Coexistence of charge-density wave and ferromagnetism in Ni_{2}MnGa

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S. W. D'Souza[1], Abhishek Rai[1], J. Nayak[1], M. Maniraj[1], R. S. Dhaka[1],
S. R. Barman[1*], D. L. Schlagel[2], T. A. Lograsso[2], Aparna Chakrabarti[3]
[1] *UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore, 452001, Madhya Pradesh, India*
[2] *Materials and Engineering Physics Program, Ames Laboratory U. S. DOE, Iowa State University, Ames, Iowa 50011-3020, USA and*
[3] *Raja Ramanna Centre for Advanced Technology, Indore 452013, Madhya Pradesh, India*

We demonstrate the existence of a charge-density-wave (CDW) associated with an incommensurate periodic lattice distortion on Ni_2MnGa surface in the ferromagnetic state. Our temperature dependent photoemission spectra provide compelling evidence of a pseudogap at the Fermi level for $T_{CDW} \leq 270$ K that appears at the onset of the pre-martensite phase and persists in the martensite phase. While the width of the pseudogap is about 25 meV, a spectral weight transfer is observed over a much wider energy range that is associated with the CDW.

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I. INTRODUCTION

Charge-density-waves (CDW) have fascinated physicists for many decades since Peierls transition was suggested in one dimensional metals coupled to an underlying lattice, where a periodic lattice distortion with wave vector $2k_F$ develops resulting in opening up of a gap at the Fermi level (E_F).[1,2] In a pioneering study, Lee, Rice, and Anderson[3] showed how fluctuations in the order parameter affect the CDW transition. They considered a model consisting of electrons in a linear chain coupled to phonons and predicted the appearance of a pseudogap in the CDW state that arises due to the thermal lattice motion. McKenzie derived a Ginzburg-Lindau free-energy functional from a microscopic theory employing a model Hamiltonian considering electron-phonon coupling and found that near the CDW transition temperature, the thermal lattice motion produces a pseudogap at E_F.[4] The density of states is symmetric about E_F.[4] Above the CDW transition temperature the pseudogap gradually fills up. CDW is a collective excitation formed by electron-hole pairs that is stabilized by a pseudogap at E_F and is a topic of active theoretical study.[5,6]

In the backdrop of intense efforts to understand the co-existence of magnetism and superconductivity, the interplay between magnetism and CDW could provide important clues to achieve a global understanding of the different degrees of freedom in a solid. Although ferromagnetism appears due to Coulomb repulsion between electrons whereas CDW is due to attractive electron-electron interaction mediated by phonons, a theoretical work by Balseiro *et al.* showed that ferromagnetism can induce a periodic lattice distortion and co-exist with CDW.[7] Subsequent calculations by Gulácsi *et al.* showed that a CDW, spin density wave and ferromagnetism could co-exist in presence of an external magnetic field.[8] On the other hand, in rare earth intermetallic $SmNiC_2$, CDW was reported to be destroyed by ferromagnetism.[9] CDW has been observed in non-magnetic metal adlayers like Sn or Pb on Ge,[10] In/Cu[11] and in bulk metal like uranium,[12] while in $Er_5Ir_4Si_{10}$ it is strongly coupled to the local moment antiferromagnetism.[13] In uranium metal, the CDW is associated with significant phonon softening that is related to the martensite transition.[14]

Ferromagnetic shape memory alloys (FSMA) exhibit ferroelastic martensite transition and constitute a new class of smart materials that are technologically important and scientifically exciting. Among the different FSMA's discovered so far, Ni_2MnGa is at the center of attention because of large (10%) magnetic field induced strain and interesting magnetic behavior.[15–17] It is an ideal model system to explore the co-existence of ferromagnetism and CDW because martensite transition (which is a diffusionless first order transition from high symmetry austenite phase to a lower symmetry martensite phase) is known to be associated with phonon anomalies.[18–22] Ni_2MnGa is ferromagnetic at room temperature with a total saturation moment of 4.17 μ_B and a large local moment of 3.6μ_B on Mn.[23,24]

Existence of a modulated crystal structure in the martensite phase of Ni_2MnGa with shuffling of the (110) planes along the $[1\bar{1}0]$ direction is well known.[23,25,26] The origin of modulation has been related to a TA_2 soft phonon mode in the transverse acoustic branch along [110] direction, which was first shown in Ni_2MnGa from diffuse x-ray scattering studies.[19] From inelastic neutron scattering, Zheludev *et al.*[20–22] found the phonon softening to occur below the pre-martensite transition temperature $T_P = 260$ K *i.e.* at temperatures higher than T_M, with wave vector $(\zeta, \zeta, 0)$, where $\zeta = 1/3$.[19–22] At T_P, the original cubic lattice becomes dynamically unstable and the lattice modulation is driven by electron-phonon interaction whose magnitude is higher than conventional shape memory alloys like NiAl or NiTiFe.[27] Density functional theory (DFT) showed that the instability of the TA_2 phonon is related to a long range anomalous contribution to the phonon frequency due to electronic screening.[28] In the martensite phase, an incommensurate wave vector with $\zeta \approx 0.43$ was obtained,[20] which is in agreement with theory.[28,29]

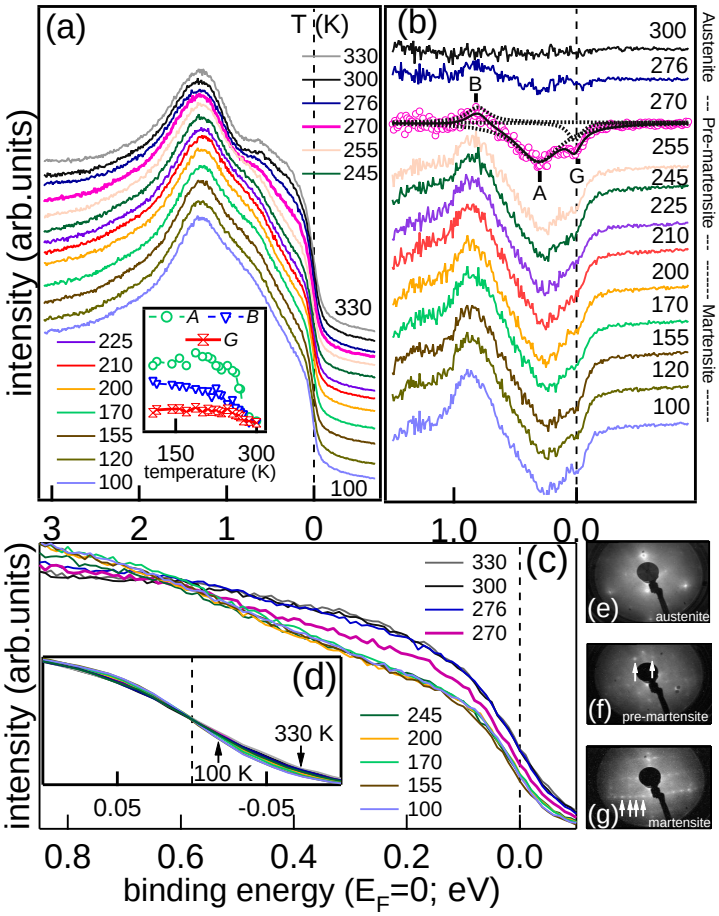

FIG. 1: (Color online) (a) The ultraviolet photoemission (UPS) spectra of Ni_2MnGa recorded with 21.2 eV photon energy as a function of temperature while cooling. The intensity of the main peak at 1.3 eV has been normalized to unity and staggered along the vertical axis. Inset shows the intensities of features A, B, and G of the (b) difference spectra obtained by subtracting the spectrum at 330 K from the other lower temperature spectra shown in (a). The near Fermi level (E_F) region of (c) Ni_2MnGa spectra in (a) and the (d) Ag UPS spectra **normalized at 0.6 eV are shown as superposed in expanded scale. In all the spectra, each temperature is represented by a particular color.** The LEED patterns at (e) 300 (f) 260 and (g) 200 K recorded with 100 eV electron beam energy. The white arrows indicate some of the satellite spots.

Photoemission spectroscopy is a standard tool to identify the CDW state.[30,31] However, in a previously published photoemission study on Ni_2MnGa, the existence of CDW was not established, although a temperature dependent variation of the spectral shape near E_F in the pre-martensite phase was observed, it was related to the density of states (DOS) in the martensite phase.[32] Suppression of the photoemission spectra near E_F in the martensite phase of Ni-Mn-Sn has been ascribed to Jahn Teller effect.[33] X-ray diffraction studies on a Ni excess Ni_2MnGa film showed that the modulation in the martensite phase is not of electronic origin, but is related to the branching of the twin variants in the tetragonal structure.[34] In contrast, a phason branch that indicates existence of CDW was identified in the martensite phase from neutron scattering.[35] In a different explanation for the phonon softenting, Wan *et al.* proposed a model Hamiltonian based on interaction of two magnons with the TA phonon that led to its damping at $\zeta = 1/3$ in the pre-martensite phase.[36] Thus, disagreement of views exist in literature about the origin of the modulation in Ni_2MnGa. In this work, we show that the incommensurate modulation in Ni_2MnGa originates from a CDW, and it exists in the ferromagnetic state. To the best of our knowledge, coexistence of CDW and ferromagnetism has not been reported in any other system until date.

II. EXPERIMENTAL

Ni_2MnGa single crystals were grown by the Bridgman method and were oriented in the austenite phase by Laue back reflection. The polishing was done mechanically using quarter micron diamond paste followed by electropolishing in nitric acid and methanol. The bulk composition of the crystal was determined by wavelength dispersive X-ray spectroscopy to be $Ni_{2.03}MnGa_{0.96}$. The surface martensitic start temperature from low energy electron diffraction (LEED) is 200 K, which is close to the bulk value of 206.5 K obtained from differential scanning calorimetry, while the Curie temperature (T_C) is 376 K.[37,38] Experiments were performed at a base pressure of about 4×10^{-11} mbar using an electron energy analyzer and a rear view LEED with four grid optics from Specs GmbH, Germany. The stoichiometric $Ni_2MnGa(100)$ surface was prepared by sputtering with 1.5 keV Ar^+ ions and annealing at 770 K for 1 hr.[39] Ni_2MnGa surface becomes Ni-rich and Mn deficient after sputtering. But, as the annealing temperature is increased, Mn segregates to the surface. Thus, by choosing appropriate annealing temperature and time, it is possible to obtain atomically clean stoichiometric surface.[39] The cleanliness was monitored and the surface composition ($Ni_{2.05}Mn_{0.96}Ga$, Mn:Ni= 0.48) was measured using x-ray photoelectron spectroscopy.[39] Sputtering and annealing technique has been used for other Mn containing ternary alloys like Al-Pd-Mn quasicrystal[40] and NiMnSb[41] to obtain atomically clean stoichiometric surface. While the analyzer is capable of 4.4 meV resolution in the gas phase, for the present experiments in the temperature range of 100- 330 K, contribution from the thermal broadening is high. So, as a compromise between counts and resolution (since the surface is highly sensitive to contamination), we use pass energy of 2 eV and 6 mm slit width. σ, which represents the Gaussian resolution broadening is obtained from least square fitting to be about 0.05 eV. The data were recorded in the normal emission (ΓX direction) with $\pm7^\circ$ angle of acceptance that provides partial Brillouin zone (BZ) integrated spectra. Besides, BZ integration could also occur due to indirect transitions that originate from disorder and defects (as depicted by the LEED patterns, Fig. 1(e-g)), the ∇.A term of the photoemission matrix element[42] and the electron-phonon interactions.[43] To obtain a single variant state in the martensite phase, the crystal was clamped along the vertical in the [01] direction of the austenite *b.c.t.* unit cell in a sample holder designed for studying complex metal surfaces.[44]

III. RESULTS AND DISCUSSION

The main peak at 1.3 eV in the ultraviolet photoemission (UPS) spectra of Ni_2MnGa (Fig. 1(a)) originates primarily from Ni $3d-$ Mn $3d$ hybridized states.[39,45] The spectra exhibit interesting modifications between 1 eV and E_F. In the austenite phase (330-276 K), the lower binding energy (BE) side of the main peak exhibits a rounded shape. At $T=270$ K, the spectrum **(bold pink line in Fig. 1(a, c))** shows a decrease in intensity centered at 0.25 eV and an increase around 0.85 eV. The difference spectra in Fig. 1(b) vividly show that a spectral weight transfer occurs from a dip A at 0.25 eV to a peak B at 0.85 eV. Most intriguingly, the difference spectra exhibits another dip (G) right at E_F. Clearly, the difference spectra can only be fitted with three Lorentzians, as shown by black dashed lines in the 270 K spectrum (Fig. 1(b)). The temperature variation has been quantified by plotting the intensities of features A, B and G of the difference spectra in the inset of Fig. 1(a). **In order to examine whether the difference spectra depends on the method of normalization of the raw spectra, we have performed the subtraction after normalizing the raw spectra in three different ways: (i) the intensity of the main peak at 1.3 eV (Fig. 1(a)), (ii) the intensity of the background on the higher BE side of the main peak at 2 eV, and (iii) the area under the spectra between E_F and 2 eV have been normalized to unity. In all cases, similar difference spectra are obtained, and in particular, the signature of the dip at E_F for T$\leq$ 270 K (feature G in Fig. 1(b)) is observed.** This dip at E_F originates from the change in the shape of the spectral function, as shown by the overlaid spectra in an expanded scale near E_F (Fig. 1(c)). In contrast, the spectra for Ag metal only show the expected thermal broadening (Fig. 1(d)).

The LEED patterns enable us to directly correlate the changes in the spectral shape at 270 K to the pre-martensite phase. For $T>270$ K, Ni_2MnGa is in the austenite (cubic) phase and the (100) surface exhibits a four fold LEED pattern (Fig.1(e)), as has been observed earlier.[39,46] Interestingly, satellite spots are clearly observed at $T\leq270$ K along [10], as well as along [01] direction (Fig. 1(f)). Similar satellite spots have been observed in transmission electron microscopy and have been ascribed to a modulated PM phase.[21,47] Thus, the pre-martensite transition temperature T_P at the surface is 270 K. By averaging the separation between the satellite spots from the line profiles at different electron beam energies, we find the modulation wave vector q to be incommensurate with value of $=0.459\pm0.002\times g_{10}$ for the pre-martensite phase, which is indicative of the occurrence of CDW. For $T\leq200$ K,(Fig. 1(g)) an array of new satellite spots appear along [10] direction as the specimen transforms to the martensite phase and the modulation wave vector is also found to be incommensurate.[48]

It should be noted that a theoretical work by Johannes and Mazin has shown that in incommensurate transitions, observation of a nesting vector does not necessarily imply CDW and the Fermi surface topology plays a secondary

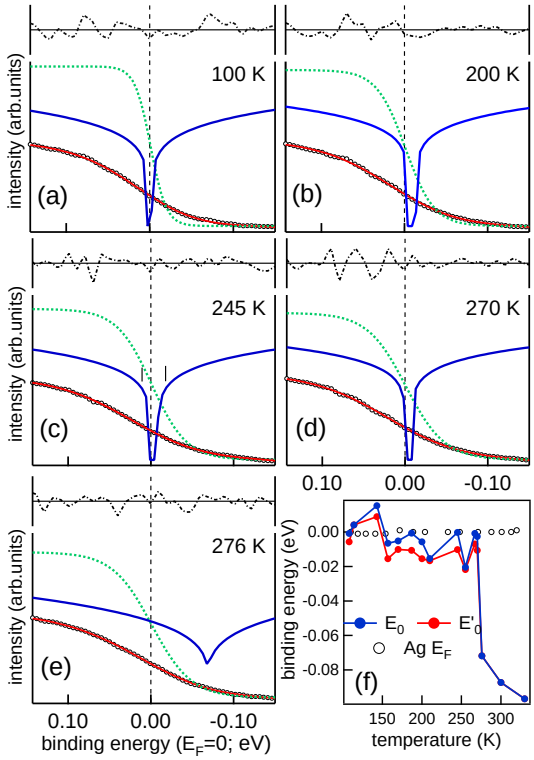

FIG. 2: (Color online) The near Fermi level (E_F) region of the UPS spectra in Fig. 1(a) fitted with Equation 1 at (a) 100 (b) 200 (c) 245 (d) 270 and (e) 276 K. The raw data (black open circles), the fitted curve (red line), the power-law spectral function (bold blue line) and the Fermi function (dashed green line) are shown. **Both the spectral function and the Fermi function are multiplied by $\sqrt{w}$.** The residuals for the fit are given at the top of each spectra. (f) The threshold energies (E_o, E_o') are compared to the E_F position.

role.[49] As discussed in the Introduction section, the hallmark of a CDW state is the pseudogap at E_F that is demonstrated on the basis of many-body calculations including the electron-phonon coupling.[3,4] So, a more reliable approach to infer about the CDW is to determine the shape of the spectral function at E_F.[30,31,50–52] Thus, in order to establish the CDW state in the pre-martensite phase, it is essential to determine the actual shape of the spectral function near E_F from the spectra in Fig. 1(a). This can be achieved by deconvoluting the Fermi function and the spectral broadening from the spectra near E_F. Note that if only the resolution broadened Fermi function ($f(E, T)$, whose position does not vary with temperature) is used to perform the least square fitting of the near E_F region, systematic deviations are observed and the fitting is not satisfactory. This shows that Ni_2MnGa is not a simple metal, since the E_F region of a photoemission spectra of a simple metal (irrespective of whether it is angle resolved, partially or fully angle integrated) can always be fitted with the Fermi function. So, on the basis of the theory for CDW,[4,7] a symmetric power law type spectral function is considered and the least square fitting has been performed using the following function

$$[w\times f(E,T)\times(|E-E_0|^{\alpha}h(E-E_0)+|E_0'-E|^{\alpha}h(E_0'-E))]\otimes G(E,\sigma) \quad (1)$$

where E_0 and E_0' are the threshold energies for left (below E_F) and right (above E_F) branches of the power law spectral function (bold blue line in Fig. 2(a-e)) and α is the exponent. h is an unit step function and w is an overall multiplicative factor. The power law function is symmetric around $(E_o+E_o')/2$. All the parameters in the above expression are allowed to vary. As in our earlier work,[53] the error minimization was performed using Levenberg-Marquardt algorithm with the tolerance for convergence given by $\chi^2<10^{-5}$. Convergence to a global minimum was tested by using different starting parameter values. The random variation of the residuals about zero indicates good quality of the fit (Fig. 2(a-e)).

It is fascinating to find that the threshold energies (E_o, E_o') are almost equal and coincide with E_F for $T\leq 270$ K (Fig. 2(a-d)). The spectral function is suppressed around E_F and becomes zero resulting in a pseudogap at E_F in the

pre-martensite phase. The pseudogap sustains in the martensite phase till the lowest temperature studied (100 K). As predicted by theory,[4] for $T > T_P$ the pseudogap at E_F fills up and the minimum of the spectral function moves above E_F (Fig. 2(e)). E_o, E_o', and the E_F position obtained from the fitting are compared in Fig. 2(f). Expectedly, the E_F position remains unchanged with temperature (see also Fig. 1(d)). The width of the pseudogap, defined as the separation between the points of inflection of the spectral function (ticks in Fig. 2(c)), is obtained to be **25±5 meV. A gap (Δ) at $T = 0$ has been defined for canonical CDW systems by the mean field treatment of the one dimensional electron-phonon Hamiltonian as $\Delta = 1.76 \times kT_{CDW}$,[2] where k is the Boltzmann constant and T_{CDW} is the CDW transition temperature. Considering $T_{CDW} = 270$ K for Ni_2MnGa, we obtain the value of Δ to be 41 meV, which is consistent with the width of the pseudogap of 25 meV that we obtain here in the temperature range 100-270 K.** Because of the thermal and resolution broadening, the pseudogap is observed in the raw spectra as the suppression of the intensity at E_F in Fig. 1(c). Angle resolved photoemission work on $ZrTe_3$,[50] partially angle integrated spectra for CuV_2S_4[31] established that if only some part of the Fermi surface exhibit pseudogap, the system is considered to be a CDW. Our fitting in Fig. 2 shows that a sizable fraction of the one-electron states of Ni_2MnGa at E_F exhibit pseudogap.

The value of α determines the shape of the spectral function and it varies from $0.14 - 0.25$. If influence of the magnons and spin density waves on the shape of the spectral function is predominant, α is expected to be about 1.5,[36] while the present value ($\alpha = 0.14$-0.25) is much less. Absence of electron-magnon effect was also shown by the presence of the TA_2 phonon anomaly above T_C.[20]

Finally, to probe the possibility whether the pseudogap and the accompanying spectral weight transfer could be related to the hybridization of the one-electron energy bands governed by the crystal structure as in Hume Rothery alloys or elemental metals like Ga[54], we have performed the DFT[55] calculations for the pre-martensite phase using its experimentally determined structure. The structure is cubic but with three fold modulation.[25] For comparison, the austenite phase is calculated with the same cubic unit cell as the pre-martensite phase, but the modulation is not considered. The parameters of the calculation are similar to those used by us recently for related FSMA's.[56,57] Along ΓX (Fig. 3) as well as along the other high symmetry directions of the BZ,[38] the energy bands for the two phases show striking similarity. Only minor differences, for example, splitting of an unoccupied band about 1 eV above E_F along ΓX (arrow in Fig. 3) are observed due to modulation. In Fig. 3, the number of bands crossing E_F

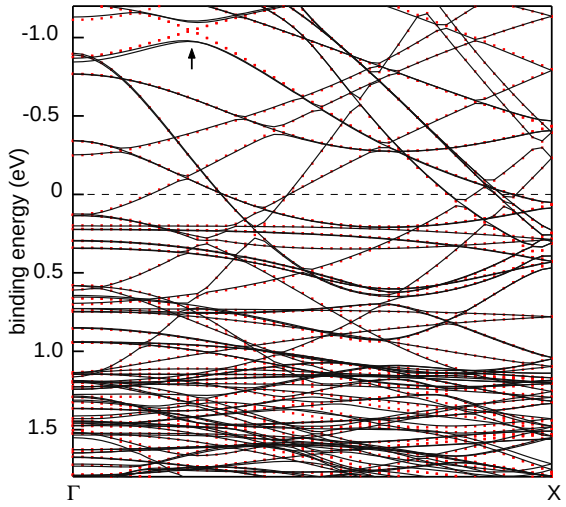

FIG. 3: (Color online) The energy bands of Ni_2MnGa along the ΓX direction for the pre-martensite (black lines) and the austenite phase (red dots).

in the pre-martensite phase is same as the austenite phase. The total DOS and the directional DOS along ΓX at E_F between the two phases are also very similar.[38] This shows that the pseudogap in the pre-martensite phase cannot be explained by one-electron band structure calculated by DFT. It also shows that the experimentally observed spectral weight transfer in the pre-martensite phase (Fig. 2) is not a band structure effect. The spectral weight transfer from below E_F to higher BE was predicted by theory of CDW[3] that considers the electron-phonon coupling. Furthermore, from the photoemission studies on other CDW systems,[30,31,50] the spectral weight transfer has been reported to occur over an energy range much larger than the pseudogap. This is also observed here: the spectral weight transfer occurs

over the energy range of 0.25 to 0.85 eV (Fig. 1(b)), while the width of the pseudogap is 25 meV. Thus, based on these earlier theoretical and experimental studies, we assign the spectral weight transfer to be a signature of the CDW state.

It has been proposed by the adaptive martensite model that if the surface energy between two orientational variants is low, the modulation in the martensite phase of Ni excess Ni_2MnGa thin film originates from a nano-twinned tetragonal structure and thus the modulation is not of electronic origin.[34] So, the variation in the UPS spectra between the austenite and the pre-martensite phase is not expected in this model, which is contrary to what we observe here. We find that the pre-martensite transition is driven by the CDW, which survives also in the martensite phase (Fig. 2(a)).

IV. CONCLUSION

To conclude, the temperature dependent photoemission spectra of Ni_2MnGa demonstrate the existence of charge-density-wave in the ferromagnetic state through the appearance of the pseudogap at the Fermi level. The pseudogap appears at the onset of the pre-martensite phase at 270 K. Concomitant with the pseudogap, a transfer of spectral weight over a much wider energy range from 0.25 to 0.85 eV binding energy is observed. The charge-density-wave state is found to persist in the martensite phase down to 100 K.

V. ACKNOWLEDGMENT

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*Electronic address: barmansr@gmail.com

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