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Critical behavior in Ni_2MnGa and $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$

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The critical behaviors of polycrystalline Ni_2MnGa and $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ have been examined through high-resolution bulk magnetization measurements. The critical exponents, β and γ , were derived from modified Arrott plots using the Kouvel-Fisher method. The values of the extracted critical exponents satisfied the scaling equation of state and associated exponent relations, indicating self-consistency of the extracted values. In Ni_2MnGa , the critical exponents ($\beta = 0.401 \pm 0.003$, $\gamma = 1.27 \pm 0.02$) indicate a deviation from the 3D-Heisenberg values toward the mean-field values, likely due to the presence of long-range Ruderman-Kittel-Kasuya-Yosida interactions. However, the critical exponents of $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ ($\beta = 0.389 \pm 0.004$, $\gamma = 1.39 \pm 0.02$) are closer to the 3D-Heisenberg values. This indicates a weakening of the long-range exchange interactions due to the substitution of Cu in the Mn site. Published by AIP Publishing.

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I. INTRODUCTION

One of the most extensively studied materials in the Heusler alloy family is the Ni_2MnGa system. This compound shows a wide variety of properties, such as magnetic field induced strain (MFIS),¹ giant magnetocaloric effects (MCE),² etc., making it attractive from both technological and scientific points of view. Ni_2MnGa undergoes two transitions upon cooling: first is a second-order magnetic (order-disorder) transition at $T_C \approx 382$ K from a cubic ($L2_1$) paramagnetic (PM) phase to a cubic ferromagnetic (FM) phase. Second, it undergoes a structural (martensitic) transition from a cubic FM phase (austenite) to a complex FM tetragonal (martensitic) phase at $T_M \approx 209$ K. There is also a premartensitic transition at $T_P \approx 260$ K, which is due to a modulation in the austenitic phase.^{3,4}

It has been observed that, in Heusler alloys, various substitution schemes and variations in stoichiometry can significantly modify the magnetic interactions. A critical exponent analysis can provide insight into the range of the exchange interactions as well as the lattice and spin dimensionalities. This is also useful in understanding the role of a particular substitution scheme or stoichiometry variation in modifying the magnetic interactions. Not surprisingly, this approach has been widely used by researchers to investigate the second-order phase transition in Heusler alloys (see Refs. 5–9). Some examples may be helpful in elucidating the scope of the critical exponent analysis. For instance, through critical exponent analysis of $\text{Ni}_{50}\text{Mn}_{50-x}\text{Sn}_x$, Phan *et al.* (Ref. 5) argued that the Sn substitution drove the system from short-range to long-range FM order. In another study, it was revealed that Gd substitution for Ni in $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$ drove the system from short-range FM order to long-range order.⁶ In a similar manner, the role of various substitution schemes in $\text{Ni}_{47}\text{Mn}_{40}\text{Sn}_{13-x}\text{Cu}_x$, $\text{Ni}_{43}\text{Mn}_{46}\text{Sn}_8\text{X}_3$ ($x = \text{In}$ and Cr), $\text{Ni}_{2.2}\text{Mn}_{0.72-x}\text{V}_x\text{Ga}_{1.08}$,

$\text{TbCo}_{2-x}\text{Fe}_x$, and so on, was investigated through critical exponent analysis.^{7–10}

In $\text{Ni}_2\text{Mn}_{1-x}\text{Cu}_x\text{Ga}$, increasing the Cu concentration drives the two transitions (T_C and T_M) towards each other and, when $x = 0.25$, the two transitions coincide at $T = 308$ K. A large MCE (magnetic entropy change) has been reported for $\text{Ni}_2\text{Mn}_{0.75}\text{Cu}_{0.25}\text{Ga}$ at this coupled magnetostructural transition.^{2,11} Over the years, experimental and theoretical investigations were carried out to better understand the mechanism behind the shift of the transition temperatures, i.e., the role of dopants, etc.^{3,11–14} Roy *et al.* investigated the role of Cu substitution in the $\text{Ni}_2\text{Mn}_{1-x}\text{Cu}_x\text{Ga}$ compound using X-ray absorption spectroscopy and X-ray magnetic circular dichroism.¹¹ They showed that the substitution of Cu enhances the Ni-Ga hybridization and shifts the martensitic transition temperature (T_M) to higher temperature. Moreover, the magnetic ordering (Curie) temperature (T_C) decreases as the Mn concentration is reduced and the system becomes more magnetically delocalized. In Ni_2MnGa , long-range Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction between Mn atoms, mediated by the Ni atoms, is responsible for the ferromagnetism.¹⁵ As pointed out previously,¹¹ the substitution of non-magnetic Cu in the Mn site significantly modifies the magnetic properties of the system. This motivated us to conduct a critical exponent analysis for these compounds.

In this investigation, the critical behavior near the second-order phase transitions in polycrystalline Ni_2MnGa and $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ has been examined. Bulk magnetization measurements were used to obtain the critical exponents, β , γ , and δ , for each system. The range of exchange interactions, lattice and spin dimensionalities, and the overall modification of the magnetic interactions due to the Cu substitution will be discussed through the critical exponents.

II. THEORETICAL BACKGROUND

The critical behavior of a magnetic material undergoing a second-order (continuous) phase transition can be

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characterized by a set of critical exponents in the vicinity of the Curie temperature (T_C). Materials with the same critical exponents belong to the same universality class, manifesting a universal behavior around the critical region. These critical exponents depend only on the dimension of the lattice (d), order parameter (n), and the range of exchange interactions.^{16–18} In the critical region near T_C , various thermodynamic quantities show power-law dependencies on the reduced temperature, $\epsilon = (T - T_C)/T_C$. The spontaneous magnetization [$M_S \equiv M_H = 0$], initial susceptibility [$\chi_0 \equiv \frac{\partial M}{\partial H}|_{H=0}$], and the critical isotherm [$M(H)_{T=T_C}$] are given by the following equations:

$$M_S(T) = M_0(-\epsilon)^\beta \quad (\epsilon < 0), \quad (1)$$

$$\chi_0^{-1} = \Gamma(\epsilon)^\gamma \quad (\epsilon > 0), \quad (2)$$

$$M = XH^{(1/\delta)} \quad (\epsilon = 0), \quad (3)$$

respectively, where, M_0 , Γ , and X are the critical amplitudes.^{17,19,20} According to the scaling hypothesis,^{17,18,21,22} various formulations of a magnetic equation of state can be expressed as

$$m = f_\pm(h), \quad (4)$$

$$H = M^\delta h(x), \quad (5)$$

$$h/m = \pm a_\pm + b_\pm m^2, \quad (6)$$

where $m \equiv |\epsilon|^{-\beta} M(H, \epsilon)$ is the renormalized magnetization, $h \equiv |\epsilon|^{-(\beta\delta)} H$ is the renormalized field, and $x \equiv \epsilon M^{-1/\beta}$. In Eq. (4), the terms f_+ for $T > T_C$ and f_- for $T < T_C$ are unspecified scaling functions.²¹ According to Eq. (4), a plot of m vs. h should collapse into two universal curves, one above and one below T_C for the correct values of the critical exponents. This feature can be used to obtain the critical exponents of a magnetic system. However, a more accurate approach is to use the Arrott-Noakes equation of state,¹⁷ which is given by

$$(H/M)^{(1/\gamma)} = A\epsilon + BM^{(1/\beta)}, \quad (7)$$

and the plot of $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$, which is known as the modified Arrott plot (MAP). For the right choices of β and γ , this plot consists of a series of parallel straight lines with the isotherm at $T = T_C$ passing through the origin. From the intercepts on the vertical and horizontal axes, the spontaneous magnetization $M_S(T)$ and the initial susceptibility $\chi_0^{-1}(T)$ can be calculated, respectively. Once the intercepts are obtained, Eqs. (1) and (2) can be used to find the values of the critical exponents, β and γ .

III. EXPERIMENTAL METHODS

Polycrystalline Ni_2MnGa and $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ ingots (approximately 5 g) were fabricated from high-purity elements (better than 99.9%) of Ni, Mn, Cu, and Ga in an induction furnace under a high purity argon atmosphere. The weight loss after melting was found to be less than 0.1%. The samples were placed inside an evacuated quartz tube and annealed at 850 °C in a tube furnace for 3 days and

slowly cooled to room temperature. X-ray diffraction (XRD) measurements were done with a room-temperature X-ray diffractometer using Cu $K\alpha$ radiation and θ – θ geometry. Magnetic measurements were carried out using a superconducting quantum interference device magnetometer (SQUID-MPMS by Quantum Design). Temperature dependent magnetization measurements, $M(T)$, were performed in a temperature interval of 10–400 K. The magnetization isotherms, $M(H)$, were measured in the vicinity of the Curie temperatures (T_C) in temperature increments of $\Delta T = 0.5$ K. At each temperature set point, a 5 min wait time was imposed for better temperature stabilization. The magnetic field was applied in increments of $\Delta H = 0.25$ T up to $H = 7$ T in no-overshoot mode.

IV. RESULTS

A. Critical behavior in Ni_2MnGa

From the temperature dependent magnetization measurement for Ni_2MnGa shown in Fig. 1(a), the initial value of T_C was calculated as the minimum of the dM/dT vs. T curve (not shown). The $M(H)$ curves (isotherms) were obtained in $\Delta T = 0.5$ K increments in the critical region as shown in Fig. 1(b). These data were rescaled according to Eq. (7) by adjusting β and γ . For $\beta = 0.5$ and $\gamma = 1$, the $M^{1/\beta}$ vs. $(H/M)^{1/\gamma}$ plot is just the conventional Arrott plot [see Fig. 2(a)]. Two things can be observed immediately from the Arrott plot: first, the non-linearity of the isotherms indicates that the mean-field theories may not be best suited to describe the critical behavior in this system and, second, the absence of negative slopes throughout the range of fields indicates that the transition from the ferromagnetic (FM) to paramagnetic (PM) phase is a second-order transition, consistent with the Banerjee criterion.²³

Known values of the critical exponents for various universality classes, such as 3D-Heisenberg, 3D-Ising, 3D-XY, etc., were used to construct corresponding modified Arrott plots (MAPs). The isotherms in the MAP constructed with the critical exponents of the 3D-Heisenberg class exhibited the most linear behavior compared to the MAPs constructed with other exponents. Therefore, theoretical values of the critical exponents for the 3D-Heisenberg model^{17,24} ($\beta = 0.365$, $\gamma = 1.336$) were taken as the initial trial values to construct an initial MAP similar to that in Fig. 2(b). The isotherms were extrapolated from high field linear regions to find the intercepts of the $M^{1/\beta}$ and $(H/M)^{1/\gamma} = (\chi_0^{-1})^{(1/\gamma)}$ axes to calculate the values of $M_S(T)$ and χ_0^{-1} shown in Fig. 3(a). From these values of $M_S(T)$ and χ_0^{-1} , a new set of critical exponents β and γ were calculated using the Kouvel-Fisher method.²⁵ This is considered to be the most reliable method in extracting accurate values of the critical exponents based on MAPs.^{17,19,22} According to this method, Eqs. (1) and (2) can be written as

$$M_S(T) \left[\frac{dM_S(T)}{dT} \right]^{-1} = (T - T_C)/\beta, \quad (8)$$

$$\chi_0^{-1} \left[\frac{d\chi_0^{-1}(T)}{dT} \right]^{-1} = (T - T_C)/\gamma. \quad (9)$$

FIG. 1. (a) Magnetization (M) vs. temperature (T) for Ni_2MnGa measured in an applied field of $H = 0.1$ T. T_M , T_p , and T_C represent the martensitic, pre-martensitic, and Curie temperatures, respectively. (b) Magnetization isotherms, $M(H)$, measured in increments of $\Delta T = 0.5$ K.

FIG. 2. (a) Arrott plot of magnetization isotherms measured in the temperature range of $T = 374.0$ – 388.0 K with $\Delta T = 0.50$ K for Ni_2MnGa . (b) Modified Arrott plot (MAP) using $\beta = 0.4000$ and $\gamma = 1.2705$. The solid red line indicates the linear fit to the isotherm at $T_C = 382.5$ K.

FIG. 3. (a) Temperature dependence of the spontaneous magnetization [$M_S(T, 0)$] and inverse susceptibility [χ_0^{-1}] obtained from the linear extrapolation of the MAP of Fig. 2(b). The lines represent best fits to Eqs. (1) and (2). (b) Kouvel-Fisher plots for Ni_2MnGa . Straight lines are linear fits to the data, from which β , γ , and T_C were calculated.

TABLE I. The critical exponent values (β , γ , and δ) and the transition temperatures (T_C) obtained from the Kouvel-Fisher (KF) method and the critical isotherms (CI). The theoretical values of the critical exponents for various universality classes are given for comparison. The experimentally calculated critical exponent values for various other materials are also provided.

Composition	Technique	β	γ	T_C	δ
Ni ₂ MnGa (This work)	KF	0.401 ± 0.003	1.27 ± 0.02	382.42 ± 5.13 K	4.17 ± 0.08
	CI				4.100 ± 0.007
Ni ₂ Mn _{0.85} Cu _{0.15} Ga (This work)	KF	0.389 ± 0.004	1.39 ± 0.02	327.45 ± 4.14 K	4.56 ± 0.08
	CI				4.66 ± 0.01
Mean Field Model ^{19,22}	Theory	0.5	1.0		3.0
3D Heisenberg Model ^{17,22}	Theory	0.365	1.336		4.66
Ni ₅₀ Mn _{50-x} Sn _x ⁵					
x = 13	KF	0.385 ± 0.035	1.083 ± 0.060	303.6 K	...
x = 14	KF	0.496 ± 0.015	1.024 ± 0.059	304.5 K	...
Ni _{50-y} Gd _y Mn ₃₇ Sn ₁₃ ⁶					
y = 1	KF	0.473 ± 0.020	1.141 ± 0.017	299.0 ± 0.02 K	...
y = 3	KF	0.469 ± 0.068	1.214 ± 0.042	302.9 ± 0.7 K	...
Ni ₄₃ Mn ₄₆ Sn ₈ In ₃ ⁷	KF	0.485 ± 0.013	0.987 ± 0.017	296.8 K	3.035
Ni ₄₃ Mn ₄₆ Sn ₈ Cr ₃ ⁷	KF	0.549 ± 0.008	0.965 ± 0.012	301.8 K	2.758
Ni _{2.2} Mn _{0.6} V _{0.18} Ga _{1.08} ⁸	KF	0.48	1.05	268 K	3.02
Ni ₄₇ Mn ₄₀ Sn _{13-x} Cu _x ⁹					
x = 0	KF	0.479 ± 0.010	1.087 ± 0.017	313.50 K	3.269
x = 0.5	KF	0.521 ± 0.008	1.061 ± 0.010	315.96 K	3.036
TbCo _{2-x} Fe _x ¹⁰					
x = 0	KF	0.380(4)	1.407(8)	224.83(7) K	4.85(3)
x = 0.1	KF	0.541(1)	1.023(2)	304.48(5) K	2.75(4)

The plots of $M_S(T)[dM_S(T)/dT]^{-1}$ vs. T and $\chi_0^{-1}[d\chi_0^{-1}(T)/dT]^{-1}$ vs. T are straight lines with slopes of $1/\beta$ and $1/\gamma$, respectively, as shown in Fig. 3(b). Next, the values of β and γ found from the Kouvel-Fisher plot were used to generate a new MAP. This process was iterated until the values converged, and a stable set of critical exponents (β , γ) and T_C were obtained. For Ni₂MnGa, after multiple iterations, the critical exponents converged to the following values: $\beta = 0.401 \pm 0.003$, $\gamma = 1.27 \pm 0.02$, and $T_C = 382.42$ K ± 5.13 K (see Table I). One notable feature of the Kouvel-Fisher method is that, unlike other methods, no prior knowledge of T_C is required, as the intercept of the straight lines with the temperature axis gives T_C .^{17,22}

A $\ln\ln$ plot of some representative isotherms in the vicinity of T_C are shown in Fig. 4. According to Eq. (3), a $\ln(M)$ vs. $\ln(H)$ plot for the critical isotherm should be a straight line with a slope of $1/\delta$. For Ni₂MnGa, the isotherm at $T = 382.5$ K was considered to be the critical isotherm as it was closest to $T_C = 382.42$ K. The exponent $\delta = 4.10$ was calculated by performing a linear fit to the critical isotherm. The β and γ values obtained through the Kouvel-Fisher method can be used to calculate δ by using the Widom relation^{18,26}

$$\delta = 1 + \frac{\gamma}{\beta}. \quad (10)$$

This relation yielded $\delta = 4.17 \pm 0.08$, which is very close to the value $\delta = 4.100 \pm 0.007$ obtained from the critical isotherm (see Table I). The values of δ obtained from the two independent methods (Kouvel-Fisher and critical isotherm) are in reasonable agreement, indicating the reliability of the β and γ values.

As discussed in Sec. II, according to Eq. (4), a plot of the reduced magnetization ($m \equiv |\epsilon|^{-\beta} M(H, \epsilon)$) vs. reduced field ($h \equiv |\epsilon|^{-(\beta+\gamma)} H$) should collapse into two separate branches, one above and one below T_C , for the correct choice of critical exponents. This behavior is seen in Fig. 5(a), where the $m(h)$ curves clearly collapsed into two symmetric curves, one above and one below that for $T = T_C$. The inset of Fig. 5(a) shows the $\ln(m)$ vs. $\ln(h)$ plot, which demonstrates the collapsed curves more clearly. This feature confirms the reliability of the critical exponents to some degree. However, the insensitive nature of the logarithms may result in the collapse of the data into two branches, even for up to

FIG. 4. A plot of $\ln(M)$ vs. $\ln(H)$ near the critical isotherm for Ni₂MnGa. The dashed red line represents the linear fit to the critical isotherm at $T_C = 382.5$ K; δ was calculated from the slope of this line.

10% deviations from the true β and γ values (see Refs. 17, 27, and 28). The reliability of the exponent values can be further verified in a more rigorous manner by using Eq. (6), which is more sensitive to the critical exponent values.^{17,19} In Fig. 5(b), the m^2 vs. h/m plot clearly collapse into two branches: one above and one below T_C . This further validates the reliability of the critical exponents obtained through the Kouvel-Fisher method.

B. Critical behavior in $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$

Experiment and analysis procedures identical to those described above were applied to $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$. The substitution of Cu reduces the second-order transition temperature from $T_C = 382.4$ K in Ni_2MnGa to $T_C = 327.5$ K in $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$. Concurrently, the first-order (martensitic) transition temperature increases from $T_M \approx 209$ K in Ni_2MnGa to $T_M \approx 273$ K in $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$. It is to be noted that the two transitions do not overlap for a 15% Cu ($x = 0.15$) substitution, whereas they do occur at the same temperature for a 25% ($x = 0.25$) Cu substitution. In order to determine whether the martensitic phase transitions affect the critical exponents calculated for the second-order transitions, we followed the analysis procedure described in Ref. 29, and constructed the universal entropy change (ΔS) vs. temperature (T) curves for both alloys. According to this approach, the influence of another phase transition (i.e., the martensitic transition in this case) would hinder the full collapse of the ΔS vs. T curves when using a single reference temperature, necessitating the usage of two well-separated reference temperatures to achieve a good collapse. For the present investigation, we observed a full collapse of the universal curves (not shown) with a single reference temperature for both alloys. This suggests that the martensitic phase transitions did not appreciably affect the calculated values of the critical exponents for the second order transitions for either system.²⁹

The $M(H)$ curves (isotherms) were collected in $\Delta T = 0.5$ K increments using the same protocol described earlier [Fig. 6(a)]. Similar to Ni_2MnGa , the critical exponents for the 3D-Heisenberg model ($\beta = 0.365$ and $\gamma = 1.336$) were used as the initial trial values to construct the first MAP. Following the same iterative Kouvel-Fisher method, the critical exponent values converged to $\beta = 0.389 \pm 0.004$, $\gamma = 1.39 \pm 0.02$, and $T_C = 327.45$ K ± 4.14 K [see Fig. 7(a) and Table I].

A linear fitting of the critical isotherm at $T = 327.5$ K yielded $\delta = 4.66 \pm 0.01$. This exponent value was also calculated by using the β and γ values obtained through the Kouvel-Fisher method in the Widom relation [Eq. (10)], which resulting in $\delta = 4.56 \pm 0.08$. As the isotherms were obtained in $\Delta T = 0.5$ K increments, there was no isotherm at exactly $T_C = 327.4$ K. Instead, the isotherm at $T = 327.5$ K was chosen to be the critical isotherm, as it was closest to T_C . This may explain the slight difference in the δ values. Still, the agreement between the δ values obtained from two independent methods indicates the reliability of the critical exponents, β and γ . In Fig. 8(a), the $m(h)$ curves collapsed into two branches, one above and one below T_C . Moreover, this collapsing feature was also observed in the m^2 vs. h/m plot [Fig. 8(b)].

For a second order magnetic transition, the peak magnetic entropy change (ΔS^{pk}) follows a power-law dependence in magnetic field, namely, $\Delta S^{pk} \propto H^n$ with $n = 2/3$.^{30,31} The scaling exponent n is related to the exponents, β and γ , through the relation³²

$$n = 1 + \frac{\beta - 1}{\beta + \gamma}. \quad (11)$$

Using the β and γ values obtained through the Kouvel-Fisher method in Eq. (11) yielded $n = 0.64$ and 0.66 for Ni_2MnGa and $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$, respectively. These values of n are quite close to the value of $2/3$ predicted for a second-order magnetic phase transition. The magnetic entropy change (ΔS) was calculated from the magnetization isotherms using

FIG. 5. (a) The renormalized magnetization [$m \equiv M|\epsilon|^{-\beta}$] vs. magnetic field [$h \equiv H|\epsilon|^{-(\beta+\gamma)}$] curves according to Eq. (4) with $\beta = 0.4007$ and $\gamma = 1.2713$ for Ni_2MnGa . The data collapse into two distinct branches, one above and one below T_C . Each color in the curves represents the contribution from a different isotherm. (Inset) A plot of $\ln(m)$ vs. $\ln(h)$. (b) The renormalized magnetization and field are plotted as m^2 vs. h/m according to Eq. (6). The data collapse into two branches, one above and one below T_C .

FIG. 6. (a) Magnetization isotherms, $M(H)$, measured in $\Delta T = 0.5$ K increments from $H = 0$ T to $H = 7$ T for $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$. (Inset) Magnetization (M) vs. temperature (T) in an applied magnetic field of $H = 0.1$ T. (b) Modified Arrott plot (MAP) using $\beta = 0.3892$ and $\gamma = 1.3869$. The solid red line indicates the linear fit to the isotherm at $T_C = 327.5$ K.

FIG. 7. (a) Kouvel-Fisher plots for $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$. Straight lines are linear fits to the data, from which β , γ , and T_C were calculated. (b) A plot of $\ln(M)$ vs. $\ln(H)$ near the critical isotherm for $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$. The dashed red line represents the linear fit to the critical isotherm at $T_C = 327.5$ K; δ was calculated from the slope of this line.

FIG. 8. (a) The renormalized magnetization $[m \equiv M|\epsilon|^{-\beta}]$ vs. magnetic field $[h \equiv H|\epsilon|^{-(\beta+\gamma)}]$ curves according to Eq. (4) with $\beta = 0.3891$ and $\gamma = 1.3867$ for $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$. The data collapse into two distinct branches, one above and one below T_C . Each color in the curves represents the contribution from a different isotherm. (Inset) A plot of $\ln(m)$ vs. $\ln(h)$. (b) The renormalized magnetization and field are plotted as m^2 vs. h/m according to Eq. (6). The data collapse into two branches, one above and one below T_C .

the integrated Maxwell relation, $\Delta S = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$. Figure 9 shows the peak entropy change (ΔS^{pk}) vs. the rescaled magnetic field (H^n) plots. These plots demonstrate the linear relationship expected for second-order magnetic phase transitions. However, for $\text{Ni}_2\text{Mn}_{0.75}\text{Cu}_{0.25}\text{Ga}$, the peak entropy change (ΔS^{pk}) does not obey any power-law dependence in magnetic field (H), as shown in the inset of Fig. 9. This behavior is expected, as $\text{Ni}_2\text{Mn}_{0.75}\text{Cu}_{0.25}\text{Ga}$ undergoes a first-order coupled magnetostructural transition, which gives rise to a giant magnetocaloric effect.

It has been observed that the presence of short-range interactions or a weakening of long-range interactions can cause a broadening of the entropy change vs. temperature (ΔS vs. T) curves.^{29,33,34} To investigate whether the Cu substitution broadens the ΔS vs. T curves, we calculated the full-width at half-maximum (δT_{FWHM}) of these curves. The relative cooling power at the full-width at half-maximum (RCP_{FWHM}) was also calculated using the relation, $RCP_{FWHM} = |\Delta S^{pk} \times \delta T_{FWHM}|$. Here, ΔS^{pk} is the maximum value of the entropy change for a particular magnetic field. Figure 10(a) shows that the δT_{FWHM} for $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ is larger at each field value compared to that of Ni_2MnGa , indicating a broadening of the ΔS vs. T curves. However, the RCP_{FWHM} remains essentially the same for both of the alloys [Fig. 10(b)]. We have also observed that the peak values of the entropy change decreased due to the Cu substitution (not shown). In $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$, a decrease in the maximum entropy change values and an increase in the width of the ΔS vs. T curves, as evident in Fig. 10(b), kept the RCP_{FWHM} values close to those of Ni_2MnGa . These facts point towards a broadening of the ΔS vs. T curves due to the Cu substitution, indicating the presence of short-range exchange interactions. Similar to ΔS^{pk} , the RCP_{FWHM} is predicted to follow a power-law dependence in magnetic field,³⁵ given by $RCP_{FWHM} \propto H^{1+1/\delta}$. The power-law fitting of the data as shown in

FIG. 9. Plots of the peak entropy change (ΔS^{pk}) vs. rescaled magnetic field (H^n) for Ni_2MnGa ($x=0$) and $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ ($x=0.15$), where $n=0.64$ and 0.66 were used, respectively. The solid lines in red and green represent linear fits. (Inset) A plot of peak entropy change (ΔS^{pk}) vs. magnetic field (H) for $\text{Ni}_2\text{Mn}_{0.75}\text{Cu}_{0.25}\text{Ga}$ ($x=0.25$).

FIG. 10. (a) The full-width at half-maximum (δT_{FWHM}) of the ΔS vs. T curves measured at various applied magnetic fields for Ni_2MnGa ($x=0$) and $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ ($x=0.15$). (b) The relative cooling power at the full-width at half-maximum (RCP_{FWHM}) for Ni_2MnGa ($x=0$) and $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ ($x=0.15$). The solid blue and dashed green lines represent power-law fits.

Fig. 10(b), resulted in $\delta=4.54$ and 4.56 for Ni_2MnGa and $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$, respectively. These values are close to the values obtained through other methods (see Table I).

V. DISCUSSION

The Heisenberg model is best suited to describe ferromagnetism in localized systems.¹⁷ Despite the localized nature of the ferromagnetism¹¹ in Ni_2MnGa , the critical exponents deviate significantly from the Heisenberg values towards the mean-field values. However, the exponents for $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ are closer to the Heisenberg values (see Table I). As mentioned previously, the critical exponents depend on the lattice dimensionality (d), spin dimensionality (n), and range of exchange interaction (σ). A relation between these quantities and the critical exponent γ [Eq. (12)] was derived through a renormalization group approach,^{19,27,36,37} and can be used to estimate the range of spin interactions. This relation is given by

$$\gamma = 1 + (4/d) \left(\frac{n+2}{n+8} \right) \Delta\sigma + \frac{8(n+2)(n-4)}{d^2(n+8)^2} \left[1 + \frac{2G(d/2)(7n+20)}{(n-4)(n+8)} \right] \Delta\sigma^2, \quad (12)$$

where $\Delta\sigma = (\sigma - \frac{d}{2})$ and $G(\frac{d}{2}) = 3 - \frac{1}{4}(\frac{d}{2})^2$.

According to this approach, the exchange interaction is long-range when $\sigma < 2$, and short-range if $\sigma > 2$. Following the procedure described by Fisher *et al.*,²⁷ and Pramanik *et al.*,¹⁹ for a particular set of values of $\{d:n\}$, the parameter σ was adjusted until the γ value from the above equation was equal to the one obtained experimentally. This value of σ was then used to calculate other exponents using the following relations: $\nu = \gamma/\sigma$, $\alpha = 2 - \nu d$, $\beta = (2 - \alpha - \gamma)/2$, and $\delta = 1 + \gamma/\beta$.

For Ni_2MnGa , $\{d:n\} = \{2:3\}$ and $\sigma = 1.216$ produced exponent values of $\beta = 0.4098$, $\gamma = 1.272$, and $\delta = 4.10$, which are close to the experimentally determined values.

Similarly, for $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$, $\{d:n\}=\{2:3\}$ and $\sigma=1.283$ resulted in critical exponent values of $\beta=0.3875$, $\gamma=1.387$, and $\delta=4.58$, also close to the experimentally determined values. These calculations suggest that the effective dimensionality of spin interactions in both alloys is less than three. This may originate from the fact that, in Mn-based Heusler alloys, the magnetic moment is mostly confined to the two-dimensional Mn sublattices, and the magnetism is governed by the Mn atoms.^{19,38} Because of the large distance between the Mn atoms ($d_{\text{Mn-Mn}} > 4 \text{ \AA}$),³⁸ there is no considerable overlapping of the Mn 3d states and, hence, no significant direct interaction between the Mn atoms.³⁹ This is why an indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction mediated by the Ni conduction electrons gives rise to the ferromagnetism in Ni_2MnGa .^{11,15,38,40} Therefore, the manifestation of long-range interactions in Ni_2MnGa is not surprising. It is clear that the Cu substitution for Mn in Ni_2MnGa decreases the values of β and T_C , while it increases the value of γ . A somewhat opposite scenario was described by Halder *et al.*,¹⁰ for $\text{TbCo}_{2-x}\text{Fe}_x$. In that case, the critical exponents for the parent compound TbCo_2 were very close to the Heisenberg values. However, for $\text{TbCo}_{1.9}\text{Fe}_{0.1}$, the T_C and the critical exponent β increased, while the value of γ decreased. Overall, the critical exponents for $\text{TbCo}_{1.9}\text{Fe}_{0.1}$ were close to the mean-field values. They argued that the Fe substitution causes the RKKY interactions to dominate over the exchange interactions. The RKKY interactions extend beyond the nearest neighbors, and this long-range interaction causes a deviation of the critical exponents from the Heisenberg values toward the mean-field values. In another investigation, Zhang *et al.*⁶ studied the role of Gd substitution in $\text{Ni}_{50-y}\text{Gd}_y\text{Mn}_{37}\text{Sn}_{13}$ through critical exponent analysis. While the parent compound ($y=0$) exhibited short-range FM interactions, the Gd-substituted compounds indicated long-range FM interactions with the critical exponents close to the mean-field values. They argued that the substitution of the rare-earth Gd atom in the Ni site reestablished the long-range RKKY-type FM interactions, drove the system towards long-range order and, hence, towards mean-field like critical behavior.

In the case of Ni_2MnGa , the deviation of the critical exponent values from the 3D-Heisenberg values toward the mean-field values could be attributed to the presence of long-range RKKY interactions.^{10,21,37} The substitution of nonmagnetic Cu in the Mn site likely weakens the RKKY interactions and hence the observed reduction in T_C in $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$. As stated earlier, Cu substitution enhances the hybridization effects between the Ni d states and Ga p states, and causes the system to be more magnetically delocalized.¹¹ This factor can cause the short-range interactions to dominate, which, along with the weakening of the long-range interactions, may explain why the critical exponents for $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ are closer to the 3D-Heisenberg values.

VI. CONCLUSIONS

In summary, we calculated the critical exponents (β and γ) of the ferromagnetic transitions in polycrystalline

Ni_2MnGa and $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ using the Kouvel-Fisher method. For both compounds, the exponent δ was obtained from critical isotherms, as well as through the Widom scaling relation. For the obtained values of the critical exponents, the reduced magnetization vs. field data collapsed into two branches, one above and one below T_C , in compliance with the scaling equation of state. In Ni_2MnGa , the critical exponents deviate from the 3D-Heisenberg values toward the mean-field values. This is consistent with the presence of long-range RKKY exchange interactions, which govern the magnetism in Ni_2MnGa . The critical exponents in $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ are close to the theoretical values of the 3D-Heisenberg model with short-range interactions. The substitution of nonmagnetic Cu in the Mn site weakens the long-range RKKY interactions and enhances the Ni-Ga hybridization. These factors may explain the similarity of the critical exponent values in $\text{Ni}_2\text{Mn}_{0.85}\text{Cu}_{0.15}\text{Ga}$ to those of the 3D-Heisenberg model. In order to obtain the desired functional properties, and to study the underlying physics in magnetic materials, various strategies, such as stoichiometry variation, elemental substitution, etc., are often employed. Although critical exponents cannot be obtained for discontinuous first-order transitions, analyzing the critical behavior in the vicinity of second-order phase transitions can be used to understand how the interactions change with substitution. This can provide some insight as to how the interactions evolve as the substitution levels increase toward values that produce coupled, first-order transitions.

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¹L. Caron, B. Dutta, P. Devi, M. Ghorbani Zavareh, T. Hickel, R. Cabassi, F. Bolzoni, S. Fabbri, F. Albertini, C. Felser, and S. Singh, *Phys. Rev. B* **96**, 054105 (2017).

²S. Stadler, M. Khan, J. Mitchell, N. Ali, A. M. Gomes, I. Dubenko, A. Y. Takeuchi, and A. P. Guimarães, *Appl. Phys. Lett.* **88**, 192511 (2006).

³M. Kataoka, K. Endo, N. Kudo, T. Kanomata, H. Nishihara, T. Shishido, R. Y. Umetsu, M. Nagasako, and R. Kainuma, *Phys. Rev. B* **82**, 214423 (2010).

⁴T. Ohba, N. Miyamoto, K. Fukuda, T. Fukuda, T. Kakeshita, and K. Kato, *Smart Mater. Struct.* **14**, S197 (2005).

⁵T.-L. Phan, P. Zhang, N. H. Dan, N. H. Yen, P. T. Thanh, T. D. Thanh, M. H. Phan, and S. C. Yu, *Appl. Phys. Lett.* **101**, 212403 (2012).

⁶P. Zhang, T. Phan, N. Dan, T. Thanh, and S. Yu, *J. Alloys Compd.* **615**, S335 (2014).

⁷W. Nan, T. D. Thanh, G. Nam, T. You, H. Piao, L. Pan, and S. Yu, *J. Magn. Magn. Mater.* **443**, 171 (2017).

⁸U. Devarajan, M. Kannan, R. Thiagarajan, M. M. Raja, N. V. R. Rao, S. Singh, D. Venkateshwarlu, V. Ganesan, M. Ohashi, and S. Arumugam, *J. Phys. D: Appl. Phys.* **49**, 065001 (2016).

⁹A. G. Varzaneh, P. Kameli, T. Amiri, K. Ramachandran, A. Mar, I. A. Sarsari, J. Luo, T. Etsell, and H. Salamati, *J. Alloys Compd.* **708**, 34 (2017).

¹⁰M. Halder, S. M. Yusuf, M. D. Mukadam, and K. Shashikala, *Phys. Rev. B* **81**, 174402 (2010).

- ¹¹S. Roy, E. Blackburn, S. M. Valvidares, M. R. Fitzsimmons, S. C. Vogel, M. Khan, I. Dubenko, S. Stadler, N. Ali, S. K. Sinha, and J. B. Kortright, *Phys. Rev. B* **79**, 235127 (2009).
- ¹²V. Sokolovskiy, V. Buchelnikov, K. Skokov, O. Gutfleisch, D. Karpenkov, Y. Koshkid'ko, H. Miki, I. Dubenko, N. Ali, S. Stadler, and V. Khovaylo, *J. Appl. Phys.* **114**, 183913 (2013).
- ¹³M. Khan, J. Jung, S. S. Stoyko, A. Mar, A. Quetz, T. Samanta, I. Dubenko, N. Ali, S. Stadler, and K. H. Chow, *Appl. Phys. Lett.* **100**, 172403 (2012).
- ¹⁴M. Khan, I. Dubenko, S. Stadler, and N. Ali, *J. Appl. Phys.* **97**, 10M304 (2005).
- ¹⁵S. R. Barman, S. Banik, and A. Chakrabarti, *Phys. Rev. B* **72**, 184410 (2005).
- ¹⁶S. Blundell, *Magnetism in Condensed Matter* (Oxford University Press, 2001), Chap. 6.
- ¹⁷P. Lampen, M. H. Phan, H. Srikanth, K. Kovnir, P. Chai, and M. Shatruk, *Phys. Rev. B* **90**, 174404 (2014).
- ¹⁸H. Eugene Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, 1971), Chap. 11.
- ¹⁹A. K. Pramanik and A. Banerjee, *Phys. Rev. B* **79**, 214426 (2009).
- ²⁰Y. Su, Y. Sui, J.-G. Cheng, J.-S. Zhou, X. Wang, Y. Wang, and J. B. Goodenough, *Phys. Rev. B* **87**, 195102 (2013).
- ²¹J. Lago, M. J. Rosseinsky, S. J. Blundell, P. D. Battle, M. Diaz, I. Uriarte, and T. Rojo, *Phys. Rev. B* **83**, 104404 (2011).
- ²²S. Kaul, *J. Magn. Magn. Mater.* **53**, 5 (1985).
- ²³B. Banerjee, *Phys. Lett.* **12**, 16 (1964).
- ²⁴M. Camprostrini, M. Hasenbusch, A. Pelissetto, P. Rossi, and E. Vicari, *Phys. Rev. B* **65**, 144520 (2002).
- ²⁵J. S. Kouvel and M. E. Fisher, *Phys. Rev.* **136**, A1626 (1964).
- ²⁶B. Widom, *J. Chem. Phys.* **43**, 3898 (1965).
- ²⁷S. F. Fischer, S. N. Kaul, and H. Kronmüller, *Phys. Rev. B* **65**, 064443 (2002).
- ²⁸P. D. Babu and S. N. Kaul, *J. Phys.: Condens. Matter* **9**, 7189 (1997).
- ²⁹M.-H. Phan, V. Franco, A. Chaturvedi, S. Stefanoski, G. S. Nolas, and H. Srikanth, *Phys. Rev. B* **84**, 054436 (2011).
- ³⁰J. Fan, L. Pi, L. Zhang, W. Tong, L. Ling, B. Hong, Y. Shi, W. Zhang, D. Lu, and Y. Zhang, *Appl. Phys. Lett.* **98**, 072508 (2011).
- ³¹H. Oesterreicher and F. T. Parker, *J. Appl. Phys.* **55**, 4334 (1984).
- ³²V. Franco, A. Conde, J. M. Romero-Enrique, and J. S. Blázquez, *J. Phys.: Condens. Matter* **20**, 285207 (2008).
- ³³X. B. Liu and Z. Altounian, *J. Appl. Phys.* **99**, 08Q101 (2006).
- ³⁴A. Wang, Y. Liu, Z. Zhang, Y. Long, and G. Cao, *Solid State Commun.* **130**, 293 (2004).
- ³⁵V. Franco, J. Blázquez, J. Ipus, J. Law, L. Moreno-Ramírez, and A. Conde, *Prog. Mater. Sci.* **93**, 112 (2018).
- ³⁶M. E. Fisher, S. Ma, and B. G. Nickel, *Phys. Rev. Lett.* **29**, 917 (1972).
- ³⁷R. Li, Z. Ma, E. A. Balfour, H. Fu, and Y. Luo, *J. Alloys Compd.* **658**, 672 (2016).
- ³⁸E. Şaşıoğlu, L. M. Sandratskii, and P. Bruno, *Phys. Rev. B* **77**, 064417 (2008).
- ³⁹J. F. Duan, Y. Long, B. Bao, H. Zhang, R. C. Ye, Y. Q. Chang, F. R. Wan, and G. H. Wu, *J. Appl. Phys.* **103**, 063911 (2008).
- ⁴⁰J. Kübler, A. R. William, and C. B. Sommers, *Phys. Rev. B* **28**, 1745 (1983).