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Hidden Mn magnetic-moment disorder and its influence on the physical properties of medium-entropy NiCoMn solid solution alloys

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The *ab-initio* Korringa-Kohn-Rostoker method (KKR) combined with the coherent potential approximation (CPA) was employed to investigate the electronic, magnetic, and transport properties of medium-entropy face-centered-cubic (fcc) NiCoMn solid solution alloys. By comparing the CPA electronic structure with that from supercell calculations, we uncovered an unconventional CPA ground state, which correctly distinguishes two equally-populated Mn CPA components – with large spin moments but opposite orientations. Using the spin spiral calculations, we further demonstrated that this ground state is most energetically favorable in the presence of spin noncollinearity and no significant longitudinal spin fluctuation is observed, justifying the applicability of the Heisenberg model. The finite temperature magnetism was further studied using different approximations based on the Heisenberg model and we found the Mn moments to be fully disordered at low temperature due to a small net effective Weiss field on Mn. In addition, the magnetic effect on the electron scattering at finite temperatures was evaluated and compared with other scattering mechanisms. Since the magnetization-induced electron scattering is almost saturated in the ground state, (full) spin disorder only yields a small addition to the resistivity whereas the thermal displacements increase it modestly. Finally, we elucidate the role of the hydrostatic pressure on the magnetic and transport properties. These findings reflect the importance of the magnetic signatures on the physical properties of alloys, and provide a window into magnetism-controlled electronic structure and energy dissipation.

I. INTRODUCTION

In a general N-component concentrated solid-solution alloy (CSA), the configurational entropy is maximal at equiatomic concentration and increases with the number of alloying elements N. When $N \geq 5$, Yeh *et al.* [1] argued that the contribution from the configurational entropy to the Gibbs free energy may be dominant, thereby facilitating the formation of highly stable, single-phase disordered solid solution alloys, of which high entropy alloys (HEAs) are exemplars [2]. Following the synthesis of the first HEA (NiFeCoCrMn) by Cantor *et al.* [3], Wu *et al.* [4] demonstrated that by taking combinations of this alloy’s 3d transition metal elements, supplemented by Pd, it is possible to obtain a series of 2-, 3-, 4- and 5-component equiatomic alloys (NiCo, NiFe, NiPd, NiFeCo, NiCoCr, NiCoMn, NiCoCrMn, NiFeCoCr, NiFeCoMn, NiFeCoCrMn, NiFeCoCrPd) that all crystallize as a single phase face centered cubic (fcc) solid solution alloy. Hereafter, this set of Ni-based fcc alloys will be referred to as Cantor-Wu alloys. Since the discovery of HEAs, many exceptional and unusual properties – mechanical [5, 6], radiation response [7, 8], transport [9–11], magnetic properties [10, 12] – have been reported for alloys having a variety of crystal structures, including fcc

[4], body centered cubic (bcc) [13], and hexagonal closed-packed (hcp) [14].

In disordered alloys composed of mid-period 3d transition metal elements, magnetism is well known to play an important role in determining their properties. Firstly, magnetic entropy makes a substantial contribution to the Gibbs free energy, thereby affecting thermodynamic phase-stability-related phenomena, such as order-disorder [15], and structural phase transitions, e.g. fcc-hcp transitions that are controlled by the stacking fault energies [16, 17]. In addition, magnetism can have a large impact on other properties, including mechanical properties [18, 19], electronic [20] and thermal transport [9, 21], thermal expansion – such as Invar effect in iron–nickel alloys [22], and also holds promise for functional applications, such as giant spin-orbit torque [23]. However, unlike mechanical properties that have been extensively explored, studies of magnetic properties and influence of magnetism on other derived properties of CSAs and HEAs remain scarce and deserve further investigation.

In this work, we study the magnetic properties of the medium-entropy CSA NiCoMn, which can be regarded as a prototype of many Mn-containing Cantor-Wu alloys (NiCoMn, NiFeCoMn, NiCoCrMn, NiFeCoCrMn), several of which exhibit complex magnetic properties, such as spin-glass state [12], frustrated Mn moments [18], longitudinal spin fluctuations (LSF) [19], and low critical temperature (T_c) [10]. Interestingly, alloying NiCoMn with Fe to form a NiFeCoMn solid solution gives unremarkable mechanical properties [24, 25], while supple-

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menting NiCoMn with Cr yields an excellent combination of strength and ductility [5]. In addition, it has been suggested that the occurrence of frustrated Mn moments [18] can eliminate the fcc-hcp energy difference, and thereby directly impact the fcc-hcp phase transition and resulting mechanical properties. Therefore, a deep understanding of magnetism in NiCoMn alloy is a prerequisite for understanding other properties of Mn-containing Cantor-Wu alloys.

Interestingly, the two most prevalent *ab-initio* theories of disordered alloys – the supercell method [26] and the coherent potential approximation (CPA) [27] – contradict each other regarding the magnetic ground state of some Mn-containing Cantor-Wu alloys. On one hand, supercell calculations found two (approximately equally-populated) groups of Mn atoms, each with sizable local moments but having opposite spin orientations [18, 20]. On the other hand, conventional single-site CPA calculations yield only *one* type of Mn atoms, all having low spin moments (hereafter called one-Mn model). Interestingly, this lattice CPA approach has been employed to study the stacking fault energies [28], magnetic transition temperatures [29], longitudinal spin fluctuations, and the impact of magnetism on the mechanical properties of NiFeCoCrMn alloys [19]. These interesting results notwithstanding, the fact that supercell and CPA calculations produce such divergent magnetic structures calls into question the validity of the results using the conventional CPA approach.

Here we employed a two-Mn model using CPA that distinguishes two types of Mn species – with opposite spin orientations but equal concentration. A similar approach has been applied to NiMn alloys by Akai *et al.* [30]. We showed this approach successfully recovers both antiparallel spin alignments and large Mn moments found in supercell calculations [20]. Furthermore, it is found that the two-Mn model is energetically favorable to the conventional one-Mn model [20]. Given that CPA methodology is specifically designed to describe the configurational averaged physical observable in the thermodynamic limit, it is desirable to justify the two-Mn model obtained from CPA by comparing the electronic structure and magnetism with supercell calculations. In addition, using a suitable model Hamiltonian to study the spin thermodynamics based on the ground state two-Mn model, we can further elucidate magnetic properties at finite temperature and pressure, and assess the effect of magnetism on electronic transport properties.

The manuscript is organized as follows: computational details are described in Sec II. Then, the electronic structure calculations for the ground magnetic state are presented in Sec. III A. Spin spiral calculations are performed in Sec. III C to sample the spin noncollinear configurations and to verify the validity of mapping magnetic interactions onto a Heisenberg Hamiltonian. The isotropic exchange parameters within the Heisenberg model are calculated in Sec. III B, based on which thermodynamic simulations are performed in Sec.

III D. The finite temperature transport properties are explored with the temperature dependent spin disorder, and temperature dependent atomic displacement been considered in Sec III E. In the Sec. III F, the magnetism and residual resistivity are calculated as a function of hydrostatic pressures.

II. METHODOLOGY

A. Computational details

Two different methods have been used to perform first-principles calculations for alloys: the supercell method and the Korringa-Kohn-Rostoker Green's function method [31, 32] combined with CPA [27] (hereafter called KKR-CPA).

The supercell calculations were carried out using the projector augmented wave method (PAW) [33] as implemented in the Vienna Ab Initio Simulation Package (VASP) [34, 35]. To mimic the disordered local environment, we constructed several conventional cubic Special Quasi-random Structures (SQS) [26] with 108 atoms included. We used a kinetic energy cutoff of 400 eV for the plane-wave expansion and a Γ -centered Monkhorst-Pack grid [36] for the Brillouin zone (BZ) integration. The ionic coordinates were relaxed while keeping the cubic cell shape and volume fixed at the experimental value for NiCoMn alloys, with lattice parameter $a = 3.60 \text{ \AA}$ [9]. To give an accurate prediction of atomic displacements, generalized gradient approximation (GGA) parametrized by Perdew, Burke, and Ernzerhof (PBE) [37] was used for the exchange and correlation. Employing the optimized structure, the electronic structure and magnetic properties were further calculated using the local density approximation (LDA). Methfessel-Paxton smearing of 0.1 eV and a Γ -centered $3 \times 3 \times 3$ ($4 \times 4 \times 4$) k-point mesh were used for ionic relaxation (density of states (DOS) calculations) within the 108-atom SQS cell. A spin collinear configuration was assumed.

The KKR-CPA method as implemented in the Munich SPR-KKR package [38] was used to calculate the effect of disorder on the electronic structure and resistivity. Consistent with the supercell electronic structure calculations, LDA has been employed for the exchange and correlation and the experimental lattice parameter was adopted. The potential is described within atomic sphere approximation (ASA). The angular momentum expansion of the Green's function employed a cutoff of $l_{max} = 4$.

Employing the self-consistent Green's function, the conductivity tensor is calculated by using the linear response Kubo-Greenwood formula [39, 40] with the configurational averaged state described within the CPA [41]:

$$\sigma_{\mu\nu} = \frac{\hbar}{\pi N \Omega} \text{Tr} \langle j_{\alpha}^{\mu} \text{Im} G^{+}(E_F) j_{\beta}^{\nu} \text{Im} G^{+}(E_F) \rangle \quad (1)$$

where j_{α}^{μ} denotes the μ -component of the current den-

sity operator j for species α with concentration c_α and $G^+(E_F)$ is the retarded Green's function at the Fermi energy. To study the effect of displacement scattering and spin disorder on ρ_0 , we used the so-called alloy analogy model (AAM) to calculate the configurational average over a discrete set of species-resolved atomic displacements and local moment orientations [42]. Two types of atomic displacements are distinguished: static atomic displacements (denoted as u_0), arising from the local atomic relaxation and thermal atomic displacements (denoted as $u(T)$), arising from the thermally-induced lattice vibrations. The former were calculated from the structurally optimized supercell, while the latter were estimated from the temperature-dependent root mean square displacements calculated using the Debye model (see Ref. 42 for details). The u_0 and $u(T)$ are assumed to be additive.

B. Magnetism

In order to evaluate the equilibrium spin configuration in the NiCoMn alloy the classical Heisenberg model is used, with the following form of Hamiltonian:

$$\hat{H} = - \sum_{i,j}^{\mu,\nu} c_\mu c_\nu J_{i,j}^{\mu,\nu} \mathbf{e}_i^\mu \cdot \mathbf{e}_j^\nu \quad (2)$$

Here the vectors \mathbf{e}_i^μ represent the normalized spin moments (or reduced moments) on site i occupied by species μ , c_μ is the concentration of species μ , and $J_{i,j}^{\mu,\nu}$ are the exchange parameters between site i (occupied by species μ) and site j (occupied by species ν). The parameters $J_{i,j}^{\mu,\nu}$ are calculated using the so-called Lichtenstein formula [43] as implemented in SPR-KKR. The summation over atomic species (μ, ν), randomly distributed over lattice sites, are weighted with their respective concentrations (c_μ, c_ν). As defined here, positive (negative) exchange parameters favor ferromagnetic (antiferromagnetic) spin alignments. We note that in Eq. 2, the exchange parameters account for the interatomic exchange interactions scaled with the size of the magnetic moments of the interacting atoms.

C. Thermodynamics

The finite temperature magnetic properties are investigated using classical mean field theory, classical pair cluster approximation, and classical Monte-Carlo simulations. The mean field approximation is expected to be reasonable due to large coordination number for the nearest spin interactions – 12 within the first *fcc* coordination shell. Moreover, Monte-Carlo simulation is also employed to estimate the correlation effect. A rigid spin approximation was used to treat magnetic moments of 3d-transition metal ions, which are considered as classical vectors.

The magnetization at finite temperature can be described within classical mean-field theory by solution of the matrix equation:

$$\langle \hat{e}_z \rangle = L(\beta \hat{h}_{eff}), \quad (3)$$

\hat{e}_z is the matrix for reduced moments (projected to the quantization axis z), which is a column vector whose components are the z -component of reduced moment on each species μ , \mathbf{e}_z^μ . $\langle \dots \rangle$ represents the thermodynamics average over the spin orientations at all sites. $L(x)$ is the Langevin function, whose argument $x = \beta h_{eff}$ is the distribution function for the spin orientation at a certain temperature T . β is $\frac{1}{k_B T}$, where k_B is the Boltzmann constant, and \hat{h}_{eff} is the effective Weiss field matrix with argument h_{eff}^μ for species μ . Specifically, $h_{eff}^\mu = \sum_\nu c_\nu \sum_j J_{i,j}^{\mu,\nu} \langle (\mathbf{e}_j^\nu)_z \rangle$. The critical temperature corresponds to the vanishing of $\langle \mathbf{e}_z^\mu \rangle$ for all species μ .

In addition, two techniques which allow to incorporate spin correlations beyond single site approximation – cluster variation method (CVM) [44, 45] and Monte Carlo simulation – have been employed. The CVM was used to calculate the thermodynamic quantities in alloys. The traditional approach – the mean field approximation (MFA) – usually overestimates the critical temperature and fails to predict stability of the correct phase. This failure is caused by the presence of strong nearest neighbor interactions and, as a result, strong interatomic correlations that are neglected in MFA. In order to incorporate the correlation effect, cluster techniques are used. In these techniques, the interactions within the maximal size cluster and its sub clusters are incorporated exactly, while the interactions of the cluster with the rest of the system are described through the effective field. The two mostly popular cluster methods are cluster variation and cluster field methods (CVM [44, 45] and CFM [46], respectively). Both methods are equivalent to each other in the case of the pair cluster approximation. Our calculation of the critical temperature of the Heisenberg model was executed using pair clusters CFM [47].

Parallel tempering Monte Carlo simulations [48, 49] are also employed to obtain the finite temperature magnetic state. The Heisenberg Hamiltonian $\hat{H} = - \sum_{i,j}^{\mu,\nu} J_{i,j}^{\mu,\nu} \mathbf{e}_i^\mu \cdot \mathbf{e}_j^\nu$ is employed for a finite-size cell, with the spins randomly distributed according to the concentration. A swap trial is performed with a Metropolis-like probability which satisfies the detailed balance condition. The transition probability from a configuration X_m simulated at temperature T_m to a configuration X_n simulated at temperature T_n is

$$W(X_m, T_m | X_n, T_n) = \min[1, \exp(-\Delta)], \quad (4)$$

$$\Delta = (1/k_B T_n - 1/k_B T_m)(\hat{H}_m - \hat{H}_n). \quad (5)$$

To take into account the effect of the critical slowing down near the phase transition, we also apply the Wolff cluster update algorithm [50]. Given a randomly chosen

direction \hat{n} , spins are iteratively added to the flipping cluster with probability

$$p = 1 - \exp \left\{ \min \left[0, \frac{2J_{ij}}{k_B T} (\hat{n} \cdot \mathbf{e}_i)(\hat{n} \cdot \mathbf{e}_j) \right] \right\}, \quad (6)$$

and then the cluster of spins is flipped with respect to the hyperplane orthogonal to \hat{n} . Therefore, a typical Monte Carlo step consists of a single spin flip trial for every spin, a cluster update for the whole system, and a replica swapping trial between neighboring temperatures.

III. RESULTS AND DISCUSSIONS

A. Electronic structure

A previous CPA study [20] found multiple magnetic states of NiCoMn that are close in total energy. Different magnetic states are distinguished depending on the spin orientation of the Mn local moment. Specifically, a state with all Mn spins parallel (antiparallel) with the Co spins was found, and is denoted as the FM (AFM) state, with only one type of Mn spin in either case. Alternatively, it has been demonstrated that the magnetic ground state corresponds to a state which distinguishes two types of Mn moments (Mn^\uparrow and Mn^\downarrow) with roughly equal populations but opposite spin orientations [20]. This is analogous to the so-called disordered local moment (DLM) state [51], with the local moment disorder only applied to Mn. For brevity, this ground state is denoted as DLM-Mn state. Using the binary pseudoalloy approximation with uncompensated collinear “up” and “down” Mn moments [30], i.e. uncompensated DLM, Fig. 1 illustrates the total energy change as a function of the relative ratio of Mn^\uparrow to the total Mn, defined as $c_{\text{Mn}^\uparrow}/(c_{\text{Mn}^\uparrow} + c_{\text{Mn}^\downarrow})$ where c_{Mn^\uparrow} and c_{Mn^\downarrow} are the concentrations of Mn^\uparrow and Mn^\downarrow , respectively. $c_{\text{Mn}^\uparrow}/(c_{\text{Mn}^\uparrow} + c_{\text{Mn}^\downarrow}) = 0, 0.5, 1$ correspond to the AFM, the DLM-Mn and the FM states, respectively. As seen from Fig. 1, the energy minimum of NiCoMn at $c_{\text{Mn}^\uparrow}/(c_{\text{Mn}^\uparrow} + c_{\text{Mn}^\downarrow}) = 0.51$ occurs around the DLM-Mn state thus we simply regard the DLM-Mn state as the ground state. Since both the AFM and the FM states have higher energies than the DLM-Mn ground state and the AFM state is slightly more energetically favorable than the FM state, we restrict ourselves to the comparison of the AFM state and the DLM-Mn state.

Besides the different spin orientations, different magnetic states obtained from KKR-CPA also possess distinct magnitudes of the local moments, particularly for Mn. For instance, a Mn moment as large as $2.20 \mu_B$ is found in the DLM-Mn state while the local moment on Mn in the AFM state is only $0.75 \mu_B$. To verify the magnetic features (orientation and magnitude of the local moments) obtained from CPA, supercell spin collinear calculations were performed as a benchmark. Similar to the DLM-Mn state, the supercell calculation distinguishes two types of Mn local moments, with large local moment magnitude but opposite spin orientations: \sim

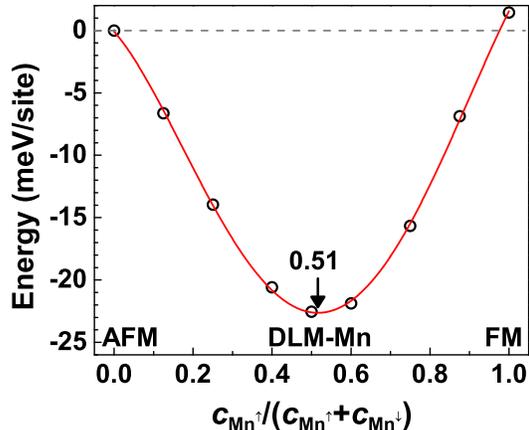


FIG. 1. Total energy (meV/site) as a function of $c_{\text{Mn}^\uparrow}/(c_{\text{Mn}^\uparrow} + c_{\text{Mn}^\downarrow})$. The zero energy corresponds to the energy of the AFM state. The black arrow labels the energy minimum at $c_{\text{Mn}^\uparrow}/(c_{\text{Mn}^\uparrow} + c_{\text{Mn}^\downarrow}) = 0.51$.

$50\% \text{Mn}^\uparrow$ and $\sim 50\% \text{Mn}^\downarrow$. This feature is insensitive to the choice of exchange-correlation functional (LDA or GGA).

We further compare the electronic structure from the supercell method and the CPA to validate the KKR-CPA ground state. Figure 2 illustrates the total density of state (DOS) and species-resolved partial DOS (pDOS) using both supercell (black lines) and the CPA methods. Two CPA solutions – DLM-Mn state (blue lines) and AFM state (green lines) – are considered here. Figure 2 (a) compares the total DOS. Notably, because the CPA directly provides the configurational averaged DOS, the fine structure of DOS as in the supercell calculations is washed out. In addition, the total DOS of DLM-Mn state is consistent with the corresponding density of state obtained from the supercell calculation, while the AFM state displays enhanced DOS around the Fermi energy, and particularly, a shallow peak in the minority-spin channel shows up just above the Fermi energy.

As for the species-resolved pDOS, Fig. 2 (b) and (c) shows pDOS of $3d$ states for Ni and Co species. The black line indicates the averaged DOS obtained from the supercell calculation and the colored smearing – quantified by the standard deviation of the DOS at each energy point – encapsulates the fluctuations of the density of state at different Ni (Co) sites due to different chemical environment of each site and local atomic relaxations that result from it. Both CPA solutions show pDOS of Ni and Co consistent with the supercell method. The on-site exchange splitting on Ni – with nearly-filled $3d$ bands – is small as is the Ni moment. On the contrary, having one less valence electron, the on-site Hund’s exchange is stronger in Co; therefore, producing a more sizable Co moment ($\sim 1\mu_B$).

As was shown in a previous study [20], the Mn mo-

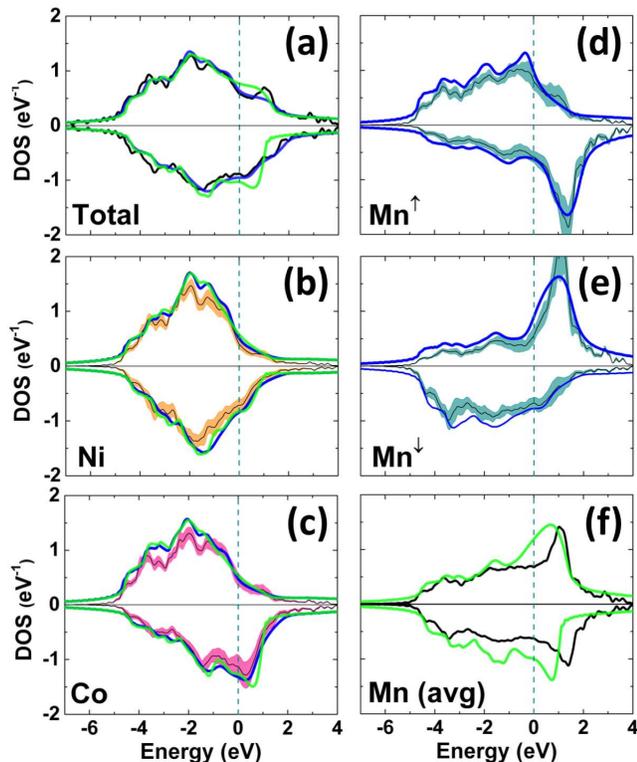


FIG. 2. (a) Total DOS (states/eV/site) and (b)-(f) species-resolved partial DOS (states/eV/site) of NiCoMn random alloy using the supercell method (black lines) and the CPA method that produces two states: the DLM-Mn state (blue lines) and the AFM state (green lines). In the supercell method, the black lines correspond to the averaged DOS in each case while their colored smearing of the partial DOS gives the standard deviation of the partial DOS at each energy point. This is obtained from sampling the partial DOS of all atoms with the same species in the supercell. (d)-(e): Mn^\uparrow and Mn^\downarrow distinguish Mn with up spins and down spins, respectively. (f) Averaged Mn partial DOS from supercell method (black lines) and from the AFM state in CPA (green lines). All DOS plots are re-scaled per atom, and the Fermi level (dashed green line) is shifted to zero energy.

ments fall into two categories, large positive (Mn^\uparrow) and large negative (Mn^\downarrow). In addition, the local moment distributions of each species in the NiCoMn supercell have only modest fluctuations: the half width at half maximum (HWHM) of the species-resolved moment distributions are $\sim 0.3 \mu_B$ for Ni, $\sim 0.4 \mu_B$ for Co, $\sim 0.5 \mu_B$ for Mn^\downarrow , $\sim 0.6 \mu_B$ for Mn^\uparrow . In Fig. 2 (d) and (e), both averaged pDOS of Mn^\uparrow and Mn^\downarrow from the supercell method are compared with that in the DLM-Mn state. Again, the DLM-Mn state agrees with the supercell calculation and captures the important magnetic signature: large Mn local moments but opposite Mn spin orientations. Unlike the single-site CPA, the supercell calculation includes the effect of the local atomic displacements. The agreement of the DOS between the supercell and CPA methods suggests that the local atomic displacements in the NiCoMn

alloy have a very minor effect on the averaged DOS.

In contrast, Fig. 2 (f) shows that the averaged Mn pDOS of the AFM state is not consistent with the supercell method, particularly the DOS at the Fermi energy. A large Mn pDOS at the Fermi energy in the AFM state is observed, suggesting a Stoner's instability towards the formation of larger Mn moment rather than the $0.8 \mu_B$ that actually is found in the AFM state.

In summary, the single-site CPA approach which assumes only one type of Mn atoms gives an inconsistent prediction of the local moments and electronic structure, as compared with the supercell calculation. In addition, it may also suffer from magnetic instability due to interatomic exchange interactions. This issue is discussed in the following two subsections.

B. Heisenberg exchange interactions

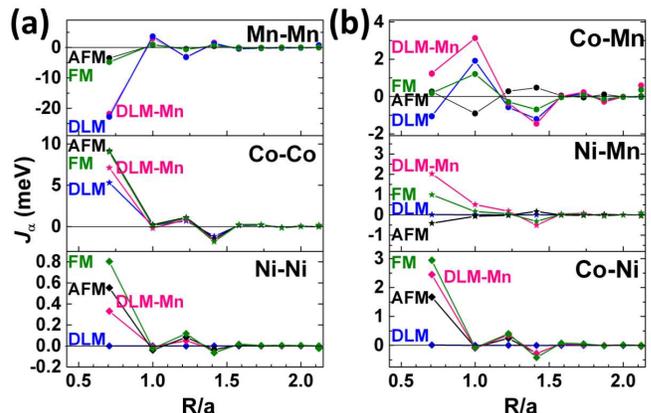


FIG. 3. The intra-species (a) and inter-species (b) exchange parameters (J_α) as a function of bond length (for a certain α th nearest neighboring shell) in random alloy NiCoMn in the following multiple states: FM state, AFM state, DLM state, and DLM-Mn state. In the DLM-Mn state and DLM state, only the interactions centered around a spin-up Mn atom are shown.

The isotropic exchange parameters are calculated for different magnetic states, FM, AFM, DLM, DLM-Mn, as defined previously. Figure 3 (a) and (b) illustrate the calculated intra-species (between the same species type) and inter-species (between different species types) exchange interactions as a function of interatomic distance (scaled by the lattice parameter). Here we use J_α to denote the exchange parameters characterizing interactions within the α th nearest atomic shell. As expected, J_α display long-range RKKY-like oscillations – between positive (ferromagnetic coupling) or negative (antiferromagnetic coupling) values – and decrease with increasing distance. The J_α become negligibly small beyond 7th nearest neighbor shell. We note that since the Ni moment collapses in the DLM state, the corresponding

inter- and/or intra-species exchange couplings vanish accordingly.

It is found that the intra-species exchange interactions are predominately determined by the first nearest neighbor exchange interactions: Co-Co and Ni-Ni exchange interactions are ferromagnetic whereas the Mn-Mn interactions are antiferromagnetic regardless of different magnetic states. While the J_1^{Co-Co} , J_1^{Ni-Ni} are only modestly modified by different magnetic states, the J_1^{Mn-Mn} is found to be sensitive to the specific magnetic states. In particular, while $J_1^{Mn-Mn}(\text{AFM}) \sim J_1^{Mn-Mn}(\text{FM})$ and $J_1^{Mn-Mn}(\text{DLM}) \sim J_1^{Mn-Mn}(\text{DLM-Mn})$, $J_1^{Mn-Mn}(\text{DLM-Mn})$ is one order of magnitude greater than the $J_1^{Mn-Mn}(\text{AFM})$.

As for the inter-species exchange coupling, the Ni-Co interactions are dominated by the nearest neighbor interaction (J_1) that favors ferromagnetic coupling. This is also true for Ni-Mn interactions. As for Co-Mn interactions, J_2 becomes dominant and the sign of J_α become more sensitive to the specific magnetic states.

It is worth noting that the exchange parameters between different species at different sites can fluctuate due to different disordered local environments, variation of the bond length due to the local relaxation, and the fluctuation of the size of the moments for each species [52]. Even though the moment size fluctuations turn out to be mild for each species, which may suggest relatively small variation of the exchange parameters, their actual fluctuations are worth a more detailed investigation. However, this is beyond the scope of this work. Here we employ the (configurationally averaged) exchange parameters to explore the thermodynamic properties.

C. Spin spiral calculation

To investigate the stability of the collinear magnetic state with respect to the formation of a non-collinear magnetic structure, and the applicability of the Heisenberg model, we carried out spin spiral calculations using the CPA method. The single-site treatment of the spin spiral state in disordered alloy, based on generalized Bloch theorem [53, 54], was implemented in SPR-KKR by Mankovsky *et al.* [55]. The self-consistent spin spiral calculation shows the relative energy scale of the collective excitation – spin wave – and the single-particle excitation – Stoner excitation. We constrained the spin spiral vector, denoted as \mathbf{q} , along $[\zeta, 0, 0]$, $[\zeta, \zeta, 0]$ and $[\zeta, \zeta, \zeta]$ directions in reciprocal lattice units (r.l.u.) to sample the Γ to X , X to Γ , and Γ to L branches of the fcc BZ. The orientation of the averaged local moment of a disordered magnetic alloy can be written as $(\sin\Omega \cdot \cos\Phi, \sin\Omega \cdot \sin\Phi, \cos\Omega)$ in the general spherical coordination, where Ω and Φ are polar angle and azimuthal angle, respectively. We studied a cone type of spin spiral state that propagates along the \mathbf{q} direction with a fixed spin cone angle Ω but a modulated azimuthal angle Φ along the \mathbf{q} direction: Φ increases by $\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_{i+1})$ between site i (at \mathbf{r}_i) and site

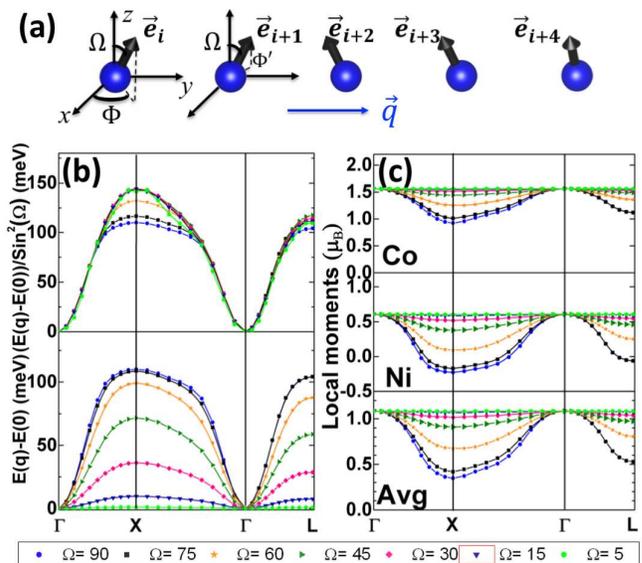


FIG. 4. (a) Sketch of the spin spiral state, propagating along the y direction for an artificial one dimensional atomic chain (blue spheres). (b) Adiabatic magnon energy (upper panel) – defined as $\frac{E(\mathbf{q})-E(0)}{\sin^2(\Omega)}$, given in meV/site – and spin spiral energy (lower panel) – defined as $E(\mathbf{q}) - E(0)$, given in meV/site – in NiCo solid solution alloy for different cone angles Ω (given in degrees). The spin spiral vector \mathbf{q} is along Γ -X $[\zeta, 0, 0]$, X - Γ $[\zeta, \zeta, 0]$ and Γ -L $[\zeta, \zeta, \zeta]$ direction. (c) Species-dependent local moments (μ_B) and averaged net moment (μ_B) for different spin spiral vectors.

$i + 1$ (at \mathbf{r}_{i+1}) (see Fig. 4(a) for a sketch). Note that in CPA, it is the *average moment* that propagates along \mathbf{q} . For multicomponent alloys, spin collinearity between different species on one site is enforced, while the spin noncollinearity between averaged moments on different sites are allowed and can be represented by the spin spiral state.

Two different definitions of the low-energy excitation and the local moments are studied in order to explore the energetic and magnetic properties in the spin spiral state. Firstly, $E(\mathbf{q}) - E(0)$ is calculated as the spin spiral energy. An additional normalized spin spiral energy – $E(\mathbf{q}) - E(0) / \sin^2(\Omega)$ is also investigated at different Ω and can be interpreted as the adiabatic magnon energy or frozen magnon energy [56]. If the magnetic interactions of the alloy are well described by the Heisenberg model, then $(E(\mathbf{q}) - E(0)) / \sin^2(\Omega)$ is independent of the polar angle Ω [56, 57]. Using the NiCo alloy as an example, Figs. 4 (b) and (c) illustrate the self-consistent spin spiral energy and the corresponding moment evolution for a set of cone angles Ω . Concentrating on the moment evolution at different spin spiral vectors, we note two important features. On one hand, in the long wavelength limit ($\mathbf{q} \rightarrow 0$), the Ni and Co local moments are stable against the spin noncollinearity, as the spin wave excitation energy is well below the energy scale of Stoner excitations. On the other hand, for large \mathbf{q} – approaching

the short wave length limit, the magnitude of the local moments on both Ni and Co atoms start to reduce, since the increased spin wave excitation energy approaches the spin-flipping Stoner excitation region. We note that this moment reduction is more pronounced for larger Ω since the angle between successive spins is larger. In particular, $\Omega = 90^\circ$ – corresponding to an antiferromagnetic helix state – gives rise to the largest moment change. A similar analysis can be performed for NiCoMn alloys.

In Figs. 5 and 6, we compare the spin spiral energy and local moment pattern of NiCoMn alloy in both AFM and DLM-Mn states. In the AFM state, the magnitude of the Mn local moment increases by a factor of three from the Γ -point towards BZ boundary (X point), exhibiting a striking longitudinal spin fluctuation that is also predicted by Niu *et al.* [19]. The moment size fluctuation is associated with a modest energy reduction, ~ 15 meV/site at $\Omega = 75^\circ$. Note that the spin spiral energy of AFM state is not continuous and is not well defined at $\Omega = 90^\circ$ due to a low-spin to high-spin transition, and is not shown here. The negative spin spiral energy at finite q indicates that the collinear AFM state is not energetically stable, compared with the spin noncollinear state with a spin spiral vector $\mathbf{q} = [\zeta, 0, 0]$ r.l.u.. The typical Stoner excitation reduces the size of the local moment in the presence of spin noncollinearity. However, here the local Mn moments in the AFM state behave oppositely – increasing the local moments with spin noncollinearity. This is because the collinear AFM state is highly frustrated due to the fact that the Mn local moments between different sites are constrained to be parallel.

As opposed to the AFM state, the spin spiral of the DLM-Mn state at the Γ point is the most energetically favorable (see Fig. 6). Moreover, in the long wavelength limit, $\zeta \leq 0.4$ along $[\zeta, 0, 0]$ direction, $(E(\mathbf{q})-E(0))/\sin^2(\Omega)$ is independent of Ω , evidently supporting the applicability of Heisenberg model in the vicinity of the DLM-Mn state. As for the local moments, the size of the local moments on Mn in this spin spiral state is relatively insensitive to the spin spiral vector and different cone angles: Mn spins are only reduced by 5% at the zone boundary (see Fig. 6). Here, in the DLM-Mn state, the strongest moment reduction comes from Co moments, whose spins decrease by 50% at the zone boundary. The relative insensitivity of the spin sizes to the spin noncollinearity validates the usage of the Heisenberg model. Therefore, the thermodynamic simulation based on Heisenberg model is only applicable for the DLM-Mn state. In the succeeding section, we explored the thermodynamics of NiCoMn using the exchange parameters (J_{ij}) from the DLM-Mn state.

D. Thermodynamics

We employ the Heisenberg model to describe the magnetic interactions, based on the J_{ij} from the DLM-Mn state. In the DLM-Mn state, all the local moments, par-

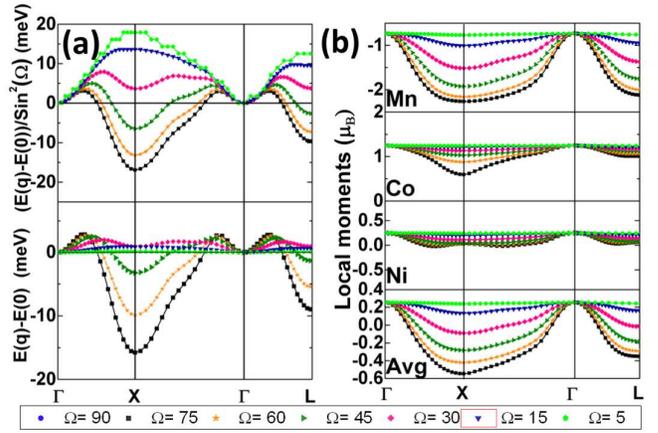


FIG. 5. (a) Adiabatic magnon energy (upper panel) and spin spiral energy (lower panel) in NiCoMn (AFM state) for different cone angle Ω (given in degrees). The spin spiral vector \mathbf{q} is along Γ -X [$\zeta, 0, 0$], X- Γ [$\zeta, \zeta, 0$] and Γ -L [ζ, ζ, ζ] direction. (b) Species-dependent local moments and averaged net moment for different spin spiral vectors.

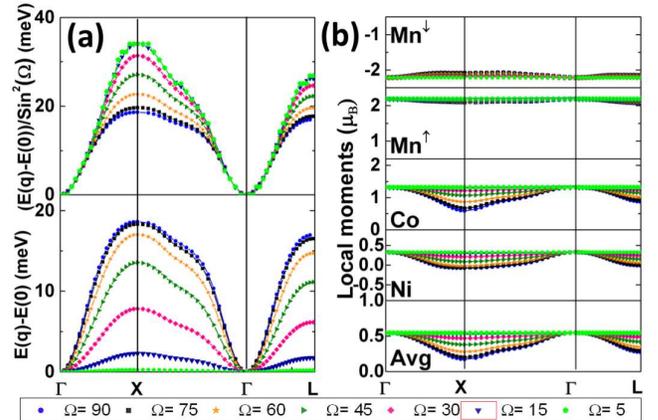


FIG. 6. (a) Adiabatic magnon energy (upper panel) and spin spiral energy (lower panel) in NiCoMn (DLM-Mn state) for different cone angle Ω (given in degrees). The spin spiral vector \mathbf{q} is along Γ -X [$\zeta, 0, 0$], X- Γ [$\zeta, \zeta, 0$] and Γ -L [ζ, ζ, ζ] direction. (b) Species-dependent local moments and averaged net moment for different spin spiral vectors. Two types of Mn species are distinguished using Mn $^\sigma$, where $\sigma = \uparrow$ or \downarrow denote the spin orientation.

ticularly Mn moments, do not exhibit strong size fluctuations, justifying the applicability of Heisenberg interactions in the assumption of rigid classical spins. We use the classical Monte-Carlo simulations to calculate the critical temperature (T_c), and compare the T_c predictions with other approximations, such as classical pair cluster approximation and classical mean-field approximation. Progressing from MF to PC, and further to MC, the spin correlations are gradually taken into account – MF has no spin correlation effect, PC only includes the pairwise correlations, and MC takes all correlations into consideration. The critical temperatures are $T_c^{MF} = 343$ K, T_c^{PC}

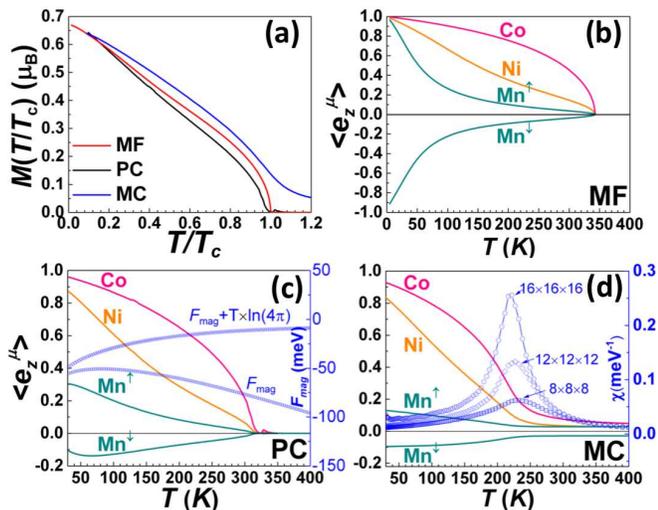


FIG. 7. (a) Simulated net magnetization $M(T)$ (μ_B/site) as a function of reduced temperature (T/T_c) using three different statistical approximations: classical mean field approximation (MF), classical pair cluster approximation (PC), and classical Monte Carlo (MC). The temperature dependent reduced species-resolved magnetization ($\langle e_z^\mu \rangle$) in (b) classical mean field approximation, (c) classical pair cluster approximation, and (d) classical Monte Carlo approximation. Magnetic free energy (F_{mag} , meV/site) and the magnetic interaction energy ($F_{\text{mag}} + T \times \ln(4\pi)$, meV/site) of NiCoMn in DLM-Mn state are plotted in (c) using PC. The temperature dependent magnetic susceptibility using $8 \times 8 \times 8$, $12 \times 12 \times 12$, $16 \times 16 \times 16$ cubic cells are displayed in (d) using MC.

= 320 K, and $T_c^{MC} = 219$ K, respectively. Figure 7(d) also illustrates the finite size effect in classical MC using a $8 \times 8 \times 8$, $12 \times 12 \times 12$, and $16 \times 16 \times 16$ cubic cell, and evidently good convergence of T_c^{MC} has been reached. The reduction of T_c from MF to PC is only 23 K. Since PC only includes the pairwise correlations compared with the MF, the small reduction of T_c indicates that the correlation effect within the pair cluster is not significant. On the other hand, T_c^{MC} is reduced by (appreciably) 31% compared with T_c^{PC} , suggesting an important correlation effect within the high order clusters. Unfortunately, there is no experimental value for T_c in NiCoMn alloy available.

The temperature dependence of the total magnetization ($M(T)$, μ_B/site) obtained using the three different statistical approximations is shown in Fig. 7(a). The variations in the shape of magnetization curves are similar in all three approaches. Figure 7 (b-d) illustrate the reduced species-resolved magnetization ($\langle e_z^\mu \rangle$) in different statistical approximations. We find that the $\langle e_z^{Co} \rangle$ is relatively stable while the $\langle e_z^{Mn} \rangle$ drops quickly with temperature due to disordered Mn moments even at low temperature. In addition, Fig. 8 shows a zoom-in of a representative spin configuration for a $12 \times 12 \times 12$ cubic cell, simulated by classical MC at 20 K. Firstly, the Mn moments (blue and light blue arrows) are disordered with random angular distribution. As opposed to Mn mo-

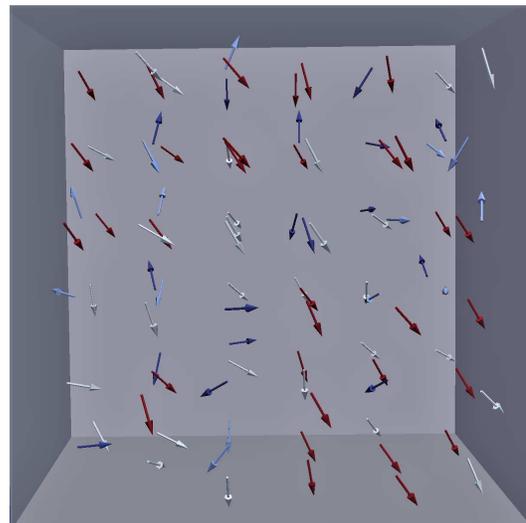


FIG. 8. A zoom-in of a representative spin configuration at 20 K for the DLM-Mn state, taken from a large $12 \times 12 \times 12$ unit cell. Red arrows indicate Co spins; silver arrows denote Ni spins; blue and light blue arrows are local moments on Mn^\uparrow and Mn^\downarrow .

ments, the Ni moments (silver arrows) and Co moments (red arrows) are (approximately) collinearly aligned. The reason for the observed disordered Mn moments is that the effective exchange field on Mn is small. This is because the Weiss fields from the neighboring Mn^\uparrow and Mn^\downarrow have opposite signs, compensating with each other (see Tab. I). As opposed to small effective exchange field on Mn, those on Ni and Co are much stronger. The effective exchange fields on each species ($J_0^\mu = \sum_\nu c^\nu J_0^{\mu,\nu}$) and the effective exchange field between species pairs ($J_0^{\mu,\nu} = \sum_j J_{ij}^{\mu,\nu}$) are listed in Table I. From this discussion, it is clear that the magnetic critical temperature is mainly determined by the effective exchange field on the Ni and Co species.

In contrast, the exchange interactions of the AFM state yield a much smaller magnetic critical temperature ($T_c^{MF} = 243$ K), as compared with that based on the DLM-Mn state: $T_c^{MF} = 343$ K. This difference mainly comes from the negative and unstable $J_0^{Co,Mn}$ contribution to the net effective exchange field in the AFM state. It is therefore anticipated that the AFM state adversely affects the Gibbs free energy through the erroneous magnetic contributions.

E. Resistivity at finite temperature

The electronic structure of the multiple metastable states of NiCoMn has a striking effect on the residual resistivity (ρ_0): ρ_0 in the DLM-Mn state is 40% greater than that in the one-Mn state in KKR-CPA [20]. Here we start from the residual resistivity and explore the transport properties at finite temperatures by including the

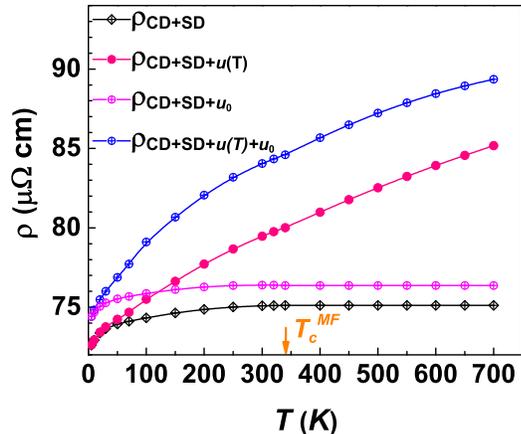


FIG. 9. Resistivity of NiCoMn alloy at finite temperatures, $\rho(T)$, given in the unit of $\mu\Omega cm$. Electron scattering due to the static displacements (u_0), thermal displacements ($u(T)$), and spin disorder (SD) are considered either separately or with different combinations (see main text for details). The chemical disorder (CD) is always included. The mean field transition temperature (T_c) is also labeled.

atomic displacements and the transverse spin fluctuations. Firstly, as previously introduced in Sec. II, we consider two types of atomic displacements – static displacements (u_0) and thermal displacements ($u(T)$). The averaged magnitudes of static displacements for each species were calculated from the supercell calculations. Thermal displacements, i.e. the mean square root displacements, are calculated using the Debye model (see Ref. 42). At finite temperature, the thermal displacements are added to the static displacements at finite temperatures (i.e., $u_{tot} = u_0 + u(T)$). In addition, the transverse spin fluctuations at a given temperature are simulated by using type-dependent $\langle \mathbf{e}_z^\mu \rangle$ within the classical mean-field simulations (Fig. 7 (b)). The resistivity due to these different scattering mechanisms is then calculated based on the above approximation.

Figure 9 illustrates $\rho(T)$ in four different cases with different electron scattering mechanisms included: (1) temperature-dependent spin disorder; (2) temperature-

TABLE I. The effective exchange interactions between species-pairs (μ, ν) $J_0^{\mu, \nu}$ (meV) and the effective exchange field on species (μ) J_0^μ (meV) are given. See main text for definitions and details.

	Ni	Co	Mn [↑]	Mn [↓]
Ni	8.28	34.9	24.9	-20.5
Co	34.9	122.4	0.32	16.9
Mn [↑]	24.9	0.32	-327.4	332.6
Mn [↓]	-20.5	16.9	332.6	-328.3
J_0^μ	15.1	55.3	9.3	-0.5

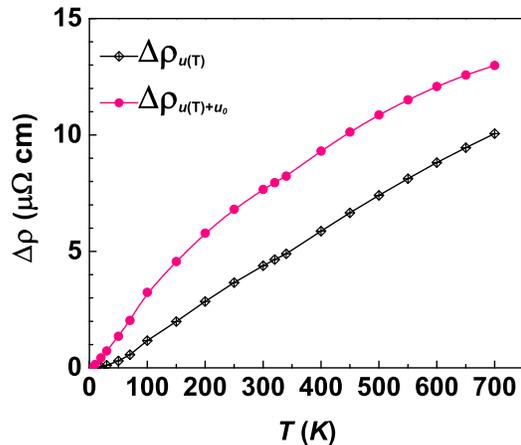


FIG. 10. The resistivity enhancement ($\Delta\rho(T)$, $\mu\Omega cm$) due to the effect of thermal displacements ($u(T)$), with (red dots) and without (black diamonds) taking into account the static displacements (u_0).

dependent spin disorder and thermal displacements; (3) static displacements and temperature-dependent spin disorder; (4) in the presence of the static displacements, thermal displacements and temperature-dependent spin disorder. We note that the electron scattering due to the intrinsic chemical disorder (CD) is always included. Assuming that Matthiessen's rule (MR) is valid, the scattering due to each individual scattering mechanism can be separated out. We first emphasize that no matter whether the static displacements are included or not, the additional electron scattering due to transverse spin fluctuation is weak. Here we define the spin disorder resistivity (ρ^{SDR}) as the resistivity enhancement when all spins are fully disordered ($T > T_c$). We found small values for $\rho^{SDR} - \rho^{SDR}(u_0 = 0) = 2.5 \mu\Omega cm$ and $\rho^{SDR}(u_0) = 2.0 \mu\Omega cm$, as seen in Fig. 9. The underlying reason for the smallness of forgoing quantities is that, even at $T=0K$, the 'local moment' scattering attendant to two antiparallel Mn spin model, over and above the large chemical disorder scattering, results in a Fermi surface that is already so washed-out (smeared out in \mathbf{k} -space) that introducing additional spin disorder scattering has a negligible effect. Due to the weak magnetic scattering in NiCoMn, $\rho(T)$ does not display a distinct kink at T_c , as in ferromagnetic Ni, Fe, NiFe, NiCo, NiFeCo [21, 42, 58]. Furthermore, the static displacements raise the residual resistivity by $1.8 \mu\Omega cm$, which is comparable to ρ^{SDR} .

The thermal displacements have a notable effect on the resistivity enhancement. Figure 10 illustrates the thermal-displacement-induced resistivity enhancements ($\Delta\rho$) as a function of temperature when static displacement is included (red dots) or not (black diamonds). In the absence of the static displacements, the thermal-displacement-induced resistivity enhancement $\Delta\rho_{u(T)}$ increases slowly in the low-temperature region ($T < 50K$),

but increases linearly in the high-temperature region – beyond the Debye temperature (T_D). This temperature dependence is normally expected in nonmagnetic metals. However, despite the fact that static displacements have a small effect on raising ρ_0 , they affect the temperature dependent resistivity remarkably when combined with the thermal displacements. At low temperatures, $\Delta\rho_{u(T)+u_0}$ increase more rapidly with temperature than $\Delta\rho_{u(T)}$. This is due to the fact that the coupling between the u_0 and $u(T)$ contributes a $u_0 \times u(T)$ term in the expansion of u_{tot}^2 , which is proportional to resistivity. This additional term greatly changes the temperature dependence of ρ , particularly when u_0 is itself substantial.

F. Pressure dependent residual resistivity and magnetism

We now examine the effect of pressure on the magnetism and the electrical transport in NiCoMn alloy. Figure 11 (a) relates the lattice parameter to the “hydrostatic” pressure – defined as the average of the diagonal terms of the pressure tensor that is calculated using GGA. The pressure tensor is calculated using the supercell method based on a 108-atom SQS cell at various lattice parameters. All internal ionic degrees of freedom are optimized at each lattice parameter. A rough estimate gives 1 *kbar* hydrostatic compressive pressure reduces the lattice parameter by 0.83 mÅ. The theoretical lattice parameter, corresponding to *zero* hydrostatic pressure, is 3.54 Å, which is 1.7% smaller than the experimental value.

The species-resolved magnetic moments in NiCoMn alloys are shown in Fig.11 (b). With reduced lattice parameter, the local moment on each species gradually decreases due to enhanced hybridization effect between 3*d* orbitals, and eventually no local moment is formed when the lattice parameter is smaller than 3.49Å. It is worth noting that the local moments on Mn[↑] and Mn[↓] are more sensitive to the lattice parameter than the Ni or Co moments. This suggests that the enhanced electron hybridization is more pronounced for Mn-3*d* orbitals, thereby effectively reducing the density of state at Fermi level and destroying the Mn local moments.

The effect of varying the lattice parameter on ρ_0 is shown in Fig. 11(a). With reduced local moments, ρ_0 decreases drastically – at a rate of 2.4 $\mu\Omega\text{ cm}$ per 0.01Å – due to magnetic scattering. On the other hand, in the nonmagnetic phase – when $a \leq 3.49\text{Å}$ – ρ_0 becomes insensitive to the lattice parameter. With reduced lattice parameter in the nonmagnetic phase, the density of state at the Fermi level (carrier density) decreases while the band dispersion across the Fermi level (carrier mobility) increases as a result of the enhanced hybridization. The above two competing effects cancel with each other, making ρ_0 relatively insensitive to the lattice parameter. This result reveals the importance of the magnetism and its dependence on the lattice parameter or pressure, on

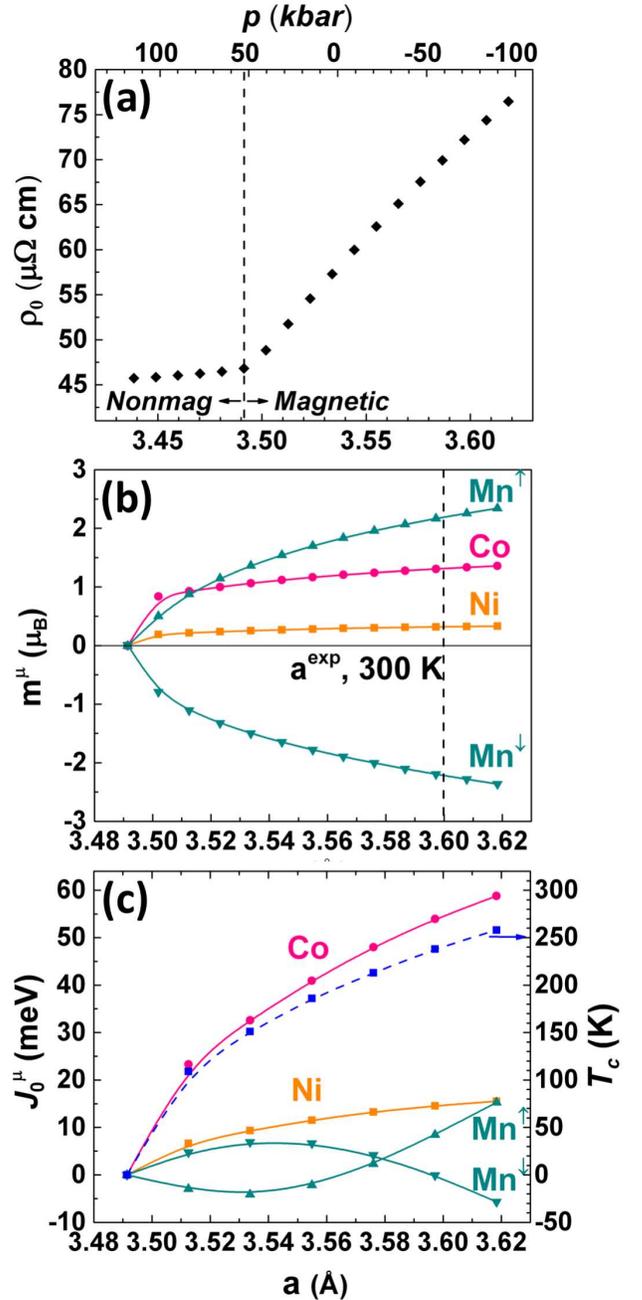


FIG. 11. (a) The residual resistivity (ρ_0 , $\mu\Omega\text{ cm}$) at different lattice parameter. The hydrostatic pressures (P , kbar) at different lattice parameters are also labeled. (b) The lattice parameter dependent local moment on different species. The experimental lattice parameter is labeled using dashed line. (c) Curie temperature (T_c , K) and effective exchange field on species μ (J_0^μ , meV) as a function of lattice parameter.

electron-mediated energy dissipation.

Figure 11(c) illustrates the effective exchange field on species μ (J_0^μ , meV) and the MC T_c as a function of lattice parameter. T_c mostly follows the more pronounced effective exchange field on Co (J_0^{Co}). Unlike J_0^{Ni} , J_0^{Co} is sensitive to the lattice parameter while the m^{Co} is rel-

atively inert in a wide range of the lattice parameters. We further confirm that the reduction of J_0^{Co} mainly comes from $J^{Co,Co}$ within the first nearest neighbor shell. While both J_0^{Ni} and J_0^{Co} decreases with lattice parameter, J_0^{Mn} exhibits non-monotonic behavior, mainly from the complex non-monotonic $J^{Mn,Mn}$. The other $J^{Mn,\mu}$ ($\mu \neq Mn$) reduce with the lattice parameter, as expected.

IV. CONCLUSIONS

By comparing with the electronic structure of the supercell method, the ground state of NiCoMn disordered solid solution alloys was verified and was denoted as the DLM-Mn state. The DLM-Mn state distinguishes two equally populated groups of Mn atoms, with large spin moments but opposite spin orientations. In contrast, the electronic structure of the AFM state, having only one type of Mn atoms, is inconsistent with that from the supercell method.

Spin spiral calculations were performed for both the AFM and DLM-Mn states of disordered NiCoMn alloys and we demonstrated:

1. that the AFM state is dynamically unstable in the sense that the energy reduces in the presence of spin noncollinearity and an unphysical enhancement of Mn moments is also observed.
2. that the DLM-Mn state is most energetically favorable in the spin spiral state and no transparent spin fluctuation is observed, associated with the transverse spin fluctuation in this state.
3. the applicability of Heisenberg model is tested, providing a justification of thermodynamic study based on the Heisenberg model.

In addition, the exchange parameters were calculated using linear response expression and the thermodynamics were simulated based on the Heisenberg model by using classical mean field approximation, classical pair cluster approximation, and classical Monte Carlo simulation. We found the spin orientation on Mn easily becomes noncollinear/disordered at low temperatures ($T \ll T_c$). This is due to relatively small Weiss field on Mn sites. We further demonstrated that a very low T_c is obtained when using exchange parameters from the (incorrect) AFM state. The magnetic transition temperature still requires experimental verification.

In the DLM-Mn ground state, the magnetic scattering is almost saturated at zero temperature due to the antiparallel spin alignments between Mn atoms. Full spin disorder, beyond the T_C does not further contaminate the Fermi surface. We also demonstrate that even though the static displacements have a small effect on raising ρ_0 , it can alter the temperature dependent ρ strikingly when combined with the thermal displacements.

Finally, we found that a hydrostatic pressure of 50 kbar quenches the magnetism of NiCoMn, and that the resistivity is strongly correlated with the magnetism. This suggests a modest and positive contribution to the resistivity from thermal expansion.

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- [1] J-W Yeh, S-K Chen, S-J Lin, J-Y Gan, T-S Chin, T-T Shun, C-H Tsau, and S-Y Chang. Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. *Advanced Engineering Materials*, 6(5):299–303, 2004.
- [2] Ming-Hung Tsai and Jien-Wei Yeh. High-entropy alloys:

a critical review. *Materials Research Letters*, 2(3):107–123, 2014.

- [3] Brain Cantor, ITH Chang, P Knight, and AJB Vincent. Microstructural development in equiatomic multicomponent alloys. *Materials Science and Engineering: A*, 375:213–218, 2004.

- [4] Zhenggang Wu, Hongbin Bei, Frederik Otto, George Mathews Pharr, and Easo P George. Recovery, recrystallization, grain growth and phase stability of a family of fcc-structured multi-component equiatomic solid solution alloys. *Intermetallics*, 46:131–140, 2014.
- [5] Bernd Gludovatz, Anton Hohenwarter, Keli VS Thurston, Hongbin Bei, Zhenggang Wu, Easo P George, and Robert O Ritchie. Exceptional damage-tolerance of a medium-entropy alloy croni at cryogenic temperatures. *Nature communications*, 7:10602, 2016.
- [6] Bernd Gludovatz, Anton Hohenwarter, Dhiraj Catoor, Edwin H Chang, Easo P George, and Robert O Ritchie. A fracture-resistant high-entropy alloy for cryogenic applications. *Science*, 345(6201):1153–1158, 2014.
- [7] Yanwen Zhang, G Malcolm Stocks, Ke Jin, Chenyang Lu, Hongbin Bei, Brian C Sales, Lumin Wang, Laurent K Béland, Roger E Stoller, German D Samolyuk, et al. Influence of chemical disorder on energy dissipation and defect evolution in concentrated solid solution alloys. *Nature communications*, 6:8736, 2015.
- [8] Chenyang Lu, Liangliang Niu, Nanjun Chen, Ke Jin, Taini Yang, Pengyuan Xiu, Yanwen Zhang, Fei Gao, Hongbin Bei, Shi Shi, et al. Enhancing radiation tolerance by controlling defect mobility and migration pathways in multicomponent single-phase alloys. *Nature communications*, 7:13564, 2016.
- [9] Ke Jin, Sai Mu, Ke An, Wallace D Porter, German D Samolyuk, George Malcolm Stocks, and Hongbin Bei. Thermophysical properties of ni-containing single-phase concentrated solid solution alloys. *Materials & Design*, 117:185–192, 2017.
- [10] Ke Jin, Brian C Sales, George Malcolm Stocks, German D Samolyuk, Markus Daene, William J Weber, Yanwen Zhang, and Hongbin Bei. Tailoring the physical properties of ni-based single-phase equiatomic alloys by modifying the chemical complexity. *Scientific reports*, 6:20159, 2016.
- [11] Brian C Sales, Ke Jin, Hongbin Bei, G Malcolm Stocks, German D Samolyuk, Andrew F May, and Michael A McGuire. Quantum critical behavior in a concentrated ternary solid solution. *Scientific reports*, 6:26179, 2016.
- [12] Oldřich Schneeweiss, Martin Friák, Marie Dudová, David Holec, Mojmír Šob, Dominik Krieger, Václav Holý, Přemysl Beran, Easo P George, Jörg Neugebauer, et al. Magnetic properties of the crmnfeconi high-entropy alloy. *Physical Review B*, 96(1):014437, 2017.
- [13] ON Senkov, JM Scott, SV Senkova, DB Miracle, and CF Woodward. Microstructure and room temperature properties of a high-entropy tanbhfrtzi alloy. *Journal of alloys and compounds*, 509(20):6043–6048, 2011.
- [14] Michael Feuerbacher, Markus Heidelmann, and Carsten Thomas. Hexagonal high-entropy alloys. *Materials Research Letters*, 3(1):1–6, 2015.
- [15] Axel Van De Walle and Gerbrand Ceder. The effect of lattice vibrations on substitutional alloy thermodynamics. *Reviews of Modern Physics*, 74(1):11, 2002.
- [16] Duancheng Ma, Blazej Grabowski, Fritz Körmann, Jörg Neugebauer, and Dierk Raabe. Ab initio thermodynamics of the cocrfemni high entropy alloy: Importance of entropy contributions beyond the configurational one. *Acta Materialia*, 100:90–97, 2015.
- [17] Shijun Zhao, G Malcolm Stocks, and Yanwen Zhang. Stacking fault energies of face-centered cubic concentrated solid solution alloys. *Acta Materialia*, 134:334–345, 2017.
- [18] Changning Niu, Carly R LaRosa, Jiashi Miao, Michael J Mills, and Maryam Ghazisaeidi. Magnetically-driven phase transformation strengthening in high entropy alloys. *Nature communications*, 9(1):1363, 2018.
- [19] Zhihua Dong, Stephan Schönecker, Wei Li, Dengfu Chen, and Levente Vitos. Thermal spin fluctuations in cocrfemni high entropy alloy. *Scientific Reports*, 8(1):12211, 2018.
- [20] Sai Mu, GD Samolyuk, S Wimmer, MC Troparevsky, S Khan, S Mankovsky, H Ebert, and GM Stocks. Uncovering electron scattering mechanisms in alloys possessing extreme disorder. *arXiv preprint arXiv:1806.03785*, 2018.
- [21] G. D. Samolyuk, S. Mu, A. F. May, B. C. Sales, S. Wimmer, S. Mankovsky, H. Ebert, and G. M. Stocks. Temperature dependent electronic transport in concentrated solid solutions of the 3d-transition metals ni, fe, co and cr from first principles. *Phys. Rev. B*, 98:165141, Oct 2018.
- [22] Mark van Schilfgaarde, IA Abrikosov, and B Johansson. Origin of the invar effect in iron–nickel alloys. *Nature*, 400(6739):46, 1999.
- [23] Tian-Yue Chen, Tsao-Chi Chuang, Ssu-Yen Huang, Hung-Wei Yen, and Chi-Feng Pai. Spin-orbit torque from a magnetic heterostructure of high-entropy alloy. *Physical Review Applied*, 8(4):044005, 2017.
- [24] Zhenggang Wu, Hongbin Bei, George M Pharr, and Easo P George. Temperature dependence of the mechanical properties of equiatomic solid solution alloys with face-centered cubic crystal structures. *Acta Materialia*, 81:428–441, 2014.
- [25] Norihiko L Okamoto, Koretaka Yuge, Katsushi Tanaka, Haruyuki Inui, and Easo P George. Atomic displacement in the crmnfeconi high-entropy alloy—a scaling factor to predict solid solution strengthening. *AIP Advances*, 6(12):125008, 2016.
- [26] Alex Zunger, S.-H. Wei, L. G. Ferreira, and James E. Bernard. Special quasirandom structures. *Physical Review Letters*, 65(3):353–356, jul 1990.
- [27] Paul Soven. Coherent-potential model of substitutional disordered alloys. *Physical Review*, 156(3):809, 1967.
- [28] Shuo Huang, Wei Li, Song Lu, Fuyang Tian, Jiang Shen, Erik Holmström, and Levente Vitos. Temperature dependent stacking fault energy of fecrconimn high entropy alloy. *Scripta Materialia*, 108:44–47, 2015.
- [29] Shuo Huang, Erik Holmström, Olle Eriksson, and Levente Vitos. Mapping the magnetic transition temperatures for medium-and high-entropy alloys. *Intermetallics*, 95:80–84, 2018.
- [30] H Akai and PH Dederichs. Local moment disorder in ferromagnetic alloys. *Physical Review B*, 47(14):8739, 1993.
- [31] J Korringa. On the calculation of the energy of a bloch wave in a metal. *Physica*, 13(6-7):392–400, 1947.
- [32] Wo Kohn and No Rostoker. Solution of the schrödinger equation in periodic lattices with an application to metallic lithium. *Physical Review*, 94(5):1111, 1954.
- [33] P. E. Blöchl. Projector augmented-wave method. *Physical Review B*, 50(24):17953–17979, dec 1994.
- [34] G. Kresse and J. Hafner. Ab initio molecular dynamics for open-shell transition metals. *Physical Review B*, 48(17):13115–13118, nov 1993.
- [35] Georg Kresse and Jürgen Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical review B*, 54(16):11169,

- 1996.
- [36] Hendrik J Monkhorst and James D Pack. Special points for Brillouin-zone integrations. *Physical review B*, 13(12):5188, 1976.
- [37] Jp Perdew, K Burke, and M Ernzerhof. Generalized Gradient Approximation Made Simple. *Physical Review Letters*, 77(18):3865–3868, 1996.
- [38] H Ebert et al. The munich spr-kkk package, version 7.7. <http://olymp.cup.uni-muenchen/de/ak/ebert/SPRKKR>, 2017.
- [39] Ryogo Kubo. R. kubo, j. phys. soc. japan 12, 570 (1957). *J. Phys. Soc. Japan*, 12:570, 1957.
- [40] DA Greenwood. The boltzmann equation in the theory of electrical conduction in metals. *Proceedings of the Physical Society*, 71(4):585, 1958.
- [41] William H Butler. Theory of electronic transport in random alloys: Korringa-kohn-rostoker coherent-potential approximation. *Physical Review B*, 31(6):3260, 1985.
- [42] Hubert Ebert, Sergiy Mankovsky, Kristina Chadova, Svitlana Polesya, Jan Minar, and Diemo Koedderitzsch. Calculating linear-response functions for finite temperatures on the basis of the alloy analogy model. *Physical Review B*, 91(16):165132, 2015.
- [43] A Il Liechtenstein, M I Katsnelson, V P Antropov, and V A Gubanov. Local spin density functional approach to the theory of exchange interactions in ferromagnetic metals and alloys. *Journal of Magnetism and Magnetic Materials*, 67(1):65–74, 1987.
- [44] Ryoichi Kikuchi. A theory of cooperative phenomena. *Physical review*, 81(6):988, 1951.
- [45] Juan M Sanchez, Francois Ducastelle, and Denis Gratias. Generalized cluster description of multicomponent systems. *Physica A: Statistical Mechanics and its Applications*, 128(1-2):334–350, 1984.
- [46] VG Vaks and NE Zein. Theory of phase transitions in solid solutions. *JETP*, 40(3):537, 1975.
- [47] VG Vaks and GD Samolyuk. On accuracy of different cluster models used in describing ordering phase transitions in fcc alloys. *Journal of Experimental and Theoretical Physics*, 88(1):89–100, 1999.
- [48] Robert H. Swendsen and Jian-Sheng Wang. Replica Monte Carlo Simulation of Spin-Glasses. *Physical Review Letters*, 57(21):2607–2609, nov 1986.
- [49] K. Hukushima and K. Nemoto. Exchange Monte Carlo method and application to spin glass simulations, 1996.
- [50] Ulli Wolff. Collective Monte Carlo Updating for Spin Systems. *Physical Review Letters*, 62(4):361–364, jan 1989.
- [51] BL Gyorffy, AJ Pindor, J Staunton, GM Stocks, and H Winter. A first-principles theory of ferromagnetic phase transitions in metals. *Journal of Physics F: Metal Physics*, 15(6):1337, 1985.
- [52] Tetsuya Fukushima, Hiroshi Katayama-Yoshida, Kazunori Sato, Masako Ogura, Rudolf Zeller, and Peter H Dederichs. Local energies and energy fluctuations? applied to the high entropy alloy crfeconi. *Journal of the Physical Society of Japan*, 86(11):114704, 2017.
- [53] LM Sandratskii. Energy band structure calculations for crystals with spiral magnetic structure. *physica status solidi (b)*, 136(1):167–180, 1986.
- [54] LM Sandratskii. Symmetry analysis of electronic states for crystals with spiral magnetic order. i. general properties. *Journal of Physics: Condensed Matter*, 3(44):8565, 1991.
- [55] S Mankovsky, G H Fecher, and H Ebert. Electronic structure calculations in ordered and disordered solids with spiral magnetic order. *Physical Review B*, 83(14):144401, 2011.
- [56] Jürgen Kübler. *Theory of itinerant electron magnetism*, volume 106. Oxford University Press, 2017.
- [57] SV Halilov, H Eschrig, A Ya Perlov, and PM Oppeneer. Adiabatic spin dynamics from spin-density-functional theory: Application to fe, co, and ni. *Physical Review B*, 58(1):293, 1998.
- [58] Aleksander L Wysocki, Kirill D Belashchenko, Julian P Velev, and Mark van Schilfhaarde. Calculations of spin-disorder resistivity from first principles. *Journal of applied physics*, 101(9):09G506, 2007.