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Importance of Doping and Frustration in Itinerant Fe-doped Cr₂Al

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Abstract

We have performed an experimental and theoretical study comparing the effects of Fe-doping of Cr₂Al, an antiferromagnet with a Néel temperature of 670 K, with known results on Fe-doping of antiferromagnetic bcc Cr. (Cr_{1-x}Fe_x)₂Al materials are found to exhibit a rapid suppression of antiferromagnetic order with the presence of Fe, decreasing T_N to ≈ 170 K for $x=0.10$. Antiferromagnetic behavior disappears entirely at $x\approx 0.125$ after which point increasing paramagnetic behavior is exhibited. This is unlike the effects of Fe doping of bcc antiferromagnetic Cr, in which T_N gradually decreases followed by the appearance of a ferromagnetic state. Theoretical calculations explain that the Cr₂Al-Fe suppression of magnetic order originates from two causes: the first is band narrowing caused by doping of additional electrons from Fe substitution that weakens itinerant magnetism; the second is magnetic frustration of the Cr itinerant moments in Fe-substituted Cr₂Al. In pure-phase Cr₂Al, the Cr moments have an antiparallel alignment; however, these are destroyed through Fe substitution and the preference of Fe for parallel alignment with Cr. This is unlike bulk Fe-doped Cr alloys in which the Fe anti-aligns with the Cr atoms, and speaks to the importance of the Al atoms in the magnetic structure of Cr₂Al and Fe-doped Cr₂Al.

Keywords: Antiferromagnetic Ordering, Magnetic Frustration, Cr₂Al

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I. Introduction

Magnetism in alloys, particularly those containing iron, has attracted much attention over the past several decades, perhaps in part motivated by the tremendous practical and engineering importance of such materials. One particular alloy system fairly well-studied is that of Fe-Cr as these alloys find numerous applications in the production of corrosion-resistant stainless steels [1], nuclear reactor containment vessels [2], and corrosion protection coatings [3]. However, most of these studies have been confined to the Fe-rich part of the phase diagram since these compositions represent the operational range of most applications. Less well-studied, though reasonably well-understood, are the features of the Cr-rich part of the phase diagram, particularly with respect to magnetic behavior. Cr alloys and compounds in particular have sparked recent interest as 3-D structured materials such as CrAs have been shown to exhibit superconductivity under pressure [4–6]. Given that a feature common to unconventional superconducting systems is the emergence of superconducting behavior from a long-range antiferromagnetically (AF) ordered state, it is imperative that these AF interactions are well-understood.

As is well-known, body-centered cubic (bcc) Cr is an itinerant antiferromagnet with a Néel temperature (T_N) of 312 K [7] with an incommensurate spin-density wave forming on the background of the AF state. The effects on the AF state with respect to alloying Cr with Fe has been the subject of some investigation which we now briefly summarize. In an early study, Mitchell and Goff [8] studied the depression of the T_N through doping Cr with Fe, finding that this rate was similar to that of Mo doping, which is perhaps surprising considering the magnetic character of Fe. A somewhat more recent study by Moze *et al.* [9] examined highly dilute (< 5 at. % Fe) alloys, finding an ordered moment on the Fe-site with little effect on the Cr atoms, a result we corroborate below. With respect to theory, an early work by Kakehashi [10] found that Fe substitution led to a loss of local moment on the Cr site in contrast to the aforementioned experimental results of Moze *et al.* [9]. In a more recent theory-based investigation, Klaver *et al.* [11] reported a somewhat variable but significant Fe moment on the Cr-rich side of the phase diagram. These works generally find that Fe atoms embedded within the Cr bcc structure carry a sizable local moment, with the T_N decreasing gradually as the Fe content increases (i.e. ~ 10 K per atomic percent

Fe [8]). Ultimately, the material transitions to a ferromagnetic state for Fe concentrations above about 20%. In this work we shall discuss experimental and theoretical findings on the Fe-alloyed Cr_2Al system that would naturally be expected to show similar response. However, the behavior exhibited by Cr_2Al is radically different from Cr. While Cr_2Al is indeed an itinerant antiferromagnet like bcc Cr, we find that alloying with Fe produces a much more rapid decrease of T_N of approximately 50 K per percent Fe added. Additionally, no magnetism is present in $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$ from above $x = 0.125$ up to $x = 0.500$. We find that we can explain these interesting behaviors in terms of a combination of two factors: charge doping with additional electrons and magnetic frustration, a feature of less prominence in the aforementioned dilute Fe-Cr system.

As depicted in Figure 1, Cr_2Al crystallizes in a tetragonal MoSi_2 -type structure (space group 139). It exhibits antiferromagnetic behavior with a T_N of approximately 670 K [12–14]. Each Cr1 atom is nearest-neighbor coordinated with 4 other Cr atoms arranged in a square, centered and vertically displaced with respect to atom Cr1. The shortest distance between Cr atoms in Cr_2Al is from Cr1-Cr2 (2.433 Å), while the next nearest neighbor distance is from Cr2 to Cr2' at 2.99 Å (cf. the a and b lattice parameters). The structure thus can be described as four Cr planes interpenetrating a body-centered tetragonal Al lattice with two planes located on either side of the body-centered atom. The inner Cr planes have their atomic positions in registry with the corner Al atoms while the outer Cr planes have their atomic positions aligned with the body-centered Al atoms. Even though the Al atoms play an important structural role, one might expect them to have little effect on the magnetism of the compound. Below we shall see that this is in fact not the case.

The antiferromagnetic ground state of Cr_2Al , as experimentally determined by Atoji [12] and Kallel and Deberge [13] and later confirmed by our first principles density functional theory calculations (below), can be described as ferromagnetic alignment within the Cr planes (i.e. next-nearest Cr neighbors) and an antiferromagnetic alignment between adjacent planes (i.e. nearest Cr neighbors). This behavior follows the pattern of magnetic interactions becoming more ferromagnetic for transition

group metals as the distance between $3d$ elements is increased. Neutron diffraction experiments (Ref. [12]) show that canted spins are aligned 65° with respect to the c axis, essentially aligned parallel to the direction of the Cr1-Cr2 bond. It was therefore proposed that the antiferromagnetic ordering in Cr_2Al is a result of the exchange coupling between nearest neighbor Cr atoms [14]. Indeed, we will see that Cr_2Al is an itinerant antiferromagnet, as careful theoretical efforts to discern the existence of a ferromagnetically ordered state (including fixed-spin moment calculations) find no such state.

A previous doping study of Cr_2Al was performed with the substitution of Fe on the Cr site [14]. The MoSi_2 crystal structure was maintained for a high level of Fe substitution, $(\text{Cr}_{0.88}\text{Fe}_{0.12})_2\text{Al}$, and the value of T_N decreased with increased doping concentration down to 310 K for the composition $(\text{Cr}_{0.925}\text{Fe}_{0.075})_2\text{Al}$. Further doping to the composition $(\text{Cr}_{0.915}\text{Fe}_{0.085})_2\text{Al}$ yielded an ambiguous value for T_N in the range 100-300 K. Antiferromagnetic ordering was suppressed altogether for the composition $(\text{Cr}_{0.88}\text{Fe}_{0.12})_2\text{Al}$. This decrease in T_N was ascribed to the increased separation distance between neighboring Cr planes in the unit cell which in turn reduced the Cr-Cr magnetic interactions and the moment they produce [14]. In $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$, a factor which has not been considered until now is the interplay of the magnetic energies in the system. The addition of a dopant such as Fe has been experimentally shown to decrease the average moment on the Cr/Fe sites [14]. The extra magnetic energy introduced by the presence of Fe in the Cr_2Al structure has been predicted to produce interesting electronic properties once the magnetism in the compound is suppressed. In this report, the magnetic effects resulting from the substitution of Fe for Cr are presented in detail. These results are complemented by theory that demonstrates the doping and magnetic frustration-induced suppression of antiferromagnetism with Fe substitution.

II. Experimental

The $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$ samples with compositions $0 \leq x \leq 0.5$ were synthesized from high purity elements (all 99.996% or greater) purchased from Alfa Aesar, Inc. The constituent elements were arc-melted under Ar atmosphere, placed in alumina crucibles, sealed in a partially evacuated silica ampoule,

and annealed for 48-72 hours at 1050°C. Table I lists all compositions and heat-treatments used in this investigation.

Structural characterization of the compositions was done using a PANalytical X'Pert Pro MPD X-ray powder diffractometer. The X-ray apparatus uses Ni-filtered Cu K_α radiation; the solid state detector has a 2.122° active length. All scans were collected from 5-90° 2θ for 40 minutes. PANalytical HighScore-Plus software was used for phase identification. Impurities were less than 5% by mass for each of the samples. Rietveld refinements were performed using FullProf 2.05 [15] and typically resulted in R_{wp} values of ~6.3-7.3 with R_{exp} values of ~5.2-5.7; a typical refinement is shown in Figure 1a and the final results are presented in Table I.

The temperature-dependent resistance was measured using a Quantum Design Physical Property Measurement System (PPMS) on specimens cut from the arc-melted and annealed ingots. The temperature sweeps (< 2 K/min) were in the range of 5 - 400 K. All compositions showed metallic behavior where $\rho(T)$ follows a T^3 dependence. The value of ρ_{300K} generally increased with doping, following Nordheim's rule for alloying [16].

The dc magnetization as a function of temperature was measured using a Quantum Design Magnetic Properties Measurement System (MPMS) SQUID magnetometer; the oven option was used to access temperatures above 400 K. Typically, the samples were cooled to 5 K after which point the magnetic field was applied (either 10^3 or 10^4 Oe) and data collected upon warming (zfc). For paramagnetic samples, the data were fitted to the modified Curie-Weiss law, $M/H = \chi = C/(T-\theta) + \chi_0$, where χ is magnetic susceptibility, C is Curie constant, θ is Weiss temperature, and χ_0 is a temperature-independent term that includes contributions from Pauli and van Vleck paramagnetism and Landau diamagnetism. The fits applied above 100 K are presented in Table II together with the estimation of effective moment, μ_{eff} , extracted using the relation $\mu_{eff} = (3Ck_B/N_A)^{1/2}$, where k_B and N_A are the Boltzmann and Avogadro constants, respectively [17].

III. Experimental Results

In Figure 1a we present a typical XRD plot measured for the $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$ system for $x=0$. It refines with tetragonal space group $I4/mmm$ (No. 139), presented pictorially in Figure 1d. The changes in the positions of the (200) and (213) reflections with increased Fe concentration are highlighted in Figures 1b and 1c. The refinements of the XRD patterns that detail these changes are presented in Table I. As more Fe is substituted for Cr, the a and b lattice parameters contract while c elongates. In Figure 2 the evolution of the refined lattice parameters with Fe content are presented. As c/a approaches 3 between $x=0.2$ and $x=0.25$, the unit cell is better described by the bcc crystal structure ($R_{wp}/R_{exp} = 1.01$) than by the MoSi_2 structure ($R_{wp}/R_{exp} = 1.39$). This is true for both $(\text{Cr}_{0.75}\text{Fe}_{0.25})_2\text{Al}$ and $(\text{Cr}_{0.5}\text{Fe}_{0.5})_2\text{Al}$ compositions. This result is not necessarily surprising given the high propensity of both Cr and Fe to form bcc solid solutions with Al, particularly at higher temperatures [18–22]. What is surprising is the retention of a single phase upon cooling to room temperature. Though the full ternary system is well-reported at higher temperatures, there is little information present in the literature relating to temperatures below 600°C [23]. From the 600°C phase diagram, however, it is predicted for this composition that two phases will form from a high temperature solid solution of Cr, Fe, and Al - Cr_2Al and a bcc solid solution of Cr, Al, and Fe. The presence of a single phase suggests that the phase diagram for the ternary Cr-Fe-Al system needs some reevaluation.

The temperature-dependence of magnetic susceptibility is plotted in Figure 3. The inset of the same figure presents the evolution of the antiferromagnetic transition temperature with increased x . Table II lists the value of T_N and the resulting fits and analyses using the modified Curie-Weiss function. The parent Cr_2Al has a $T_N = 670(8)$ K, in accord with the previously reported value of 663 K [14]. With the addition of a very small quantity of Fe (i.e. for the composition $(\text{Cr}_{0.975}\text{Fe}_{0.025})_2\text{Al}$), the value of T_N falls to ≈ 565 K (Table II). Further increases in doping concomitantly decrease T_N until there is no apparent antiferromagnetic transition above 5 K at the composition $(\text{Cr}_{0.875}\text{Fe}_{0.125})_2\text{Al}$.

In Figure 3 it is also shown that as Fe concentration increases to $x=0.125$ and beyond, the samples become increasingly paramagnetic. Referring to the results from the Curie-Weiss listed in Table II, it is evident that the effective magnetic moment per Cr/Fe (i.e. transition metal element or TM) increases from ≈ 0 for $(\text{Cr}_{0.875}\text{Fe}_{0.125})_2\text{Al}$, to $0.39(3) \mu_B/\text{TM}$ for $(\text{Cr}_{0.5}\text{Fe}_{0.5})_2\text{Al}$. It is interesting that the system continues with metallic behavior as gauged by resistive measurements even though μ_{eff} is increasing so dramatically. From the same Curie-Weiss fits, we note that the values of θ become less negative with x , behavior which accents the diminishing of long-range antiferromagnetic interactions induced by Fe substitution. No other magnetic ordering is exhibited. The resulting magnetic phase diagram of the $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$ system is plotted in Figure 4 and includes our experimentally obtained values of T_N and μ_{eff} . The data from previous works [14] which include T_N and the values of the ordered moments, μ , from neutron diffraction experiments at 1.5-4.2K are also included for completeness. We find that the antiferromagnetic region lies between $x=0$ and $x=0.125$, after which point the system shifts to paramagnetic behavior. It is quite surprising that Fe does not make a greater contribution to the formation of a new magnetic phase once the antiferromagnetic ordering of the parent Cr_2Al is suppressed, as is found in similar alloys [24]. The principal goal of the next section of this paper is to explain this unexpected behavior.

IV. Discussion

In order to understand why antiferromagnetic Cr_2Al that is doped with ferromagnetic Fe generates a non-magnetic ground state, we have performed first principles density functional theory calculations on Cr_2Al using the linearized augmented planewave all-electron code WIEN2K [25] and compared these findings with results from the same analysis performed on Cr-Fe alloys. In performing our calculations we have used the generalized gradient approximation of Perdew, Burke and Ernzerhof [26] throughout with well-converged basis sets ($RK_{\text{max}}=9.0$, where R is the smallest sphere radius and K is the magnitude of the largest planewave vector) for all calculations.

We calculated the experimentally-determined antiferromagnetic (AF) ground state (cf. Fig. 1d) in which neighboring nearest-neighbor Cr planes are antiferromagnetically aligned and ferromagnetic alignment is present *within* the Cr planes. In addition, we have conducted fixed-spin moment calculations to search for a possible ferromagnetic state. No such ferromagnetic state was found; indeed, the calculated energy increased monotonically from the AF value as the moment was increased such that the magnetism in Cr_2Al can clearly be described as itinerant, and the energy of the AF state relative to a non-spin-polarized (NSP) state is reflective of the actual ordering energy of the system. This is unlike local moment formation, in which the actual ordering energy is much less than the energy difference of AF and NSP states. In this case we find an actual ordering energy of 560 K/Cr, which agrees relatively well with the experimental T_N of ≈ 670 K. For comparison, we performed analogous calculations for a nearest neighbor AF state in bcc Cr. As with Cr_2Al , we find this to be an itinerant state, with a substantially lower ordering energy of 276 K/Cr, again in good agreement with the experimental T_N of bcc Cr of 313 K. We have not attempted to model the actual spin-density-wave ground-state of Cr, but note that this effect is a relatively small one and seems to have comparatively little impact on the effect of Fe alloying.

Next, to study the effects of Fe alloying in these two systems, we have performed calculations within the virtual crystal approximation. Here we have added electrons to simulate the effect of Fe addition. In addition, we have performed supercell calculations in which one of the four equivalent Cr atoms is substituted by a Fe atom (we considered a $2\times 2\times 2$ supercell of bcc Cr, which as an fcc structure has 4 Cr sites in the Wigner-Seitz primitive cell). While this situation represents a somewhat higher Fe concentration than those at which the Cr_2Al -Fe alloy remains antiferromagnetic, the results of this calculation provide much useful insight into the origin of these disparate behaviors.

For virtual crystal approximation (VCA) calculations, depicted in Table III are the ordering energies for a series of $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$ and $\text{Cr}_{1-x}\text{Fe}_x$ alloys, with the experimental antiferromagnetic order assumed for both cases. The table shows a rapid reduction in ordering energies with charge doping for the $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$ series, but no such effect for $\text{Cr}_{1-x}\text{Fe}_x$. In fact, for this material, the ordering energy actually

increases with x . This is consistent with a large local moment energy created by the additional charge as a means of simulating Fe alloying.

For our purposes, it is illustrative to consider a comparison between these calculations. Fig. 5 presents three densities-of-states (DOS) studied within VCA: pure metallic Cr, Cr_2Al , and $(\text{Cr}_{0.75}\text{Fe}_{0.25})_2\text{Al}$; we plot the non-spin-polarized DOS for clarity since the effects are evident in these. With the exception of a likely Van Hove singularity [27] in the pure Cr DOS at approximately 1.5 eV above the Fermi energy, the plots exhibit, at first glance, comparatively similar behavior. A more careful observation, however, finds important differences. The middle plot of non-magnetic Cr_2Al shows significantly wider bands than the pure Cr plot, with regions of significant DOS even 5 eV above the Fermi energy. This is consistent with our finding of Cr_2Al as an itinerant antiferromagnet; accordingly, the T_N of 670 K is much higher than the 311 K value for pure Cr. Upon doping with Fe, however, the bands become significantly narrower. For example, the broad maximum centered at 1.75 eV above the Fermi energy in Cr_2Al moves to 1 eV in the VCA plot. Some, but not all, of this shift is attributable to a rigid-band-like effect motion of the bands relative to E_F with doping; however, the narrowing of the bands with doping is characteristic of weakening magnetism in an itinerant system. Accordingly, the VCA calculation, when performed as a spin-polarized calculation, converges to a non-spin polarized result which is indicative of a lack of magnetism in $(\text{Cr}_{0.75}\text{Fe}_{0.25})_2\text{Al}$. This phenomenon is experimentally observed above.

In order to study this result in more detail, as well as check the applicability of the VCA, we performed spin-polarized calculations (including fixed-spin moment, FSM, calculations) of $(\text{Cr}_{0.75}\text{Fe}_{0.25})_2\text{Al}$ in a cell with 3 Cr and 1 Fe atoms. The ground state is magnetic, but has an observed ordering energy (relative to the non-spin-polarized case) of only 30 % of the value of Cr_2Al . In addition, from the FSM calculations we find at least one metastable solution only 4 meV above the ground state in a different magnetic arrangement. This near-degeneracy of states hints at possible frustration. In fact, in the ground state the Fe prefers to align parallel to its nearest neighbor Cr. This arrangement will tend to

frustrate the Cr system's desire to order antiferromagnetically because we find that the Fe atoms have a strong tendency, roughly 3000 K/Fe, to align ferromagnetically with neighbors. This means that any clusters of adjacent Fe (whose frequency increases with the *square* of the Fe concentration) will cause the surrounding Cr atoms to tend towards FM order, which will in turn be frustrated by the AF ordering preferred by the Cr. The net result is a highly disordered, degenerate state with T_N quickly driven to zero, as observed experimentally.

To demonstrate this quantitatively, in Figure 6 below we present the results of these fixed spin moment calculations for both situations – Cr_3FeAl_2 (i.e. $x=0.25$ for $(\text{Cr}_{1-x}\text{Fe}_x)\text{Al}$) and Cr_3Fe (i.e. $x=0.25$ for $\text{Cr}_{1-x}\text{Fe}_x$). The results demonstrate a radical difference in the behavior of these putatively similar systems. In particular, the base Cr_3Fe alloy demonstrates a single minimum at a moment value of approximately $0.45 \mu_B/\text{TM}$. From the same figure we readily see that energies rapidly increase away from this point. This means that in this system there is only one stable state. Hence, the system will choose this magnetic state, with robust ordering, as its groundstate. The situation is radically different for Cr_3FeAl_2 . This system shows a pair of nearly degenerate minima, only a few meV apart, for moments of approximately $0.23 \mu_B$ and $0.45 \mu_B/\text{TM}$. Hence, at finite temperatures both of these states will be stable and accessible. Since these represent very different configurations, the system will have difficulty choosing an electronic groundstate. Effective frustration will result and the value of T_N will be quickly reduced, again as observed in the experimental results.

Conclusions

A doping investigation of the Cr_2Al antiferromagnet and a comparative theoretical investigation of Fe alloying of this compound in relation to Fe-alloyed bcc Cr was carried out. In the experiment, antiferromagnetic ordering was reduced rapidly with Fe alloying and completely destroyed at the composition $x=0.125$ with a paramagnetic state prevailing at doping concentrations above this point. Theoretical calculations explain this rapid suppression of magnetism, as well as a lack of magnetism in

the more heavily alloyed samples, as stemming from a combination of charge doping and magnetic frustration arising from competing near-degenerate states. This is quite unlike the situation in Fe-alloyed Cr, in which local moments develop on the Fe atomic site, the magnetism disappears more slowly with Fe doping, and magnetism transitions directly from antiferromagnetism to weak ferromagnetism.

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List of Tables

Table I. Sample compositions and resultant lattice parameter refinements of $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$. For compositions $0 \leq x \leq 0.2$ the structure refines as tetragonal $I4/mmm$; for compositions $x \geq 0.25$ the structure refines as cubic $Im\bar{3}m$.

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Table III. Comparison of $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$ and $\text{Cr}_{1-x}\text{Fe}_x$ ordering energies, with x .

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x	a (Å)	c (Å)	c/a	V (Å ³)
0.00	3.0042(2)	8.647 (1)	2.878	78.04 (1)
0.025	3.0016(3)	8.692(1)	2.896	78.31(1)
0.050	2.9849(2)	8.699 (1)	2.914	77.51(1)
0.075	2.9795(4)	8.717(1)	2.926	77.38(2)
0.100	2.9735(3)	8.711(1)	2.930	77.02(1)
0.125	2.9688(3)	8.716(1)	2.936	76.82(1)
0.150	2.9648(3)	8.725(1)	2.943	76.69(1)
0.200	2.9542(3)	8.740(1)	2.959	76.28(1)
0.250	2.9403(3)	-	1	25.420(4)
0.500	2.9069(2)	-	1	24.564(3)

Table II. Magnetic properties of $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$ samples; TM: transition metal

x	T_N (K)	C (10^{-3} emu K mol $^{-1}$ Oe $^{-1}$)	μ_{eff} (μ_B/TM)	θ (K)	χ_0 (10^{-4} emu mol $^{-1}$ Oe $^{-1}$)
0	670(8)	--	--	--	--
0.025	565(11)	--	--	--	--
0.050	466(15)	--	--	--	--
0.075	344(6)	--	--	--	--
0.100	170(7)	--	--	--	--
0.125	--	0.43(18)	0.03(6)	-34.4(3)	4.32(5)
0.150	--	13.3(6)	0.16(3)	-10.9(3)	4.47(2)
0.250	--	26.9(4)	0.23(2)	-7.2(8)	5.11(1)
0.500	--	74.8(4)	0.39(3)	-6.1(3)	6.27(1)

Table III. Comparison of $(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$ and $\text{Cr}_{1-x}\text{Fe}_x$ ordering energies, with x .

x	VCA ordering energy/ $3d$ (K)	
	$(\text{Cr}_{1-x}\text{Fe}_x)_2\text{Al}$	$\text{Cr}_{1-x}\text{Fe}_x$
0	560	276
0.025	398	329
0.05	258	367
0.075	146	367
0.10	60	354
0.125	<1	332

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6