

Stabilization of the hcp structure in the ruthenium-substituted high-entropy Cantor alloys $\text{Cr}_{20}\text{Mn}_{20}(\text{Fe}_{20-x}\text{Ru}_x)\text{Co}_{20}\text{Ni}_{20}$ ($0 \leq x \leq 20$) and their magnetic and structural properties

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While the valence electron concentration (VEC) of the system $\text{Cr}_{20}\text{Mn}_{20}(\text{Fe}_{20-x}\text{Ru}_x)\text{Co}_{20}\text{Ni}_{20}$ ($0 \leq x \leq 20$), where Fe is partially substituted by Ru, remains at eight electrons per atom (e/a), the structure undergoes a change from single-phase fcc ($x = 0$) to a two-phase fcc/hcp system as x increases, with the VEC of both phases remaining at or very close to 8 e/a. The hcp phase forms already at 5 at% Ru substitution. From studies on thermal expansion determined through x-ray diffraction, magnetization, and Mössbauer spectroscopy, we find that the fcc phase is magnetically active and possesses moment-volume instabilities with energetically close-lying low-spin and high-spin states, while the hcp phase is nonmagnetic in accordance with the predictions of theory. The results show that the hcp phase can be stabilized at a volume fraction of up to 80% under ambient conditions in a predominantly 3-d alloy with VEC = 8 e/a.

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I. INTRODUCTION

Alloys made up of five or six elements with equiatomic stoichiometry are known as high-entropy alloys (HEAs) [1,2]. Many of these stabilize in a single-phase, high-symmetry crystal structure such as fcc, bcc, or hcp [3–5]. In many cases, such multi-element systems with nonequiatomically stoichiometry can also be stabilized as single- or multiphase alloys. These are referred to as compositionally complex alloys (CCAs) and can also acquire the σ phase next to high-symmetry crystal structures [6–8].

Initially, the main interest in HEAs and CCAs was in their favorable mechanical and corrosion-resistant properties [3,9–12]. It eventually expanded towards interest in the magnetic [7,13–16], transport [17–19], and crystallographic properties, all of which are interrelated through fundamental electronic properties [20–22]. Today, such studies are widely undertaken both theoretically and experimentally to understand the basic physical phenomena underlying both the macroscopic and microscopic properties of these complex alloy systems. On the theory side, *ab initio* calculations provide information on the ground-state properties and the results can be used as a guide for synthesizing new materials [23]. Machine-learning techniques are also particularly useful for this purpose [24–26].

The basic physical properties of alloys and compounds of 3-d elements and, to a large extent, their alloys and compounds with the main group elements are governed by

the valence electron concentration VEC, calculated as the concentration-weighted number of s and d electrons of the individual constituent elements making up a crystallographically single-phase alloy. For multiphase alloys, the VEC is not valid for the whole of the alloy and should be considered for each individual phase. The VEC scheme is a well-established experimental fact that reaches back to the foundation of the Slater-Pauling rule, which provides a systematic scheme for the compositional variation (namely, the VEC variation) of the magnetic moment and of the stability ranges of crystal structures, particularly of fcc and bcc [27–30]. The use of this rule has become indispensable also for interpreting and understanding the general physical properties of HEAs and CCAs.

Among the HEAs, studies of alloys having high-symmetry crystal structures fcc and bcc date back as the earliest. The fcc phase is readily formed by combining various 3D elements, whereas the bcc phase is obtained by adding a main group element from group 13 or 14 [31–33]. HEAs with the hcp structure were obtained somewhat later. These were first formed by combining hcp rare-earth elements in equiatomic compositions [5,34]. Later combinations of various elements in group 3 and 4 and some combinations of 4D and 5D elements with close-packed structures led to the stabilization of hcp-structured HEAs [35–49], some even having superconducting properties [50–55]. Elements from group 2 can also be incorporated into these so that equiatomic and off-equiatomic alloys in the hcp state are formed [56]. Therefore, in most cases, some combination of hcp elements are required to form an hcp HEA or a CCA.

It has been shown, however, that applying hydrostatic pressure of about 14 GPa to the fcc Cantor alloy (containing no hcp elements other than Co) will cause it to transform into the hcp state [57]. The question then arises as to whether the

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hcp phase of the Cantor alloy can also be stabilized in the hcp structure by substitution of other elements with the condition that the VEC remains as 8 e/a (electrons per atom). This makes up the theme of this work. Here we gradually substitute Fe with the equi-electronic 4D hcp element Ru and investigate the conditions for the stability of the hcp structure through x-ray diffraction (XRD), scanning electron microscopy (SEM), magnetization, and Mössbauer spectroscopy studies. Before presenting the results, we provide a brief background on the subtleties of the hcp phase at VEC = 8 e/a, especially in relation to magnetic properties.

II. BACKGROUND

The periodic system of the 3D, 4D, and 5D transition-metal elements shows a systematic variation in the ground-state crystallographic structures when followed from group 3 to group 12 [27]. Groups 3 and 4 are hcp, and 5 and 6 are bcc. Groups 7 and 8 are hcp, except for Mn and Fe. Mn has a complex cubic structure and Fe is bcc. It has been shown by thermodynamic considerations that the structure of Fe in the ground state would have also been hcp had bcc-Fe been nonmagnetic [28]. On further following the transition series, groups 9–11 are fcc, except for Co, which is hcp.

Group 8 elements have VEC = 8 e/a and are hcp. Also, for the high-entropy Cantor alloy CrMnFeCoNi, VEC = 8 e/a is equivalent to that of Fe. However, the Cantor alloy is fcc in the ground state instead of being bcc as Fe is. Therefore, according to the VEC scheme, the Cantor alloy could electronically represent fcc-Fe and have structural and magnetic properties similar to those predicted for fcc-Fe. Indeed, as expected and verified for fcc-Fe, the ground-state magnetic structure of the Cantor alloy is also antiferromagnetic (AFM) and possesses a highly enhanced thermal expansion that is observed in the temperature dependence of the thermal expansion coefficient due to the presence of a small-volume–low-spin/high-volume–high-spin (LS/HS) instability in the ground state as in fcc-Fe [7,16,58], known as the moment-volume instability. The HS state lies energetically higher than the LS state, but is thermally accessible. By using a Boltzmann activation model, it is possible to describe the anomalous thermal behavior of thermodynamic quantities such as the thermal expansion coefficient and the specific heat of 3D fcc alloys and fcc-Fe.

Since this work aims to stabilize and study an hcp HEA with VEC = 8 e/a, we also focus on the properties of hcp-Fe. As such, the results of *ab initio* calculations show that hcp-Fe also possesses LS and HS states, with the HS state lying 17 mRy/atom higher in energy, comparable to the case of fcc-Fe with the energy difference of 6 mRy per atom [59–61]. However, a nonmagnetic (NM) state is yet lower in energy so that this state is the ground state of hcp-Fe in contrast to the AFM state being the ground state in fcc-Fe. A collection of experimental facts for hcp-Fe and its alloys can be found in chapter 2 of Ref. [27]. Just as an analogy can be established between the properties of fcc-Fe and those of the Cantor alloy through their isoelectronic nature, it may also be possible to establish an analogy between hcp-Fe and a Ru-incorporating hcp Cantor alloy, which we find, in the course of this work, stabilizes as a two-phase fcc/hcp system.

Therefore, throughout this work, we provide interpretations to the data by assuming that the ground state of the hcp phase of this alloy would be NM as in case of hcp-Fe. The validity of this assumption is supported by the results of *ab initio* calculations that indicate that the Cantor alloy in the hcp phase is indeed nonmagnetic [23].

The VEC scheme appears to be applicable for understanding the properties of the Cantor alloy. However, its structure not being hcp, as would be expected for a system with VEC = 8 e/a, is a limitation for a full understanding. Additionally, just as Fe becomes hcp and superconducting under 14 GPa [62], the Cantor alloy also becomes hcp under practically the same pressure.

III. EXPERIMENT

Cr₂₀Mn₂₀(Fe_{20–x}Ru_x)Co₂₀Ni₂₀ samples were prepared by arc melting under Ar atmosphere in a Cu crucible using 99.99% pure Cr, Mn, Fe, Co, Ni, and Ru. The nominal target compositions are $x = 0, 3, 5, 10, 18$, and 20. The melting was repeated four times with the sample turned each time, and the ingots were then homogenized at 900°C for 14 days in sealed quartz tubes under Ar gas. The ingots were subsequently quenched in water at room temperature. The chemical compositions and homogeneities of the samples were determined by energy-dispersive x-ray analysis (EDX) using a scanning electron microscope (SEM).

X-ray diffraction (XRD) was carried out at room temperature (RT) and as a function of temperature (T) using two separate diffractometers. Cu $K\alpha$ radiation was used for the RT measurements with a Panalytical X'Pert Pro diffractometer. Temperature-dependent XRD were recorded in the range $240 \leq T \leq 420$ K using a custom-built diffractometer with a closed-cycle cold-finger He cryostat, employing Mo K-alpha radiation and a Mythen 1 K R detector [63]. The results were refined with Le Bail refinement using the jana software [64].

⁵⁷Fe Mössbauer spectroscopy was performed in transmission geometry in the absence of a magnetic field in a closed-cycle He cryostat using a ⁵⁷Co(Rh) radiation source mounted on a driving unit operating in constant acceleration mode. The Mössbauer spectra were fitted by a least-squares approach using the software program pi [65], while potential effects of overabsorption have been described using the transmission integral [66,67]. The values of the isomer shift δ_{iso} are given relative to an α -Fe reference foil at room temperature ($\delta_{\text{iso}}^{\alpha\text{-Fe}} = -0.107$ mms^{–1}). Except for $x = 18$, all measurements have been performed on samples with the natural abundance of ⁵⁷Fe. Only the sample with $x = 18$ has been enriched by ⁵⁷Fe by an amount sufficient to attain an acceptable signal-to-noise ratio.

IV. RESULTS

A. Structure and composition

The XRD results for the nominal compositions $0 \leq x \leq 20$ are shown in Fig. 1. The samples with compositions $x = 0$ and 3 are fcc, whereas those with $x = 10, 18$, and 20 are mixed fcc and hcp. $x = 5$ is mainly fcc; however, a peak with a relatively weak intensity emerges around 46° corresponding to the (101)

TABLE I. Chemical compositions and VEC in fcc and hcp phases in $\text{Cr}_{20}\text{Mn}_{20}\text{Fe}_{20-x}\text{Ru}_x\text{Co}_{20}\text{Ni}_{20}$.

x (nominal)	fcc	VEC _{fcc} (e/a)	hcp	VEC _{hcp} (e/a)
0	$\text{Cr}_{19.4}\text{Mn}_{21.3}\text{Fe}_{18.6}\text{Co}_{20.7}\text{Ni}_{20.0}$	8.0		
3	$\text{Cr}_{20.2}\text{Mn}_{19.7}\text{Fe}_{17.8}\text{Ru}_{3.1}\text{Co}_{20.0}\text{Ni}_{19.2}$	8.0		
5	$\text{Cr}_{20.1}\text{Mn}_{20.3}\text{Fe}_{14.9}\text{Ru}_{5.7}\text{Co}_{19.6}\text{Ni}_{19.4}$	8.0	Close to composition of fcc	
10	$\text{Cr}_{19.9}\text{Mn}_{20.3}\text{Fe}_{10.0}\text{Ru}_{11.2}\text{Co}_{18.7}\text{Ni}_{19.8}$	8.0	$\text{Cr}_{20.7}\text{Mn}_{19.6}\text{Fe}_{10.0}\text{Ru}_{12.4}\text{Co}_{18.9}\text{Ni}_{18.4}$	8.0
18	$\text{Cr}_{18.4}\text{Mn}_{22.6}\text{Fe}_{2.3}\text{Ru}_{16.1}\text{Co}_{17.5}\text{Ni}_{23.7}$	8.1	$\text{Cr}_{23.3}\text{Mn}_{13.2}\text{Fe}_{2.6}\text{Ru}_{27.8}\text{Co}_{17.4}\text{Ni}_{15.6}$	8.0
20	$\text{Cr}_{17.6}\text{Mn}_{21.3}\text{Ru}_{18.2}\text{Co}_{19.7}\text{Ni}_{23.3}$	8.1	$\text{Cr}_{22.1}\text{Mn}_{16.3}\text{Ru}_{26.4}\text{Co}_{18.8}\text{Ni}_{16.4}$	7.9

hcp peak. The refinement data and the results are provided in the Appendix.

The samples with the nominal compositions $x = 0$ and 3 are seen to be homogeneous from electron mapping studies. For $x = 5$, the resolution of the mapping is not sufficient to resolve the small amount of hcp phase detected by XRD. The mapping images of the samples with the nominal compositions $x = 10, 18$, and 20 are shown in Figs. 2, 3, and 4, respectively. The image scale bars are given as 30 μm in Fig. 2 and as 10 μm in Figs. 3 and 4. The Fe and Co compositions are distributed uniformly in all three images, whereas contrasts are observed for Cr, Mn, Ni, and Ru in a manner that segregated regions rich in Cr along with Ru and Mn along with Ni are found. The contrast in the segregated regions in Fig. 2 is weaker than those in Figs. 3 and 4. A contrast in the electron image (EI) is essentially not observable in Fig. 2, whereas a clear contrast arising from the different secondary electron emission characteristics from the fcc and hcp phases can be observed in Figs. 3 and 4. In these figures, the increase in the size of the Ru-rich areas correlate with the increase in the hcp peak intensities in the XRD data in Fig. 1. Therefore, the hcp phase is the phase that is richer in Ru. The list in Table I shows the compositions of the fcc and hcp regions obtained from these electron mapping results along with their

respective VEC values. In all cases, the VEC is close to the value of 8 e/a corresponding to that of elemental Fe and Ru. The lattice parameters a for the fcc phase and a' and c for the hcp phase along with the volume-phase fractions of the individual phases are collected in Table II. The phase fraction of the hcp phase increases with increasing nominal Ru concentration.

The concentration dependence of the lattice parameters and the atomic volume of the corresponding fcc and hcp phases are shown in Figs. 5(a) and 5(b). The atomic volume for the fcc and hcp phases $V_{\text{at}}^{\text{fcc}}$ and $V_{\text{at}}^{\text{hcp}}$ are calculated as

$$V_{\text{at}}^{\text{fcc}} = a^3/4 \quad \text{and} \quad V_{\text{at}}^{\text{hcp}} = \sqrt{3}(a')^2c/4, \quad (1)$$

respectively. a , a' , and c increase monotonically with increasing Ru composition, as seen in Fig. 5(a). The behavior is similar for V_{at} , as seen in Fig. 5(b). Although the atomic radius of Ru is larger than that of Fe, V_{at} for the fcc phase is larger than that of the hcp phase for all Ru concentration. The inset in Fig. 5(b) represents the case when all elements in the alloy are gradually replaced by Ru, by which the lattice parameters of pure hcp Ru are reached practically in a linear manner.

The temperature dependence of the lattice parameters for the sample with the nominal composition $x = 20$ in the range $240 \leq T \leq 420$ K are plotted in Fig. 6. The lattice parameters increase essentially linearly with increasing temperature in

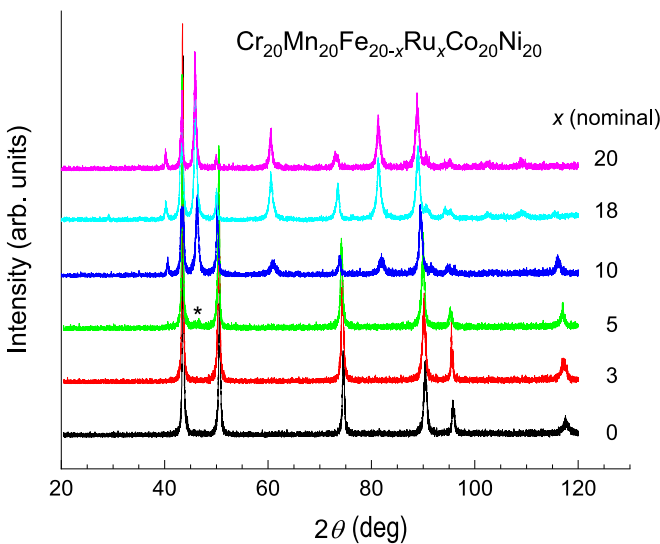


FIG. 1. XRD for $\text{Cr}_{20}\text{Mn}_{20}(\text{Fe}_{20-x}\text{Ru}_x)\text{Co}_{20}\text{Ni}_{20}$ at room temperature with the nominal compositions $x = 0, 3, 5, 10, 18$, and 20 at% (see Table I for compositions of individual phases). A weak peak shown with an asterisk for $x = 5$ emerges around 46° , corresponding to the (101) hcp peak.

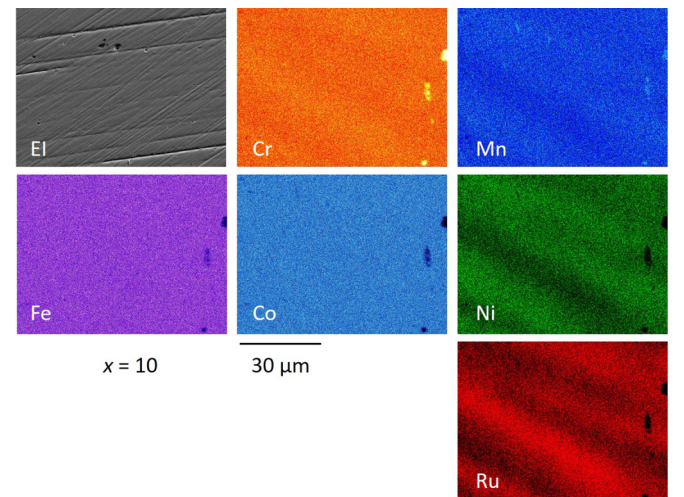


FIG. 2. Electron mapping images for $x = 10$. Fe and Co are uniformly distributed, whereas the contrasts appearing in the Cr, Mn, Ni, and Ru images indicate enrichment of Cr along with Ru for the hcp phase and Mn along with Ni for the fcc phase. The scale bar is given as 30 μm . A contrast in EI is not observable.

TABLE II. Lattice parameters and volume phase fractions of fcc and hcp. The error in the lattice parameters is estimated to be ± 0.0002 nm.

Label x (nominal)	Lattice parameters			Volume-phase fractions	
	fcc	hcp	hcp		
	a (nm)	a' (nm)	c (nm)	fcc	hcp
0	0.3602			1	0
3	0.3610			1	0
5	0.3619	0.2555	0.4166	0.99	0.01
10	0.3637	0.2573	0.4164	0.52	0.48
18	0.3650	0.2594	0.4179	0.31	0.69
20	0.3652	0.2596	0.4177	0.18	0.82

the measured temperature range. The green lines are linear fits from which an average thermal-expansion coefficient α is estimated from the slope using

$$\alpha_{av} = \frac{1}{a(240)} \frac{\Delta a}{\Delta T}, \quad (2)$$

where α_{av} is the average thermal-expansion coefficient at about 330 K. For the fcc phase, $\alpha_{av}^{fcc} = (16.6 \pm 0.4) \times 10^{-6} \text{ K}^{-1}$ is similar to the estimated enhanced value of $17.0 \times 10^{-6} \text{ fcc-Fe}$ [68]. The enhancement is due to the presence of moment-volume instabilities. α_{av} for the hcp phase for a polycrystalline sample is estimated from

$$\alpha_{av}^{hcp} = (2/3)\alpha_{av}^{a'} + (1/3)\alpha_{av}^c \approx 12.5 \times 10^{-6} \text{ K}^{-1}. \quad (3)$$

This considerably lower value than that of the fcc state suggests that moment-volume instabilities that would lead to an enhanced thermal expansion are not present in the hcp state, as also suggested by the results of *ab initio* calculations. These α_{av} values for the fcc and hcp phases can also be estimated through the temperature dependence of the atomic volume shown in Fig. 7. The volume thermal-expansion coefficient

β is obtained from the slope of the linear fits from

$$\beta = \frac{1}{V_{at}(240)} \frac{\Delta V_{at}}{\Delta T}. \quad (4)$$

The values of α and β for both phases are given in the figure. Assuming isotropic expansion for a polycrystal specimen,

$$\alpha = \frac{1}{3}\beta. \quad (5)$$

From this, we obtain $\alpha_{fcc} = (16.7 \pm 1.1) \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{hcp} = (12.5 \pm 0.3) \times 10^{-6} \text{ K}^{-1}$, in agreement with those obtained using Eqs. (2) and (4), respectively.

B. Magnetic properties

We have investigated the magnetic properties of these heterogeneous alloys through magnetization and Mössbauer spectroscopy measurements. We first present the results of the magnetization measurements and subsequently those for the Mössbauer spectroscopy. From the results, we aim to provide an understanding of the magnetic properties of the individual fcc and hcp phases.

1. Magnetization

We have measured the temperature and field dependence of the magnetization, $M(T)$ and $M(H)$, in magnetic fields up to 5 T. We first present $M(T)$ measured under 5 mT in Fig. 8. The

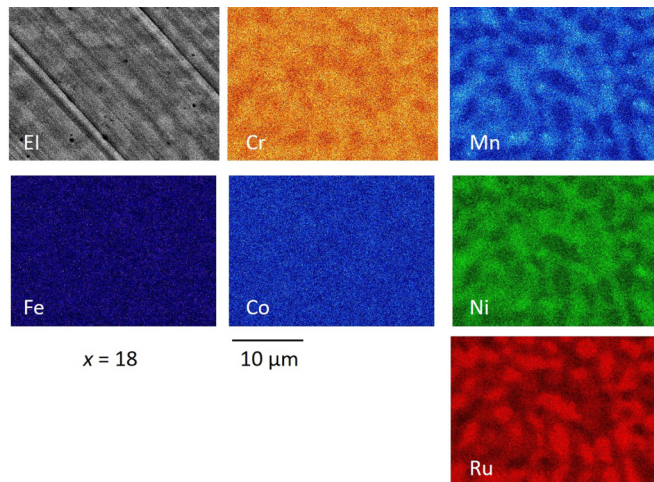


FIG. 3. Electron mapping images for $x = 18$. Fe and Co are uniformly distributed, whereas the contrasts appearing in the Cr, Mn, Ni, and Ru images indicate enrichment of Cr along with Ru for the hcp phase and Mn along with Ni for the fcc phase. The scale bar is given as 10 μm . A contrast in EI can also be seen.

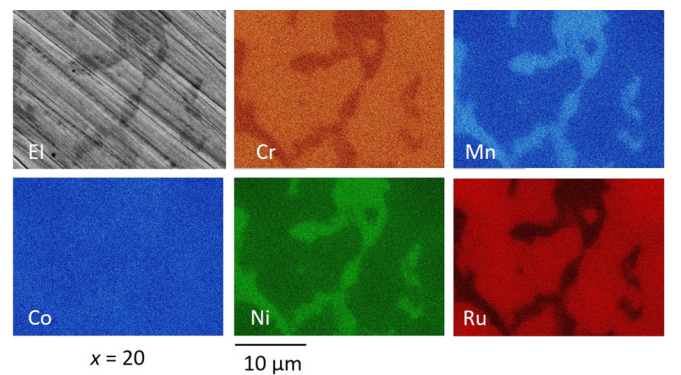


FIG. 4. Electron mapping images for $x = 20$. Fe and Co are uniformly distributed, whereas the contrasts appearing in the Cr, Mn, Ni, and Ru images indicate enrichment with Cr with Ru and Mn with Ni. The scale bar is given as 10 μm . A contrast in EI can also be seen.

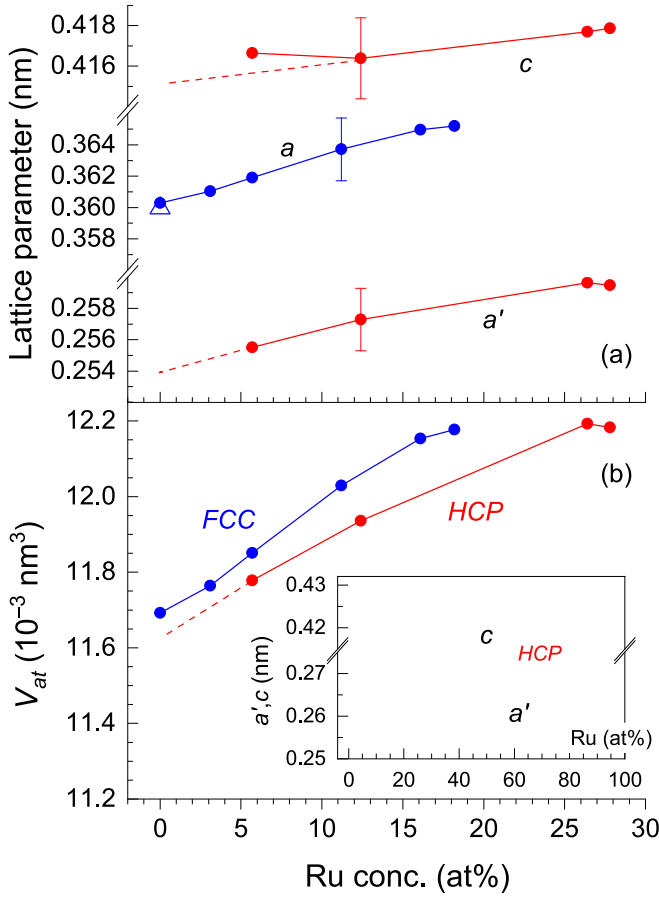


FIG. 5. The room-temperature true Ru-concentration dependence of the lattice parameters and atomic volume for the fcc and hcp phases, where the concentrations and lattice parameters are taken from Tables I and II, respectively. (a) Lattice parameters; (b) atomic volume. The open blue triangle is from Ref. [14].

measurements are made such that the sample is first cooled to the lowest temperature in zero field (zero-field cooled, ZFC), and a field of 5 mT is subsequently applied. The data are then taken on warming to the highest measurement temperature. Subsequently, without removing the field, the data are taken on cooling (field cooled, FC) down to the lowest temperature.

$M(T)$ measured in 5 mT for the Cantor alloy $x = 0$ is shown in Fig. 8(a), and in Fig. 8(b), expanded in the mid-temperature range. The splitting point between the ZFC and FC measurements is denoted as the freezing temperature T_f , below which the spins are frustrated. The directions of these measurements are indicated by the red arrows (the arrows are omitted in the other panels for clarity). On lowering the temperature from 380 K, $M(T)$ gradually increases down to about 80 K, showing paramagnetic (PM) behavior. Below this temperature, a cusp is observed for $x = 0, 3$, and 5, denoted as the Néel temperature T_N , where long-range antiferromagnetic (AFM) ordering sets in. This has also been evidenced in earlier magnetization and neutron-diffraction studies [7,16]. T_N decreases with increasing Ru concentration, as indicated in Figs. 8(a), 8(c), and 8(d). On further lowering the temperature, ferromagnetic (FM) ordering begins below a Curie temperature T_C of about 44 K (shown with an arrow only in Fig. 8(a)).

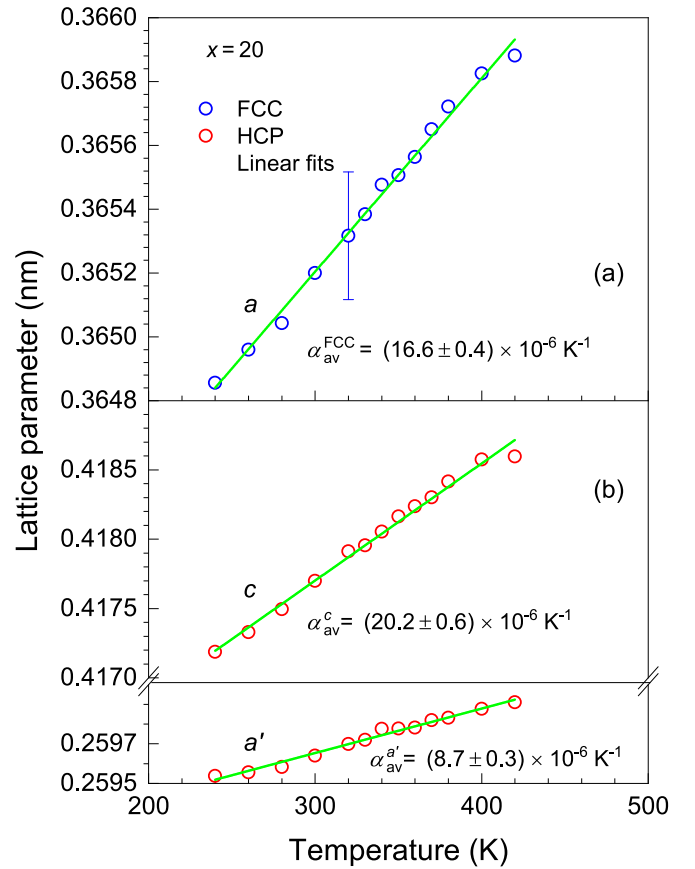


FIG. 6. The temperature dependence of the lattice parameters for the fcc and hcp phases in $x = 20$. (a) fcc, (b) hcp. The green lines are linear fits of which the slopes are used to estimate the average thermal-expansion coefficients in the temperature range of the measurements, which are given in the panels.

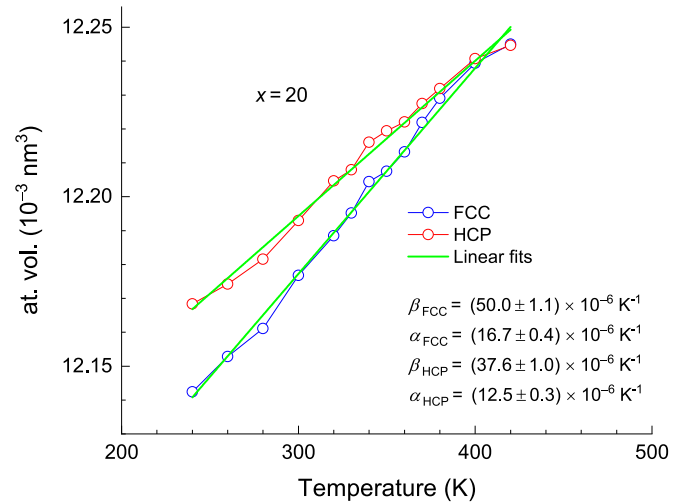


FIG. 7. The temperature dependence of the atomic volume for the fcc and hcp phases in $x = 20$. The green lines are linear fits of which the slopes are used to estimate the average volume and linear thermal-expansion coefficients in the temperature range of the measurements, which are given in the figure.

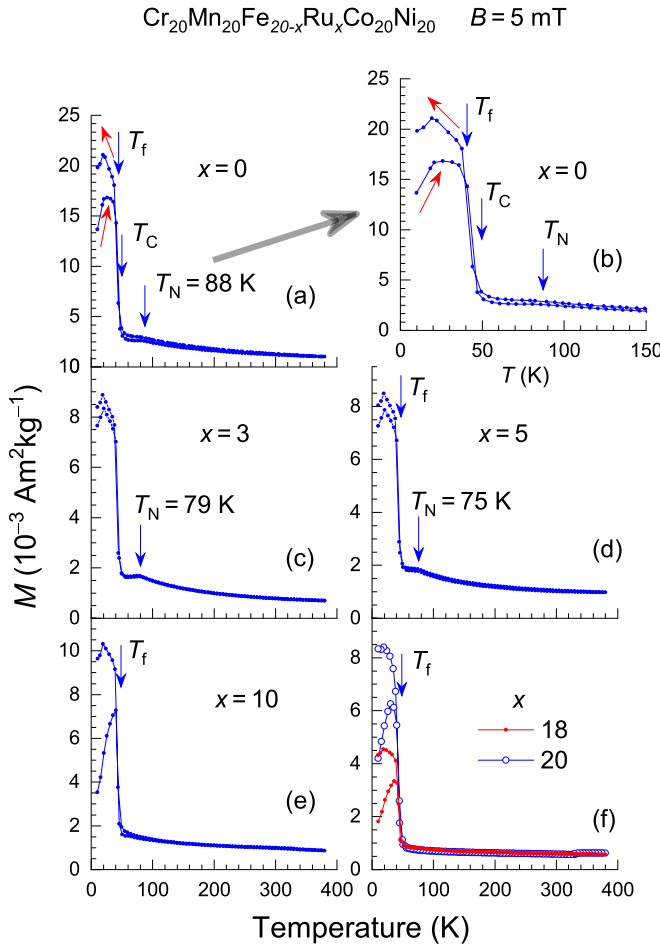


FIG. 8. ZFC and FC $M(T)$ in 5 mT for (a) $x = 0$ and (b) $x = 0$, expanded around the mid-temperature region indicated by the dark arrow, (c) $x = 3$, (d) $x = 5$, (e) $x = 10$, and (f) $x = 18$ and 20. The measurement directions are indicated by the red arrows for $x = 0$ only. T_N and T_f are shown with vertical black arrows.

for clarity), below which a sharp rise in $M(T)$ is observed, persisting down to T_f . T_C is essentially independent of the Ru concentration. In this temperature range, AFM and FM interactions coexist, leading to spin frustration below T_f . T_f remains as about 35 K for all samples when measured under 5 mT. Such frustration is also observed in $M(T)$ of Ref. [16], but with somewhat different features. This could be related to different heat-treatment conditions or slight variations in composition of the sample giving rise to different homogeneities. This reference reports that the sample was homogenized at 1473 K, whereas ours was homogenized at 1173 K.

$M(T)$ for $x = 3$ and $x = 5$, shown in Figs. 8(c) and 8(d), respectively, behave similar to $M(T)$ of $x = 0$, with T_N decreasing from 88 K for $x = 0$ to 75 K for $x = 5$. T_N is attributed to the fcc phase and is not resolved in $M(T)$ for $x \geq 10$ since it could be merging close to the sharp-increase feature associated with the onset of FM coupling just above T_C , as seen in Figs. 8(e) and 8(f), respectively. The feature can also be weakening concurrently due to the overwhelming amount of NM hcp phase for these compositions as evidenced by the phase fractions (see Table II). The remaining fcc phase

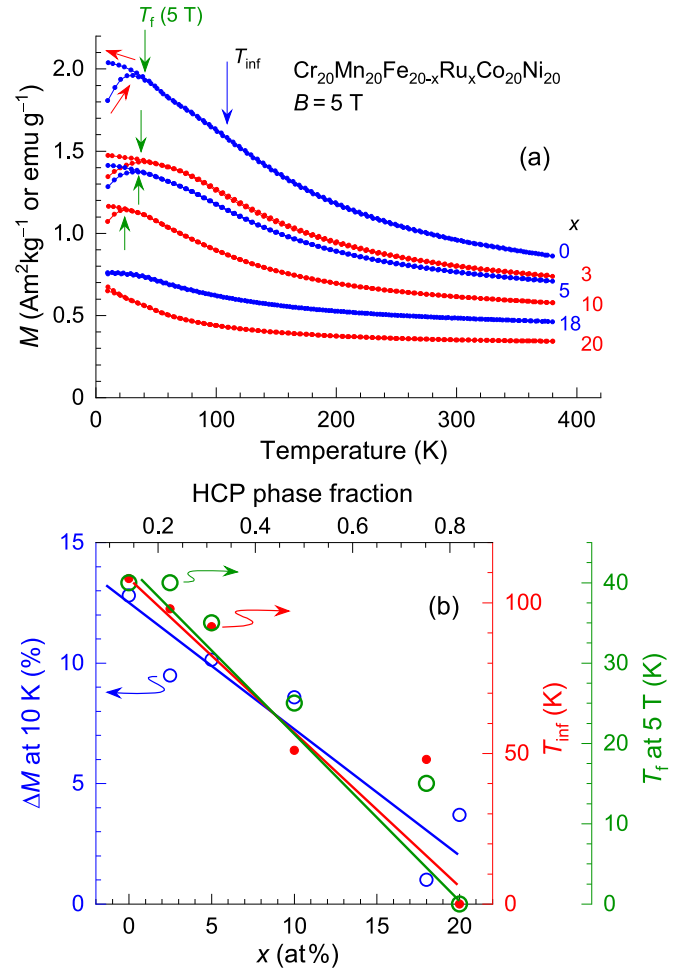


FIG. 9. (a) ZFC and FC $M(T)$ in 5 T for all samples. The measurement directions are indicated by the red arrows and T_{inf} by the black arrow, both for $x = 0$ only. $T_f(5\text{ T})$ are indicated by the vertical green arrows. (b) The nominal Ru-concentration dependence of ΔM , T_{inf} , and $T_f(5\text{ T})$.

in the samples $x \geq 10$ would then be the magnetically active phase. Therefore, the splitting in $M(T)$ at T_f , which is still present at these concentrations, should then be due to the presence of mixed AFM/FM exchange present in the fcc phase. However, this point requires further verification, which can be provided by investigating $M(T)$ in high fields and, along with it, $M(H)$. We present these next.

$M(T)$ measured in 5 T are shown in Fig. 9(a). These data show four features that can contribute to the verification of the NM nature of the hcp phase: With increasing nominal Ru concentration or increasing hcp phase fraction, (1) $M(T)$ at all temperatures runs at lower values, (2) T_f decreases in these high fields, (3) the relative change in the ZFC and FC magnetization ΔM at 10 K decreases, and (4) an inflection point in $M(T)$ occurring at T_{inf} (shown only for $x = 0$ for clarity) also decreases. These points are presented individually below.

(1) The decrease in the overall $M(T)$ at all temperatures for $x = 3$ and 5, for which the amount of hcp phase is marginal if none at all, could be related to a smaller effective moment

than that of Fe contributed by Ru in an fcc environment. This would weaken the effect of moment-volume fluctuations. It can also be due to any nonmagnetic residual hcp phase in these samples.

(2) The fact that the splitting below T_f prevails in these high-field measurements instead of disappearing, as would be expected for the case of a spin glass, indicates that the nature of interactions differs from those leading to a simple spin frustration. For splitting in high fields to prevail, the AFM coupling should be strong enough to cause a pinning of FM components in configurations that differ under ZFC and FC conditions. The splitting at T_f is present in all samples, except that it weakens and shifts to lower temperatures with increasing Ru concentration, as can be seen in Fig. 9(b). It is practically absent for $x = 18$ and 20.

(3) Along with T_f , ΔM estimated at 10 K also decreases with increasing Ru concentration. If we consider the hcp phase to be nonmagnetic, the concentration dependence of T_f and ΔM has to be attributed mainly to the properties of the magnetically active fcc phase along with its composition and phase fraction (Tables I and II). As seen from Table I, the Fe/Ru compositional ratio within the fcc phase decreases with increasing Ru concentration. In this respect, magnetic interactions within the fcc phase can be expected to weaken as nonmagnetic Ru replaces Fe.

(4) Applying a high magnetic field of 5 T smears out any feature in T_N and T_C , but a new feature arises at T_{inf} , which is an inflection point, below which field-induced FM coupling emerges, making the presence of any short-range FM correlations detectable in $M(T)$. T_{inf} decreases with increasing Ru concentrations for reasons given in point (3) above.

The arguments related to the four points can give a general characterization of the present systems. This would be that a nonmagnetic contribution arising from the hcp phase causes an overall decrease in the magnetization, whereas the magnetically active fcc phase is responsible for the changes in ΔM , T_f , and T_{inf} .

To more closely study the magnetism of this mixed fcc/hcp system, we have measured the field dependence of the magnetization $M(H)$ at 10 K in the range $0 \leq B \leq 5$ T. The results are shown in Fig. 10. The data are shown in the full-field range in Fig. 10(a) and in the low-field region in Fig. 10(b). To be able to estimate $M(H)$ for a 100% hcp alloy using the volume-phase fraction, the $M(H)$ data are provided in units of emu cm^{-3} . These are obtained by multiplying $M(H)$ of each alloy by its density. The density is approximated as the concentration-weighted average of the individual elements in the alloy. To obtain $M(H)$ for 100% hcp, we interpolate the values of $M(H)$ at 5 T for $x = 0$ and 20 to determine the interpolation constant and use this to obtain $M(H)$ at 5 T for a 100% hcp alloy. Since AFM and FM interactions weaken with increasing Ru (Figs. 8 and 9), these would be expected to diminish at low temperatures. The estimated behavior is shown with the dashed red line in Fig. 10(a). From the $M(H)$ values at 5 T, volume-phase fractions for the hcp phase of $x = 10$ and 18 can be estimated as 0.36 and 0.75, respectively. These values are in line with those obtained from the XRD values (Table II) in that the hcp fraction increases with increasing Ru concentration. However, the substantial differences in the values obtained from XRD and magnetization lie mainly on

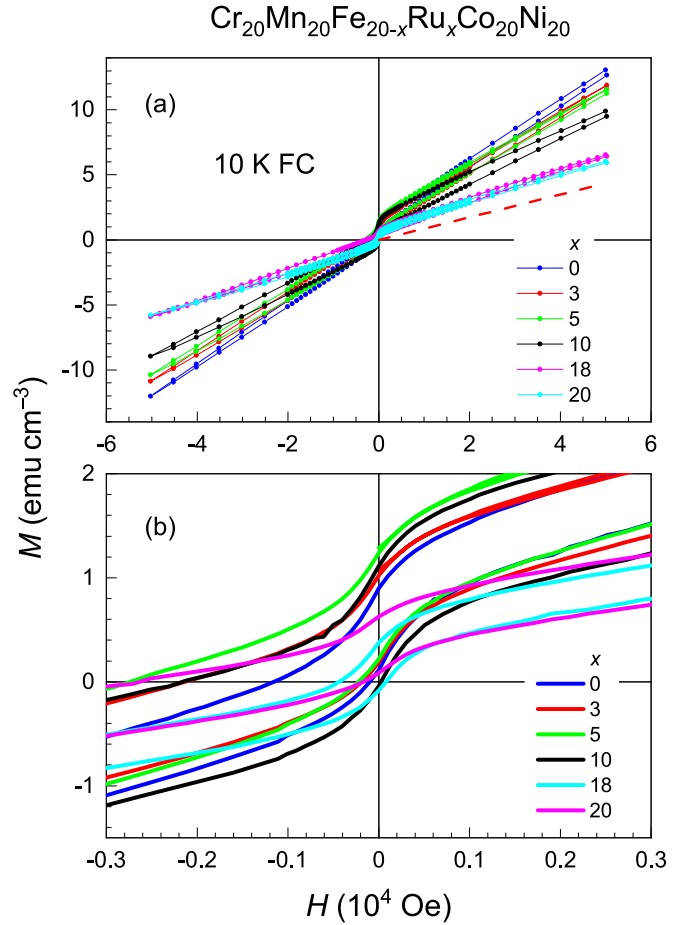


FIG. 10. $M(H)$ at 10 K for all samples. (a) $M(H)$ in the full-field range. The dashed red line is the behavior of $M(H)$ estimated for a 100% hcp alloy. (b) $M(H)$ focused on the low-field range.

the uncertainty in the values obtained from the magnetization data, mainly by the choice of the field at which the estimation is made. In this case, the data obtained from XRD are more reliable.

The data feature behavior that is related to FM coupling in small fields and a high-field susceptibility χ_{hf} featured by a linear increase in $M(H)$ with increasing field up to the highest fields caused by the AFM contribution from the fcc phase and any PM contribution coming from the hcp phase. The data do not retrace on decreasing and increasing field, hence the curves are minor loops. The minor-loop character can be further evidenced by the fact that the data are vertically displaced around zero field, as can be seen in Fig. 10(b). Nevertheless, χ_{hf} decreases with increasing Ru concentration so that at any given field above about 1 T, the total volume magnetization M_{tot} can be written as

$$M_{\text{tot}} = \sum f(M_{\text{FM}}^{\text{fcc}} + M_{\text{AFM}}^{\text{fcc}}) + (1 - f)M_{\text{PM}}^{\text{hcp}}, \quad (6)$$

where f is the volume-phase fraction of the fcc phase, and $M_{\text{FM}}^{\text{fcc}}$, $M_{\text{AFM}}^{\text{fcc}}$, and $M_{\text{PM}}^{\text{hcp}}$ are the magnetizations from the fcc-FM, fcc-AFM, and hcp-NM components, respectively.

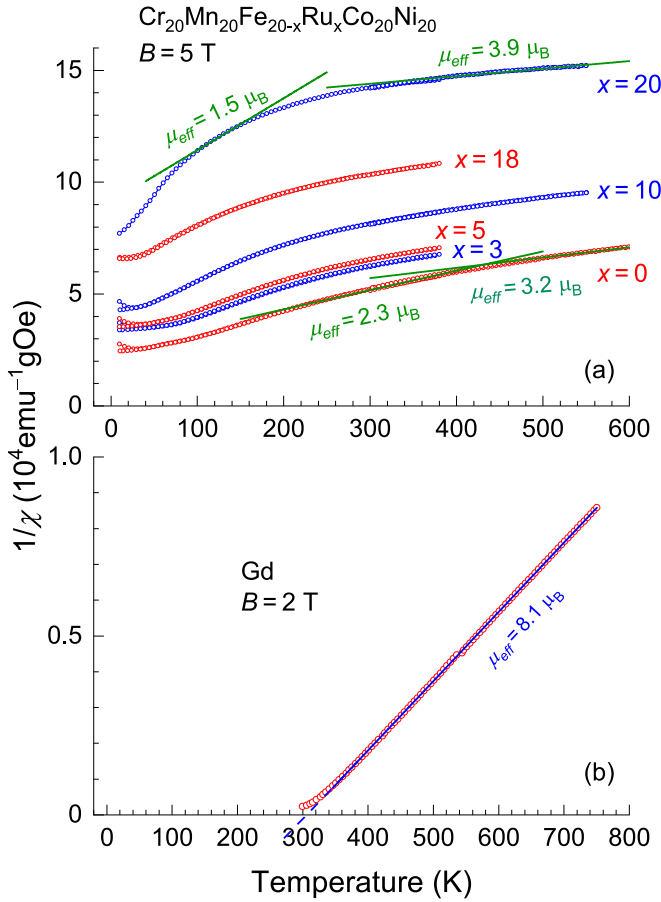


FIG. 11. The inverse susceptibility (a) for 5 T measuring field for all samples. The curves do not conform to Curie behavior in the PM ranges above 150 K. μ_{eff} varies with the chosen fitting range within the PM regime (green lines). (b) For Gd above T_C , $1/\chi(T)$ is linear in T in the full PM regime, yielding $\mu_{\text{eff}} = 8.1 \mu_B$.

2. Inverse susceptibility

The Curie law is given by

$$\chi(T) = \frac{N\mu_{\text{eff}}^2}{3AkT}, \quad (7)$$

where N is Avagadro's number and A is the molecular weight, k is the Boltzmann's constant, and T is the temperature. $(1/\chi)(T)$ is then linear in T with a slope proportional to a unique μ_{eff} .

The temperature dependence of the inverse susceptibility, $(1/\chi)(T)$, for all samples is plotted in Fig. 11(a). All samples are well in the PM regime for $T > 100$ K. For convenience, we use, in the following analysis of $(1/\chi)(T)$, the CGS system of units. Here, the data show that $(1/\chi)(T)$ do not show linear behavior with T so that they do not obey the Curie law. Despite this, fitting $(1/\chi)(T)$ to the Curie law in the ranges 190–380 K and 540–750 K for $x = 0$ and 100–150 K and 350–550 K for $x = 20$ yield very different values for μ_{eff} for each fit range of each sample. The obtained values are labeled in the figure. The data are compared to those of Gd obtained using the same magnetometer. Here, a typical linear dependence is observed over the full PM regime in accordance with the Curie law, whereby a unique value of

$8.1 \mu_B$ is obtained for μ_{eff} as expected. Therefore, to understand the behavior of $(1/\chi)(T)$ particularly for $x = 0$, we consider a temperature-dependent effective magnetic moment $\mu_{\text{eff}}(T)$ instead of a constant μ_{eff} , as expressed in the Curie law. The Curie law would then be modified to take the form

$$\chi(T) = \frac{N\mu_{\text{eff}}^2(T)}{3AkT}. \quad (8)$$

We showed in Sec. IV A that α is enhanced so that LS/HS fluctuations can be expected to be present in these systems. The nonconformity of these systems to the Curie law should then have its origins in these coupled moment-volume fluctuations. Since these fluctuations would be expected to be coupled to the phonons, the temperature dependence can be described with a Boltzmann activation model, where the population $n(T)$ of the energetically higher-lying state HS is given by

$$n(T) = \frac{1}{1 + (g_{\text{LS}}/g_{\text{HS}})\exp(\Delta\epsilon/kT)}, \quad (9)$$

where $g_{\text{LS}}/g_{\text{HS}}$ is a degeneracy ratio and $\Delta\epsilon$ is the energy difference between the LS and HS states [69]. $\mu_{\text{eff}}(T)$ can then be written as

$$\mu_{\text{eff}}(T) = [1 - n(T)]\mu_{\text{LS}} + n(T)\mu_{\text{HS}}, \quad (10)$$

where μ_{LS} and μ_{HS} are the LS and HS magnetic moments at their respective equilibrium volumes V_{LS} and V_{HS} . From the extrapolation of the fcc branch of the Slater-Pauling curve to VEC = 8 e/a [58] and the results of *ab initio* calculations [70], we take $\mu_{\text{HS}} = 2.8 \mu_B$ and $\mu_{\text{LS}} \approx 1 \mu_B$. We take the remaining parameters as $g_{\text{LS}}/g_{\text{HS}} \approx 0.8$ [68] and $\Delta\epsilon \approx 1500$ K, but vary them as fitting variables in Eq. (9). Since the magnetization measured in a magnetometer pertains to the whole of the sample, an analysis of $1/\chi(T)$ would only be meaningful for a single-phase system so that we focus first on the analysis for $x = 0$, which is single-phase fcc. The analysis is made for $T > 200$ K, which should be well above T_{inf} and within the PM temperature range. The data and the fits obtained by using μ_{eff} in Eq. (8) are shown in Fig. 12(a) for $\chi(T)$ and in Fig. 12(b) for $1/\chi(T)$ in the range $200 \leq T \leq 600$ K. We see in the figure that the model fits well to the data for $x = 0$ by using $\mu_{\text{LS}} = 1.42 \mu_B$ and $\Delta\epsilon = 1700$ K. 1700 K corresponds to about 150 meV (~ 10 mRy), which is similar to the value obtained from *ab initio* calculations.

Similar analysis can also be carried out for the other samples, but their heterogeneity would not allow a sound determination of the characteristic parameters even if the magnetization data were corrected for the phase fraction. However, the form of their $1/\chi(T)$ curves being similar to that of $x = 0$ suggests that moment-volume instabilities, and therefore LS/HS fluctuations, can also be present in the fcc phase of the remaining alloys and even in the $x = 20$ sample, which contains no Fe in the fcc phase. The behavior of $1/\chi(T)$ of this sample would be dominated by the magnetically active fcc phase.

3. Mössbauer spectroscopy

To further investigate the Ru-substituted Cantor alloys, we performed ^{57}Fe Mössbauer spectroscopy to bring clarity to the changes in the electronic and magnetic structure. Mössbauer

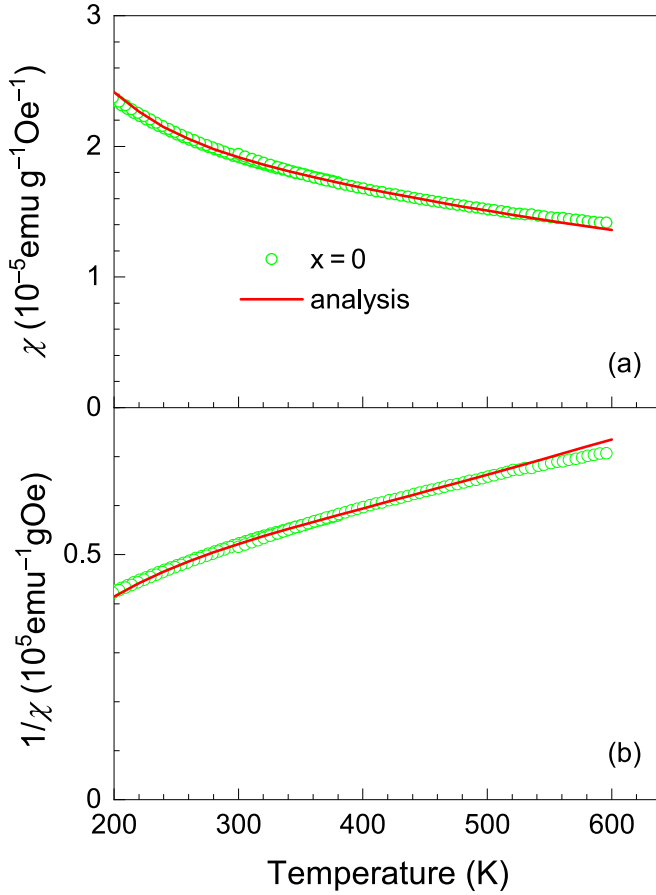


FIG. 12. Results of the analysis of $\chi(T)$ and $1/\chi(T)$ for $x = 0$.

spectroscopy is an isotope-specific technique that probes slight deviations in the energy levels of the ^{57}Fe nuclei due to the presence of hyperfine interactions and reveals electronic and magnetic properties through the isomer shift δ_{iso} and the hyperfine field B_{hf} . Figures 13(a)–13(e) show the Mössbauer spectra obtained at 5 K. All spectra exhibit a broad, singlet absorption. Due to the small hyperfine splitting and the lack of spectral fine structure, the spectra have been described by a single Lorentzian, where the full width at half maximum, Γ , can be associated with the mean magnetic hyperfine field B_{hf} and the magnetic moment of Fe. The Mössbauer spectrum of the Ru-free sample [Fig. 13(a)] exhibits similar hyperfine field parameters compared to fcc-Fe grown on Cu [71–73], namely, an isomer shift close to -0.09 mms^{-1} and a hyperfine field splitting $B_{\text{hf}} = 4.5 \text{ T}$, while in earlier works on fcc-ordered high entropy alloys with $\text{VEC} \approx 8 \text{ e/a}$, similar spectral fingerprints [14] occur. The spectrum with the highest Ru content resembles the spectra obtained from Ru-rich ϵ -FeRu [74] with a relatively small hyperfine field splitting.

The comparison of hyperfine field parameters, as shown in Figs. 14(f) and 14(g), reveals a reduction of full width at half maximum Γ and an increase of the isomer shift δ_{iso} with increasing Ru content. The decrease of FWHM Γ can be interpreted as a reduction of the Fe magnetic moment associated with the lack of magnetic ordering in the hcp structure. Combining the Mössbauer and XRD results, we can correlate the increased isomer shift δ_{iso} with the volume expansion.

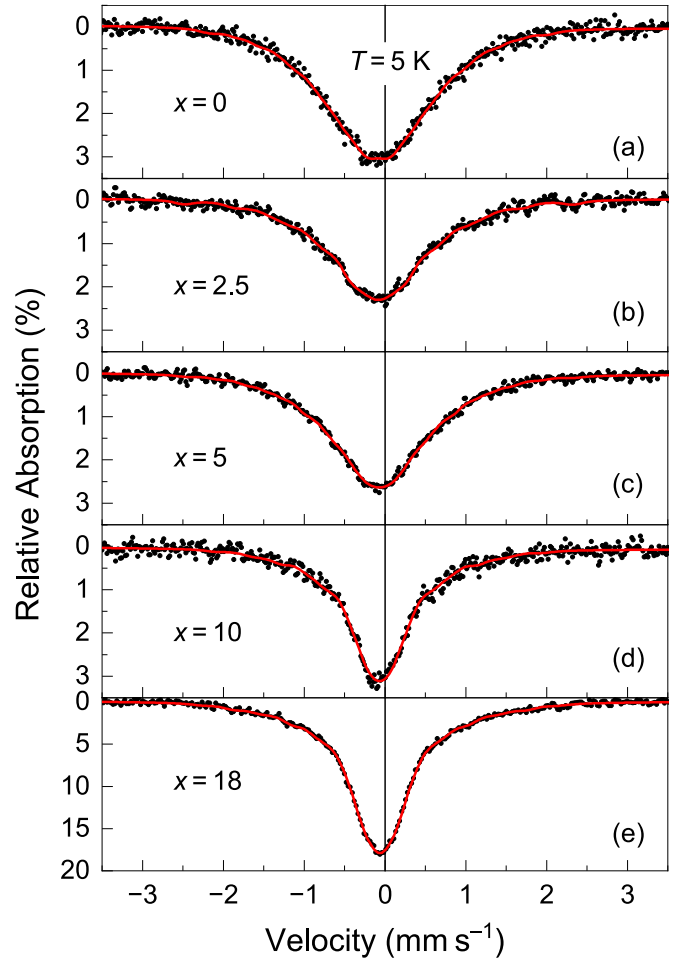


FIG. 13. (a)–(e) Zero-field Mössbauer spectroscopy measurements and the corresponding results obtained by least-squares fit. Measurements performed at $T = 5 \text{ K}$. (f), (g) Evolution of the mean hyperfine field (B_{hf}) and the isomer shift δ_{iso} corrected for the second order Doppler shift.

$B_{\text{hf}}(T)$ for $x = 18$ is plotted in Fig. 15. The sharp increase in $B_{\text{hf}}(T)$ below 60 K occurs at a temperature similar to that observed in $M(T)$ in Fig. 8(e), so that this feature can be associated with the onset of T_C within the fcc phase. Any feature related to a T_N at temperatures around 80 K is not observed so that the presence of any AFM coupling cannot be resolved.

V. DISCUSSION

A. Predicted properties of the fcc and hcp phases of Fe and the Cantor alloy

The two fundamental properties of the Cantor alloy $\text{Cr}_{20}\text{Mn}_{20}\text{Fe}_{20}\text{Co}_{20}\text{Ni}_{20}$ in relation to the electronic and crystallographic structure is that $\text{VEC} = 8 \text{ e/a}$, and the crystal structure is fcc. Since the VEC reflects the electronic and structural properties of the 3D elements and alloys, the Cantor alloy can be considered to be electronically equivalent to fcc-Fe, except that it is stable throughout the solid-state temperature range unlike fcc-Fe, which is stable only for $1184 \leq T \leq 1665 \text{ K}$. On the other hand, according to

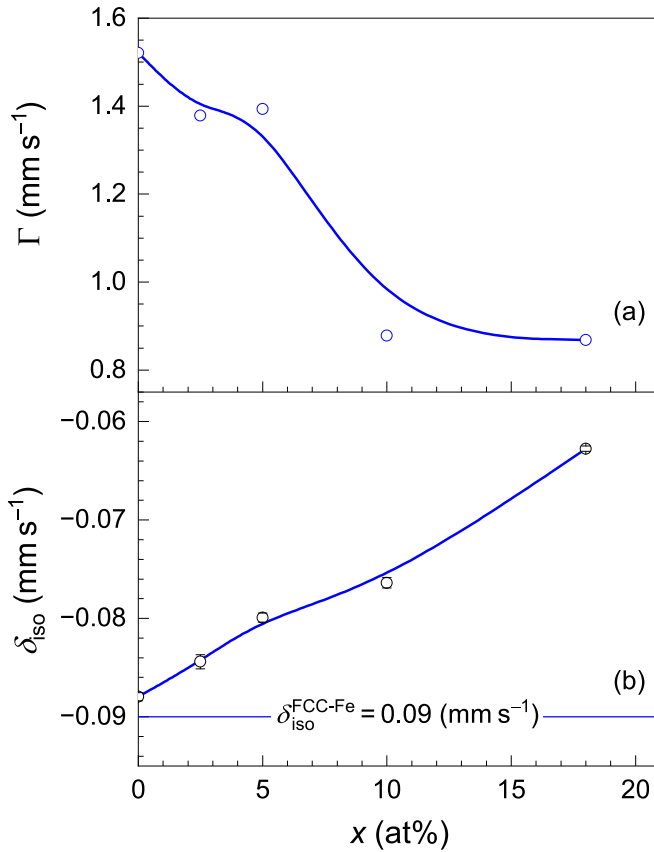


FIG. 14. Composition dependence of the hyperfine parameters at 5 K. (a) Γ , (b) δ_{iso} .

the periodic scheme of the elements, the structure of 3D elements and alloys at VEC = 8 e/a should be hcp. However, the hcp phase of both Fe and the Cantor alloy are attained only under nonambient conditions, namely, at pressures around 14 GPa. fcc-Fe possesses a moment-volume instability in the ground state with close-lying LS and HS states, with the HS state being energetically higher but accessible through thermal volume fluctuation. This gives rise to an enhanced lattice anharmonicity leading to an anomalously large thermal

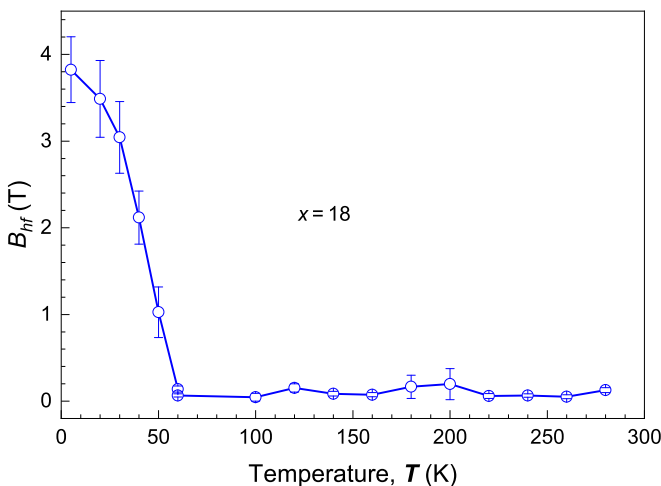


FIG. 15. Temperature dependence of B_{hf} for $x = 18$.

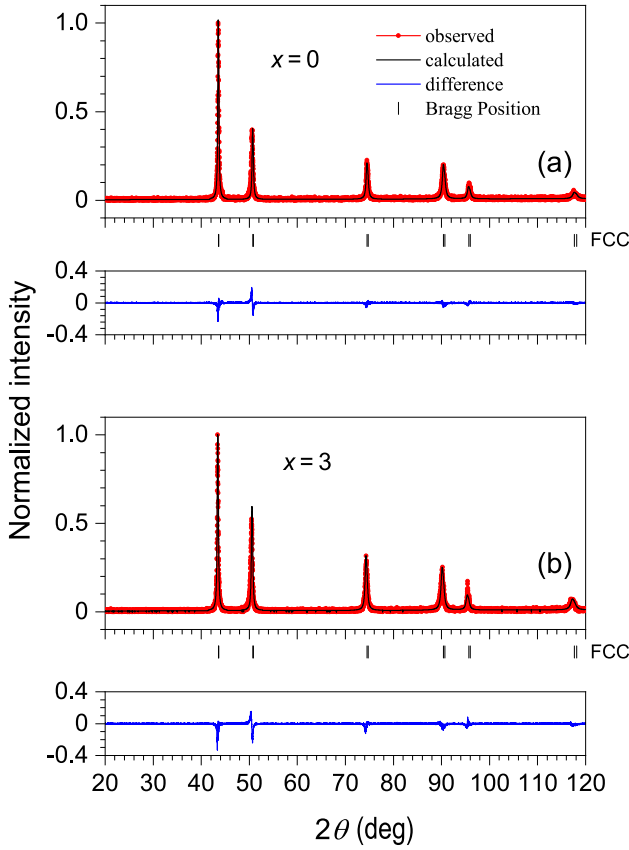
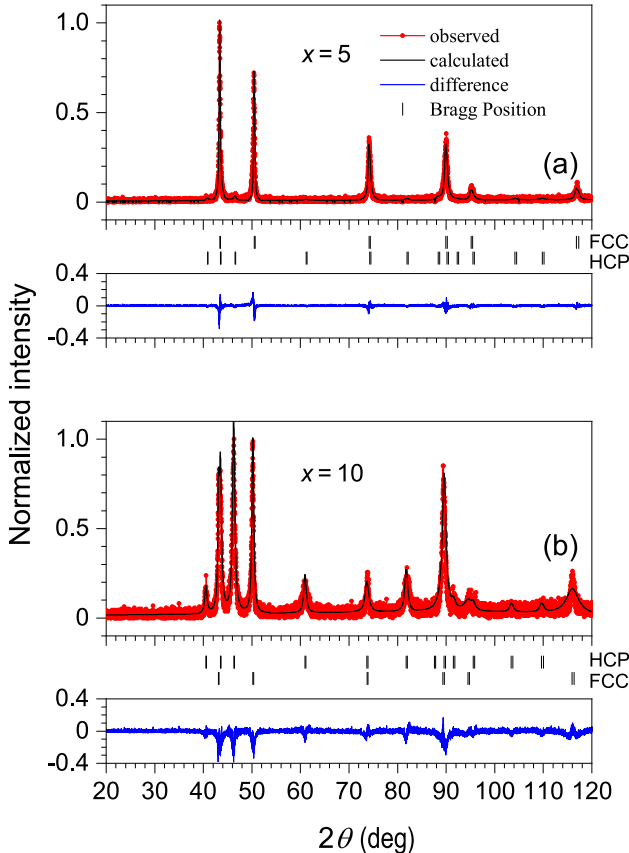
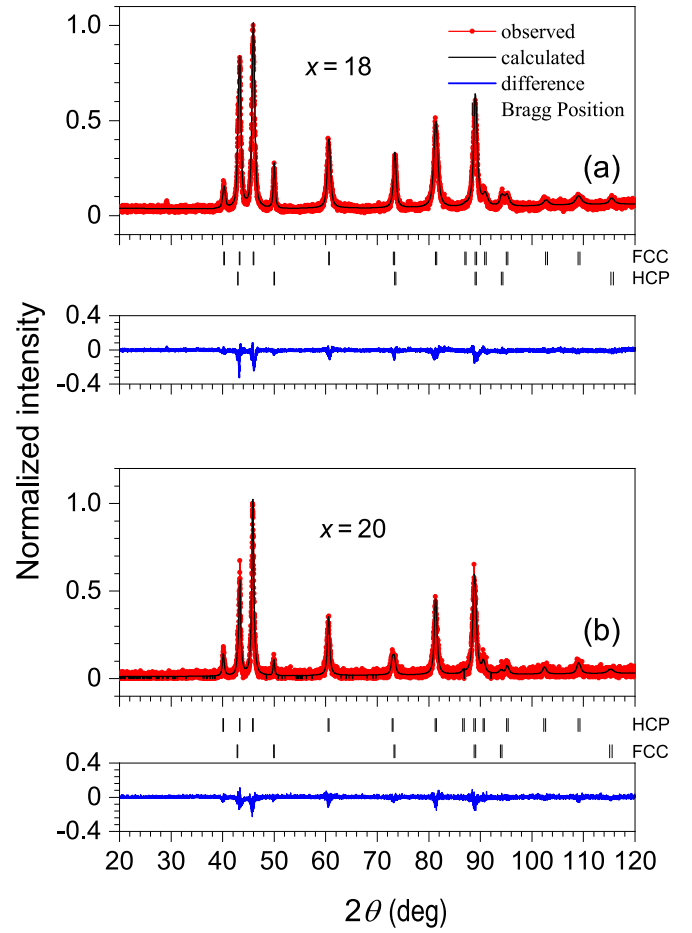
expansion. Thermodynamic considerations had shown that the stabilizing agent of the bcc state of Fe over the hcp phase is the FM coupling that is already present above T_c [28]. On the other hand, the stabilizing agent of the fcc phase over the hcp phase at high temperatures is the partial attainment of the HS state at these temperatures given by Eq. (9) [68].

Since the Cantor alloy also exhibits a similar anomaly in the thermal expansion, and therefore, also an enhanced lattice anharmonicity, its ground state should carry similar characteristics to those of fcc-Fe. Recent findings have indeed shown that this is the case [58]. However, the question still remaining is why the ground state of the Cantor alloy is not hcp. Very little is known experimentally about the hcp phase at VEC = 8 e/a, in particular for 3D systems, since samples in this state cannot be readily prepared. On the other hand, theory predicts that the stable hcp phase of both Fe and the Cantor alloy would be NM in the ground state [23,61], but this phase in the Cantor alloy is thought not to be stabilized because of possible kinetic limitations in experimental samples.

B. The contributions to fcc and hcp phase stabilities by the alloying effect of hcp Ru and by moment-volume fluctuations in the fcc state

We have shown in this work that the $\text{Cr}_{20}\text{Mn}_{20}(\text{Fe}_{20-x}\text{Ru}_x)\text{Co}_{20}\text{Ni}_{20}$ system forms a two-phase fcc/hcp alloy with each phase preserving the VEC as 8.0 ± 0.1 e/a, but with different elemental compositions. XRD resolves the formation of the hcp phase already at $x = 5$. However, even for $x = 20$, the hcp phase is not fully stabilized, although it comprises a large percentage of the sample with a phase fraction of more than 80%. It is known that the structure of individual elements influences the stability of the final structure of an alloy, and in this sense, 20 at% of hcp Ru would be strongly contributing as a stabilizing agent of the hcp structure in the present alloys. For the $x = 20$ sample, the fcc phase is still present, although the phase fraction may be down to 0.18. However, it appears that a total of 37.9 at% of Ru and Co together in the fcc phase of this sample is not capable of fully stabilizing the hcp phase, whereas the hcp phase in $x = 10$ is already stabilized with a total of 31.3 at% of Ru and Co.

Ru substitution may have an effect of stabilizing the hcp phase through its own structure, but one may have to look beyond this alloying effect and also consider the destabilization of the fcc phase to be due to the weakening of the effect of moment-volume fluctuations. The two effects would then be complementary for stabilizing the hcp phase. The effect of weakening moment-volume fluctuations by the incorporation of Ru into the fcc phase is reflected in the weakening of FM and AFM interactions as the Ru concentration in the fcc phase of the alloys increases. The similarity of the behaviors of the anomalous $\alpha(T)$ of fcc-Fe and the equielectronic Cantor alloy, both with VEC = 8 e/a, had suggested that a moment-volume instability should be present in the ground state of this alloy [58]. In the case of Fe, the presence of such an instability leads to the stability of the fcc state over the hcp state. An analogy of the behaviors of $\alpha(T)$ and the same value VEC = 8 for Fe and the Cantor alloy would then suggest the presence of such an instability also in the ground state of the fcc-Cantor alloy so that this would be a contributing agent for the stability of

FIG. 16. Refinements for samples (a) $x = 0$ and (b) $x = 3$.FIG. 17. Refinements for samples (a) $x = 5$ and (b) $x = 10$.FIG. 18. Refinements for samples (a) $x = 18$ and (b) $x = 20$.

the fcc next to the established configurational entropy effect. This would be an alternative argument for the stability of the fcc phase in the Cantor alloy due to kinetic limitations.

VI. CONCLUSION

The high-entropy Cantor alloy system $\text{Cr}_{20}\text{Mn}_{20}(\text{Fe}_{20-x}\text{Ru}_x)\text{Co}_{20}\text{Ni}_{20}$ comprises two-phase fcc/hcp structures with the fcc phase being magnetically active through the presence of moment-volume instabilities, and the hcp phase is NM, with both properties in accordance with theoretical predictions. Ru can contribute to the stability of the hcp phase by the alloying effect through its own hcp structure, but it can also destabilize the fcc phase by weakening the effect of the moment-volume instability,

TABLE III. Figure of merit of the refinement.

x	GoF	R_p	wR_p
0	1.28	28.27	37.71
2.5	1.33	28.45	37.20
5	1.30	28.34	37.37
10	1.20	28.07	37.67
18	1.20	13.05	16.71
20	1.13	25.30	35.54

which is the stabilizing agent of the fcc structure. Thermal expansion, magnetization, and Mössbauer spectroscopy studies suggest that the fcc and hcp entities are essentially noninteracting.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX

The XRD refinement results are shown in Figs. 16–18. The figure-of-merit goodness of fit (GoF), profile R-factor (R_p), and wR_p (weighted profile R-factor) are collected in Table III.

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