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Note: This paper was presented at the 2019 Joint MMM-Intermag Conference.
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ABSTRACT

We measured the change in the average hyperfine field strength of several high entropy alloys in relation to small compositional deviations from the equiatomic alloy, FeCoNiCuMn. Mössbauer spectra of four psuedo-binary systems, in which Mn content is increased and another element was decreased in equal measure, reveal several discrete peaks in the hyperfine field distribution that show evidence of the discrete exchange interactions between magnetic elements in the alloy. A simple linear regression modelling the perturbation of the average hyperfine field when the composition is altered calculates the contribution of each atom to the overall average. The average hyperfine field is linear with T_c, so these values allow us to estimate T_c for alloys with more complex compositional variation within the window of linearity (<24% Mn based on other alloys). The results were confirmed experimentally by calculating T_c of two new alloys, $Fe_{19}Co_{20}Ni_{19}Cu_{19}Mn_{23}$ and $Fe_{19}Co_{20}Ni_{19}Cu_{20}Mn_{22}$.

I. INTRODUCTION

Magnetocaloric refrigeration at room temperature is a topic of great interest due to the fact that it has been shown to be up to 20% more efficient than conventional vapor compression refrigeration, and it has the additional advantage of being environmentally friendly because ozone depleting and warming refrigerants are not used.[1,2] Much work has been done to explore materials with transition temperatures around room temperature, but the majority of them contain rare earth (RE) metals, the scarcity and high price of which is prohibitive for large scale production.[3–6] Our past work has explored the RE-free transition metal-based high entropy alloy (HEA) system FeCoNiCuMn for this reason, building on the work of Lucas et. al on FeCoCrNi alloys.[7–9] The multiple similarly sized atoms mixed in relatively equiatomic amounts in these alloys lead to a 2nd order magnetic transition, which is broadened due to the distributed exchange interactions arising from the disorder,[10–14] and

allows T_c tuning and control of the refrigeration capacity, which leads to a broader transition range than seen in traditional alloys. This is a novel approach to increasing the refrigeration capacity of a magnetocaloric material that does not rely on physical processing (ball milling, cold rolling, etc) to broaden the temperature range.

Though our past work considers the distributed exchange interactions qualitatively as the cause of the broad transition, Mössbauer spectroscopy offers us a unique method of quantifying the individual exchange interactions between each magnetic element present.[15]

Mössbauer spectroscopy relies on the absorption and emission of gamma rays from the sample's atomic nuclei. These transition energies are influenced by the atom's compositional, electronic, and magnetic environment. In a recoilless event, a nucleus that absorbs a gamma ray of a certain energy will then emit a gamma ray of the same energy. For an absorber nucleus in a different environment, the emitted gamma ray must be altered using the

Doppler effect; the emitting source is moved forward or backwards at specific speeds on the order of mm/s, and because the change in energy is so small, the transmission spectra are typically reported in terms of intensity of transmission versus source velocity for simplicity.[16] It is important to note that this technique investigates the environment surrounding one specific atomic species.

There are three primary environmental factors that will influence the energy levels of the absorber nuclei: isomer shift, quadrupole splitting, and Zeeman splitting. The isomer shift (δ) corresponds to the electric monopole interaction between the nuclear charge distribution and the potential generated by the electronic charge distribution penetrating the nucleus. Quadrupole splitting occurs due to the presence of an electric field, and it results in the splitting of the central peak, a singlet, into two peaks, a doublet. Zeeman splitting is the splitting in energy levels due to the presence of magnetic dipoles, resulting in six peaks, a sextet. The transmitted Mössbauer spectrum is a superposition of singlets, doublets and sextets which need to be deconvoluted to obtain the Mössbauer parameters corresponding to the hyperfine interactions present.[17] The hyperfine field surrounding the absorber nucleus can be thought of as the effective magnetic field of the sample at the location of the nucleus. When the hyperfine parameters fluctuate from one site to another, they give rise to hyperfine magnetic field distributions (HFD), which are obtained through fitting of each peak in the spectrum.[18]

The Mössbauer spectra obtained for our alloys were taken using a ^{57}Co gamma ray source embedded in a Rh matrix. This emitter nucleus' gamma rays will be absorbed by Fe atoms, so all spectra and hyperfine field distributions are explorations of the local environment surrounding Fe atoms in our alloys. The compositional data for each alloy was obtained using ICP analysis, and all magnetic measurements were performed using a vibrating sample magnetometer (VSM) mounted on a physical properties measurement system (PPMS). Our alloys are produced by melting high-purity bulk elemental samples in a mini arc melting system MAM-1 (Edmund Buhler GmbH) into an ingot, which is then melt-spun using an SC melt spinner (Edmund Buhler GmbH). This results in a single phase alloy produced through rapid quenching. These alloys were previously confirmed to be single phase using both x-ray diffraction (XRD) and electron dispersive spectroscopy (EDS) for compositional mapping.[7] Cu tends to phase separate at large concentrations[19]–we postulate that a combination of extended solubilities due to entropic effects in multicomponent FCC solid solutions[20] and the lower concentration of Cu in quinternary HEAs versus quaternary HEAs allows us to retain a single phase.

II. EXPERIMENTAL RESULTS

The Mössbauer spectra, when fit for Zeeman splitting, reveal a complex hyperfine field distribution containing several discrete peaks. The peaks are not coherent enough to fit individually, which prohibits us from quantifying the amount in each distribution or assigning specific field values to each peak. However, their presence allows for some qualitative discussion of these alloys. The four pseudo-binaries probed, Cu-Mn, Ni-Mn, Co-Mn, and Fe-Mn, produce a range of alloys with T_c spanning from 400K to 265K, and the average hyperfine field of these alloys decreased with T_c (Tab. I) but is still non-zero for the compositions with T_c lower than room

TABLE I. Mössbauer spectroscopy data for FeCoNiCuMn pseudo-binaries.

Composition	T_{peak} (K)	$\langle HFD \rangle$ (T)	δ (mm/s)
$FeCoNiCuMn$	395	12.68	-0.051
$FeCoNiCu_{0.975}Mn_{1.025}$	321	6.68	-0.056
$FeCoNiCu_{0.95}Mn_{1.05}$	297	5.07	-0.086
$FeCoNiCu_{0.925}Mn_{1.075}$	279	3.73	-0.09
$FeCoNiCu_{0.9}Mn_{1.1}$	264	3.41	-0.08
$Fe_{0.975}CoNiCuMn_{1.025}$	299	6.24	-0.079
$Fe_{0.95}CoNiCuMn_{1.05}$	292	4.43	-0.09
$FeCoNi_{0.975}CuMn_{1.025}$	319	7.08	-0.025
$FeCoNi_{0.95}CuMn_{1.05}$	280	4.45	-0.094
$FeCo_{0.975}NiCuMn_{1.025}$	320	7.33	-0.037
$FeCo_{0.95}NiCuMn_{1.05}$	292	4.79	-0.09

temperature. This is evidence that our materials undergo a broad, second order magnetic transition, as a first order transition would result in a sharp drop in the average hyperfine field. In BCC solid solutions, exchange interactions extend to several next nearest neighbor shells, whereas in close packed FCC solid solutions the exchange interactions are more localized.[21] The AFM interactions in fcc and bcc-derived structures may exhibit non-collinear spin wave interactions, complicating the interpretation of the HFD.[22]

Each HFD exhibits a handful of peaks at several values of field strength, some which are obscured and appear as shoulders on other peaks. Several identifiable peaks are indicated by red arrows in Fig. 1. Though we cannot definitively quantify the number of peaks in each distribution, we can note that the number of peaks and shoulders identified for each alloy is around six; there are six ferromagnetic pairwise interactions in each alloy (Fe-Fe, Co-Co, Ni-Ni, Fe-Co, Fe-Ni, and Co-Ni). These peaks show evidence of these individual pairwise interactions, demonstrating that the magnetic behavior is an average over these interactions and is responsible for the broad magnetocaloric response in these alloys. Past work by Kimball et. al. has shown that Mössbauer spectroscopy can identify antiferromagnetic behavior in Fe-Mn alloys, even with spectra that do not have fully resolved six peaks due to Zeeman splitting.[18] The FeCoNiCuMn spectra are weak because they are obtained at room temperature, near T_c for these alloys, but spectra taken at a lower temperature could allow us to examine the antiferromagnetic interactions in these alloys as well.

A. Addition perturbation model

Though the hyperfine field distributions for the Mössabauer spectra are too weak to fit, we can use the corresponding average hyperfine fields to reveal the contributions from each atom to the changing values. Table I lists the average hyperfine fields in each alloy, $\langle HFD \rangle$, which gives us a value for the average strength of the exchange interactions between each atom, alongside the transition temperature, T_{peak} (or T_c) for each alloy and the isomer shift, δ. Because the isomer shift is a measure of Coulomb interactions in the alloy, it should be larger as the density of the s-orbit electrons increase. We see this reflected in the isomer shift values for
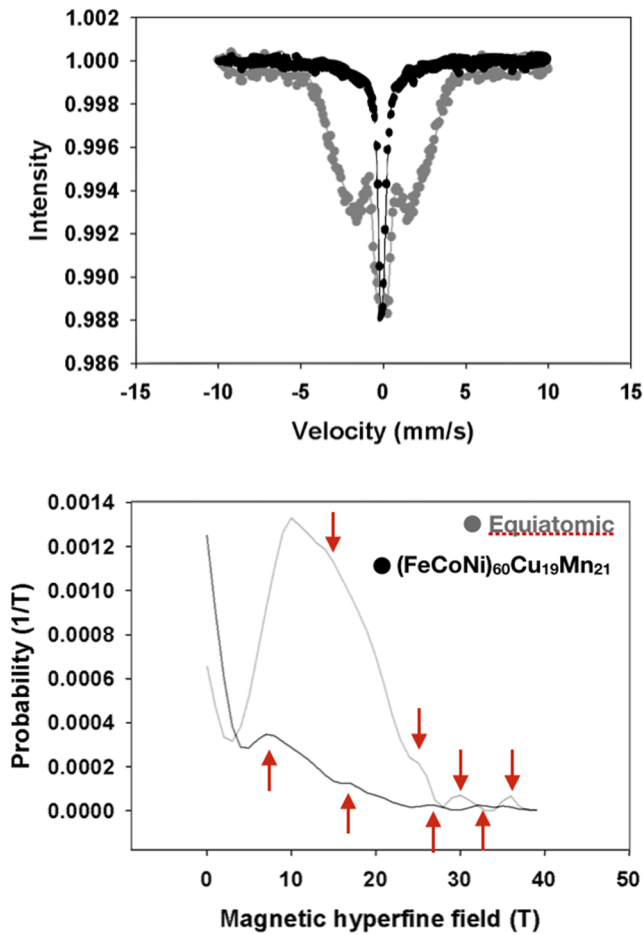
FIG. 1. Top: Mössbauer spectra for two HEA alloys. Bottom: Corresponding HFDs, with discrete peaks and shoulders denoted with red arrows. Reprinted with permission from Perrin et al., Journal of Metals **69**, 2125–2129 (2017). Copyright 2017 Springer.[8]
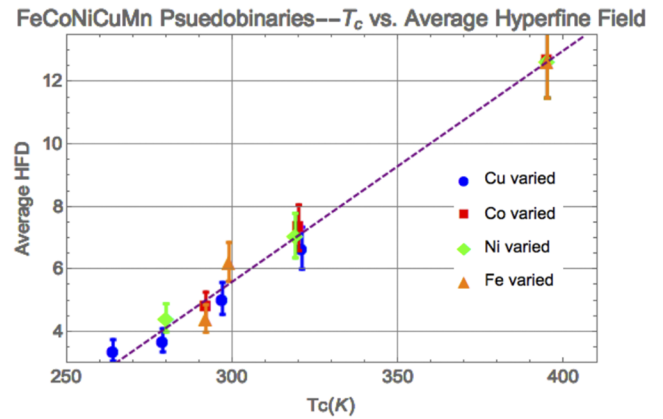

FIG. 2. T_c of pseudo-binary alloys plotted against average hyperfine field, demonstrating that the relationship is composition-independent for small variational changes.

these alloys, which increase with Mn content as Mn contains fewer d-orbital electrons than the other atoms present.

The average hyperfine fields are generally linear with the T_{peak} values, which is easier to see when the data is plotted (Fig. 2). The majority of the data lies on a line with a maximum deviation of ± 0.35T, so a calculated or experimental value of the average hyperfine field can be used to estimate T_c of an alloy, and vice versa.

To calculate the contribution from each element to the average hyperfine field, we follow the model laid out in Brent Fultz' 1993 paper, which investigates the change in hyperfine fields experienced by Co atoms in BCC solid solutions as a function of the composition of the nearest and next nearest neighbors, also known as the addition perturbation model.[23] The model begins by defining the hyperfine field of the solid solution as the hyperfine field of pure Co, H_o, plus a perturbation, ΔH:

$$H = H_o + \Delta H \tag{1}$$

This perturbation can be broken into three terms:

$$\Delta H \approx n_1 \Delta H_1^x + n_2 \Delta H_2^x + \kappa c \tag{2}$$

where n_1 and n_2 refer to the number of nearest and next nearest neighbors, respectively, and ΔH_1^x and ΔH_2^x refer to the contributions from each set of neighbors. All further neighbors, whose contributions to the hyperfine field are relatively weak, are wrapped into the κc term, where κ is the average concentration dependence of the perturbations, and c is the concentration of solute atoms. This model is easily extended to our alloys; to model an FCC crystal, the neighbor terms are changed to $n_1 = 12$ and $n_2 = 6$. The H_o term is now defined as the average hyperfine field of the equiatomic FeCoNiCuMn alloy, and the ΔH contribution is broken into several solute terms:

$$\Delta H = \Delta H_{Ni} + \Delta H_{Fe} + \Delta H_{Mn} + \Delta H_{Cu} + \Delta H_{Co} \tag{3}$$

and it follows that the average contribution from all is a sum of the average of each:

$$\langle \Delta H \rangle = \langle \Delta H_{Ni} \rangle + \langle \Delta H_{Fe} \rangle + \langle \Delta H_{Mn} \rangle + \langle \Delta H_{Cu} \rangle + \langle \Delta H_{Co} \rangle \tag{4}$$

Because we cannot get accurate variance information from the HFDs, we do not have enough information to distinguish between nearest and next nearest neighbor. However, as long as our alloys are truly randomly distributed solid solutions, the terms in our ΔH expressions can be lumped together into one new value, G_x:

$$\langle \Delta H \rangle = \sum_x c_x \left(12 \Delta H_1^x + 6 \Delta H_2^x \right) \quad = \sum_x c_x G_x \tag{5}$$

Thus the final expression for the perturbations due to the change in composition for our alloys simplifies to:

$$\langle \Delta H \rangle = c_{Fe} G_{Fe} + c_{Cu} G_{Cu} + c_{Mn} G_{Mn} + c_{Ni} G_{Ni} + c_{Co} G_{Co} \tag{6}$$

With enough different alloys, and accurate compositional data for each alloy, the values of G_x for each atom can be calculated using the average hyperfine field values listed in Table I. The resulting values of G_x are listed in Table II. These values validate the assumptions we have made about each element's contribution the system based on their elemental properties. The largest positive contributions

TABLE II. Contributions to average hyperfine field from each element.

Element	$G_x \left(\frac{T}{atom\%} \right)$
Co	2.165
Fe	0.215
Ni	0.839
Cu	0.136
Mn	-3.058

come from Co and Ni, which are ferromagnetic with large magnetic moments, and the larger moment and T_c of Co over Ni correlates to a larger contribution. Fe has a noticeably smaller contribution, and we suggest that this is due to the decreased atomic distance between Fe atoms in these alloys. While BCC Fe is ferromagnetic, antiferromagnetic Fe is FCC, so it is likely that the closer packing in these alloys approaches the crossover point. This gives us further insight into the antiferromagnetic interactions in the alloy, which are lowering both the magnetization and T_c. Cu is not expected to change the hyperfine field drastically as it is diamagnetic, but the small amount of RKKY coupling Cu experiences does give it a slightly positive contribution. Finally, antiferromagnetic Mn causes a large, negative contribution.

We developed alloys in the FeCoNiCuMn system with more than two elements varied, allowing us to assess the validity of these results, as well as the limits of the linearity of the average hyperfine field versus T_c. The alloys $Fe_{19}Co_{20}Ni_{19}Cu_{19}Mn_{23}$ and $Fe_{19}Co_{20}Ni_{19}Cu_{20}Mn_{22}$ were estimated to have T_c=248K and T_c=294K from the calculated values, while the experimental values of T_c were found to be 225K and 319K. This demonstrates that the Fultz model can estimate T_c values within 25K for this system.

This approach could also be used to characterize and make predictions in other similar systems (for example, a system with Cr replacing some Mn) provided that some data about an alloy in the system, or the Mössbauer spectra, has been obtained, but we have not done further work to confirm this experimentally.

III. CONCLUSION

We present Mössbauer spectra obtained for four psuedo-binary alloy systems branching from equiatomic FeCoNiCuMn. The hyperfine field distributions calculated for these spectra have several distinct peaks which is evidence of the discrete exchange interactions between the magnetic components of the alloys, and we demonstrated a simple model for calculating the contributions of each atom to the average hyperfine field. We found that the values estimated T_c within 25K for two new alloys in the system.

ACKNOWLEDGMENTS

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