with much higher values of T_C (not shown). By applying the Curie–Weiss law to the high temperature part ($T > 200$ K) where $\chi^{-1}(T)$ is linear, one can obtain the paramagnetic Curie temperature θ_p and the effective moment μ_{eff}, see Table 1. Compared to those reported previously, all our samples show much higher values of θ_p indicating greatly enhanced ferromagnetic interaction, though the values of μ_{eff} are all similar.

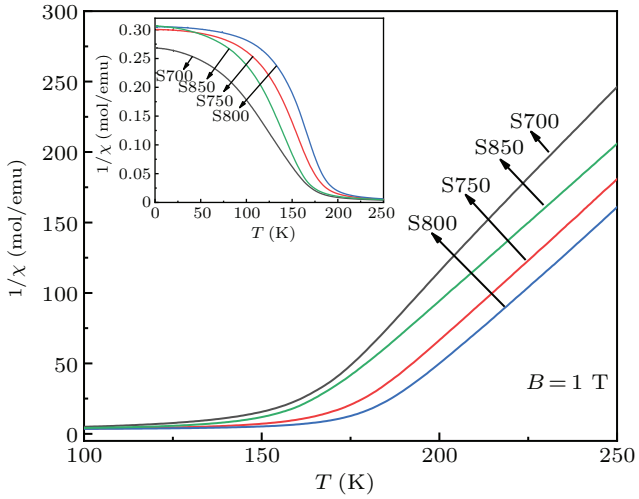


Fig. 2. The magnetic susceptibility $\chi(T)$ (inset) and the corresponding inverse magnetic susceptibility $\chi^{-1}(T)$ (main panel) as a function of temperature. The applied external field was 1 T.

To shed more light on the tunable ferromagnetism, in Fig. 3(a) we show the isothermal magnetization $M(B)$ measured at various temperatures for the S800 sample, with the highest T_C in this work. Re-plotting these data as M^2 versus H/M (the Arrott plot) in Fig. 3(b), one can accurately derive the values of μ_0 and T_C : μ_0 is obtained by linearly extrapolating isothermal M^2 versus H/M to $H/M = 0$ (see the dotted line in Fig. 3(b)), and T_C as the temperature where $\mu_0(T)$ reduces to zero, see Fig. 3(b) inset. Here, we obtain $\mu_0 = 0.66\mu_B$ and $T_C = 170$ K for S800. The varied strengths of the itinerant ferromagnetism in different CrAlGe samples are demonstrated in Fig. 3(c), where the $M(B)$ isotherms measured at 2 K for all the samples are compared. The $M(B)$ curve measured at 5 K for the sample with $T_C = 80$ K is reproduced from the literature[5] and shown in Fig. 3(c), too. It is apparent that the samples with higher values of T_C also have larger spontaneous moments. Moreover, a remarkable two-shoulder feature is observed in all the $M(B)$ curves, manifested as two inflections in the dM/dB versus B curves (Fig. 3(c) inset). The first one at 170 Oe marks the coercive field of the complex ferromagnetic state with glass-like clusters,[7] and the second one at 1.3 T is presumably related to the suppression of the ferromagnetic cluster state. Similar features are also discernible from the data reported previously,[5,7] though not discussed before. Finally, a roughly linear correlation between the values of T_C and μ_0 is depicted in Fig. 3(d). This is reminiscent of the Rhodes–Wohlfarth relation for ferromagnetic metals[9] that relates the ordered moment to T_C, offering a strong evidence that the highly tunable ferromagnetism is of an intrinsic feature of CrAlGe. Taking the magnetization value at $T = 2$ K and $B = 5$ T as an approximation to the saturation moment μ_s (Table 1) for all the samples investigated, one can readily estimate the Rhodes–Wohlfarth ratio μ_{eff}/μ_s, which is expected to be unity for typical ferromagnets with local magnetic moment. As shown in Table 1, while this ratio is much larger than unity in all the samples indicative of dominant itinerant character of the ferromagnetism, it becomes smaller as the value of T_C increases (for example, 3.22 for S700 versus 2.78 for S800). This observation offers a compelling evidence of the competition from local magnetism,[11] i.e., the local character in CrAlGe is slightly enhanced in the samples with higher values of T_C.

Figure 4 shows the resistivity for all the annealed samples as $\rho - \rho_0$ versus T. Here ρ_0 is the residual resistivity. The magnetic transitions can be confirmed as a slope change at T_C, see the derivative $d\rho/dT$ shown in the inset. The values of T_C obtained here are in good agreement with those determined from the magnetic measurements. The residual resistance ratio $RRR = \rho_{300\ K}/\rho_{2\ K}$ is rather small in all samples, partially due to the atomic disorder between Al and Ge. It, however, has an apparent correlation with T_C: the larger the value of RRR, the higher the magnetic transition temperature, see Table 1. Similarly, one can also recognize a correlation between the overall values of ρ–ρ_0 and T_C. This feature, like the correlation between the Rhodes–Wohlfarth ratio and T_C as discussed above, suggests again that the itinerant ferromagnetism in CrAlGe suffers competition from the partially localized character of the 3d band. The low temperature resistivity at $T < 20$ K was fitted to the Fermi-liquid description $\rho = \rho_0 + AT^2$ and all the fitting parameters are shown in Table 1. The A values, which are in the range of (1.5–1.7) $\times 10^{-2}$ μΩ·cm·K^{-2}, are three orders of magnitude larger than those of typical ferromagnetic elements[12] like Fe and Ni, indicative of strong spin fluctuations persisting deep into the ordered state of CrAlGe.

The specific heat measured between 2 and 200 K is shown in Fig. 5 for the sample S800. The ferromagnetic transition at $T_C = 170$ K manifests itself as only a weak and broad hump. This is in line with the strong spin fluctuations and the consequently reduced spontaneous moment of this material, considering that the magnetic contribution at T_C is proportional to μ_0^2/T_C. The low-temperature specific heat, shown in Fig. 5 inset, follows the description of $C/T = \gamma + \beta T^2$, with the electronic specific heat coefficient $\gamma = 12$ mJ/mol·K^2 and $\beta = 0.4$ mJ/mol·K^4, from which the Debye temperature $\theta_D = 244$ K can be obtained.

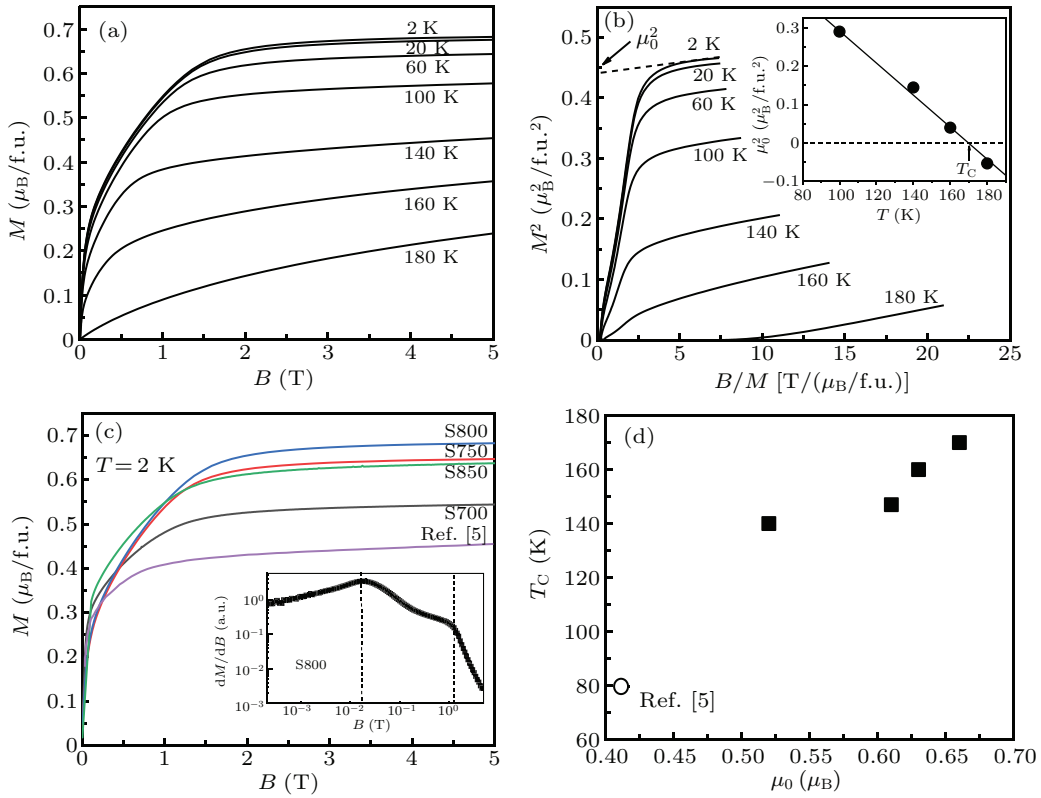


Fig. 3. (a) Isothermal magnetization $M(B)$ measured at various temperatures for the sample S800. (b) The same data of panel (a) shown as M^2 versus H/M plots, i.e., the Arrott plot. The spontaneous magnetic moment μ_0 is obtained by extrapolating H/M to zero, see the dashed line. Inset shows μ_0^2 versus temperature, from which T_C is read as the temperature where $\mu_0 = 0$. (c) $M(B)$ measured at 2 K for all the samples investigated in this work, as compared to the literature value of the sample with $T_C = 80$ K. Inset shows the corresponding field derivative dM/dB for S800. (d) T_C versus μ_0 for various CrAlGe samples investigated.

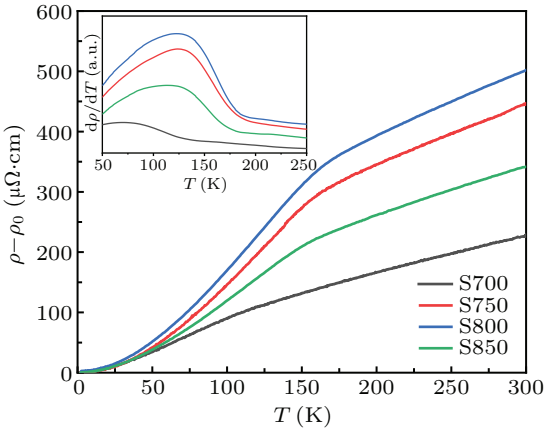


Fig. 4. The electrical resistivity of CrAlGe as a function of temperature. Inset shows d$\rho(T)$/dT, where a kink can be observed at T_C.

The Seebeck coefficient $S(T)$, as a sensitive transport probe of spin fluctuations, is shown in Fig. 6 for the samples S800 and S850. The $S(T)$ values of S800 ($T_C = 170$ K) are roughly 5 μV/K higher than those of S850 ($T_C = 147$ K) at $T > 100$ K. The room-temperature Seebeck coefficient of S800, $S = 45$ μV/K, is considerably large compared to that of typical d-electron ferromagnetic metal, like Fe (17 μV/K, Ref. [13]) and Ni (−20 μV/K, Ref. [14]). This is consistent with the conclusion of the recent studies that have pointed out the existence of enhanced Seebeck effect in itinerant magnetic systems with strong spin fluctuations.[15,16] The absence of clear signature at T_C in the $S(T)$ curves is related, at least partially, to the complex magnetic state due to ferromagnetic cluster glass.[7]

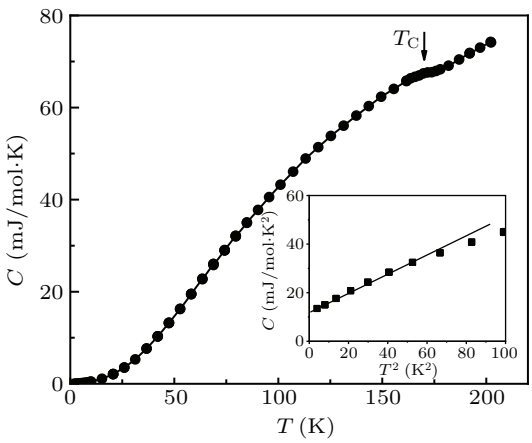


Fig. 5. The specific heat as a function of temperature for the CrAlGe sample S800. The ferromagnetic transition at $T_C = 170$ K is marked by a broad and weak hump. Inset shows C/T versus T^2 for $T < 10$ K.

First-principles total energy calculations[17] predict a ferromagnetic ground state of CrAlGe with ordered moments of $1.0\mu_B$. Although the values of μ_0 observed in our work are significantly larger than the previously observed one, they are still smaller than the theoretical expectation by more than 30%. By contrast, in MnAlGe where Al and Ge occupy two distinct atomic sites, the calculated magnetic moment per formula unit $\sim 1.7\mu_B$ is in well agreement with the observations.[8,17]

Markedly, the disorder between Al and Ge in CrAlGe can cause the magnetic moment on Cr varying locally from site to site, albeit with an unchanged average moment per formula unit.[17] The locally varied magnetic moments caused by Al/Ge disorder indicate a strongly varied hybridization between Cr 3d band and conduction bands of Al or Ge. This feature can likely be rooted in the crystal structure of CrAlGe,[7] where the Cr–Al/Ge bond (2.563 Å) in the *ab* plane is much stronger than the Cr–Cr bond (3.218 Å). This situation is different from MnAlGe that has much stronger Mn–Mn bond in *ab* plane ($\sim$ 2.8 Å).[17] On the other hand, the Cr–Cr bond along *c* is even weaker, with the interatomic distance 4.747 Å.

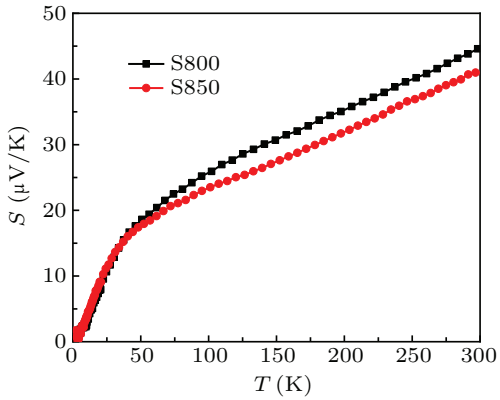


Fig. 6. The Seebeck coefficient as a function of temperature for the CrAlGe samples S800 and S850.

CrAlGe has been predicted to be half metallic with a high spin polarization ratio $P = 99\%$ (Refs. [17,18]), where the electronic density of states of the spin-up channel is nearly fully gaped. Looking carefully into the spin resolved electronic density of states,[17] one can find a sharp feature at the gap edge of the spin-up channel, near which the Fermi level is located. This band feature indicates that a local fluctuation of the Fermi level due to the locally varied hybridization of the Cr–Al/Ge bonds may cause a significant change of spin polarization ratio. This provides a naive explanation to the strong tunability of the itinerant ferromagnetism in CrAlGe.

In conclusion, we have found that the itinerant ferromagnetism in CrAlGe is strongly tunable with annealing heat treatment, with the values of T_C and the spontaneous moment being much higher than those reported in literature. A good correlation between the spontaneous moment and T_C indicates that the magnetic tunability is an intrinsic feature of this compound, hinting at a strong instability of the cooperative magnetism in response to the varied local crystallographic surroundings caused by Al/Ge disorder. Such disorder-induced instability offers a framework to interpret the competition between the itinerant and the localized character of the 3d band. This inference appears to be reasonable in view of the unique crystal structure where Cr is strongly bonded with Ge/Al, a feature highlighting the importance of the hybridization between Cr 3d band and conduction bands of Al or Ge. More efforts along this line are called for to further extend the range of tunability, towards an even stronger or even weaker ferromagnetism.

Acknowledgements

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References

[1] Pfleiderer C, Uhlarz M, Hayden S M, Vollmer R, Löfhneysen H V, Bernhoeft N R and Lonzarich G G 2001 *Nature* **412** 58
[2] Imada M, Fujimori A and Tokura Y 1998 *Rev. Mod. Phys.* **70** 1039
[3] Stewart G R 2001 *Rev. Mod. Phys.* **73** 797
[4] Brando M, Belitz D, Grosche F M and Kirkpatrick T R 2016 *Rev. Mod. Phys.* **88** 025006
[5] Yoshinaga S, Mitsui Y, Umetsu R Y and Koyama K 2015 *Phys. Procedia* **75** 918
[6] Yoshinaga S, Mitsui Y, Umetsu R Y, Uwatoko Y and Koyama K 2017 *J. Phys.: Conf. Series* **868** 012018
[7] Khan M U, Brock J A, Provino A, Belfortini C and Manfrinetti P 2017 *Phys. Rev. Mater.* **1** 034402
[8] Kamimura T, Ido H and Shirakawa K 1985 *J. Appl. Phys.* **57** 3255
[9] Rhodes P and Wohlfarth E P 1963 *Proc. R. Soc. A* **273** 247
[10] Masumitsu H, Yoshinaga S, Mitsui Y, Umetsu R Y, Hiroi M, Uwatoko Y and Koyama K 2019 *J. Magn. Magn. Mater.* **492** 165677
[11] Li R, Li F, Fang J, Tong W, Zhang C, Pi L and Zhang Y 2013 *J. Alloys Compd.* **577** 303
[12] Jacko A C, Fjærestad J O and Powell B J 2009 *Nat. Phys.* **5** 422
[13] Blatt F J, Flood D J, Rowe V, Schroeder P A and Cox J E 1967 *Phys. Rev. Lett.* **18** 395
[14] Abadlia L, Gasser F, Khalouk K, Mayoufi M and Gasser J G 2014 *Rev. Sci. Instrum.* **85** 095121
[15] Tsujii N, Nishide A, Hayakawa J and Mori T 2019 *Sci. Adv.* **5** eaat5935
[16] Sun P, Kumar K R, Lyu M, Wang Z, Xiang J and Zhang W 2021 *The Innovation* **2** 100101
[17] Fukuda Y and Fujii S 2016 *J. Alloys Compd.* **687** 17
[18] Eto S, Fukuda Y, Mitsui Y, Ito M, Koyama K and Fujii S 2019 *J. Phys. Soc. Jpn.* **88** 064709