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$Ni_2MnGa(100)$ ferromagnetic shape memory alloy: A surface study

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ABSTRACT

$Ni_2MnGa(100)$ single crystal studied using low energy electron diffraction (LEED) and ultraviolet photoemission spectroscopy (UPS) exhibits interesting modification of the surface properties that are mainly influenced by surface composition as well as intrinsic effects. In the martensite phase, the LEED spot profiles show presence of an *incommensurate* modulation for the stoichiometric surface. In contrast, a *commensurate* modulation is observed for Mn-excess Ni–Mn–Ga surface. A pre-martensite phase is identified at the surface. Both the surface martensitic and pre-martensitic transition temperatures decrease as the Mn content increases. The UPS spectra in the austenite phase exhibit systematic change in shape as a function of surface composition that can be related to changes in the hybridization between Ni and Mn 3*d* states. The spectra in the martensite phase exhibit interesting modifications near the Fermi level, which has been compared to density of states calculated for a modulated structure by ab-initio density functional theory. Intrinsic surface properties dissimilar from the bulk are enhanced hysteresis width of the martensite transition and increased pre-martensitic transition temperature.

1. Introduction

There is a surge of interest in the basic physics of Ni–Mn–Ga ferromagnetic shape memory alloy because of its potential as a functional material with large magnetic field induced strain [1,2], as an energy material with giant magnetocaloric effect [3] and as a magnetic sensor with large negative magnetoresistance [4]. Ni–Mn–Ga exhibits magnetic field induced strain because of its fundamental properties like large magnetocrystalline anisotropy and high mobility of the twin boundaries. The latter is related to low twinning stress, which is associated with a modulated structure in the martensite phase [1,2]. Neutron scattering studies of stoichiometric Ni_2MnGa single crystal showed that the modulation is related to a phonon anomaly [5]. Shapiro et al. identified well-defined phasons associated with charge-density-wave (CDW) excitation below 200 K in the martensite phase [6]. Theoretically, it has been shown from density functional theory (DFT) that in the martensite phase, an instability in the TA2 phonon mode related to Fermi surface nesting assists the formation of CDW [7]. Recently, an alternative explanation of the modulation has been suggested from X-ray diffraction studies on a Ni excess Ni_2MnGa film [8]. This is based on the adaptive martensite model that comprises of the branching twin variants with small surface energy [9]. Recent photoemission study on Ni_2MnGa showed temperature dependent variation of the spectra in the pre-martensite phase and evidence of pseudogap was observed at 0.3 eV below the Fermi level (E_F) [10].

Ni_2MnGa, which is ferromagnetic with Curie temperature of 375 K, has a cubic $L2_1$ structure in the austenite phase. Around 200 K, it undergoes a first order structural transformation to the lower symmetry martensite phase. Generally, Ni–Mn–Ga compositions that display modulated structure have low twinning stress and exhibit magnetic field induced strain [2]. However, whether the modulation exists at the surface of the bulk single crystal is an interesting question that has not been studied till date. In general, how a bulk first order transition manifests itself at the surface constitutes an interesting study. Furthermore, surface study of Ni_2MnGa is important because it could modify the magnetic and structural properties of the adlayers grown on it. Recently, we have reported low energy electron diffraction (LEED) and photoemission studies on stoichiometric surface of Ni_2MnGa and Mn_2NiGa at room temperature where the surface was found to be Mn–Ga terminated [11]. Very recently, the (001)-oriented surface of epitaxial off-stoichiometric Ni–Mn–Ga ferromagnetic shape memory alloys was studied and they also observed that the surface is Mn–Ga terminated [12]. In this work, we report temperature dependent LEED study on the (100) surface of a bulk stoichiometric Ni_2MnGa single crystal and identify the pre-martensite and martensite phases. Periodic modulation in the martensite phase of Ni_2MnGa is observed. The nature of the modulation depends on the surface stoichiometry: it is incommensurate for the stoichiometric surface, while it is commensurate for the Mn

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excess surface. The width of the hysteresis in the martensitic transition at the surface is found to be five times larger than the bulk value. The surface martensitic and pre-martensitic transition temperatures decrease as the Mn content increases. The photoemission spectra exhibit systematic change in shape as a function of surface composition.

2. Experimental

Ni_2MnGa single crystal was grown at the Materials Preparation Center of the Ames Laboratory by the Bridgman method [13]. The ingot was oriented in the austenite phase by Laue back reflection and the sample was spark cut. The polishing was done mechanically using quarter micron diamond paste followed by electropolishing in nitric acid and methanol. The bulk composition was confirmed by wavelength dispersive X-ray spectroscopy. LEED was performed at a base pressure of about 4×10^{-11} mbar using ErLEED 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 h. The cleanliness and the surface composition were ensured using X-ray photoelectron spectroscopy (XPS). The photoemission studies were performed by using a commercial electron energy analyzer (Phoibos 100 from Specs GmbH, Germany). For ultraviolet photoemission spectroscopy (UPS) measurements, He I (21.2 eV) radiation was used. The analyzer was set at a pass energy of 2 eV and medium area lens mode with collection angle of $\pm7°$ was used. To obtain a single variant state in the martensite phase, the crystal was cut along [10] direction (corresponds to [100] direction of body centered tetragonal unit cell with *I*4/*mmm* space group in the bulk) and clamped along the vertical i.e. [01] direction in a sample holder designed for studying complex metal surfaces [14]. To check this, we recorded LEED patterns as a function of position over a grid on the crystal at 12 different positions. In each case, the patterns in both martensite and austenite phases remained unaltered. In this sample holder, the thermocouple is placed below the sample for reliable temperature measurement. The martensite transition temperatures for the bulk crystal have been determined using differential scanning calorimetry. The latent heat is 0.2 kJ/mole in agreement with literature [15].

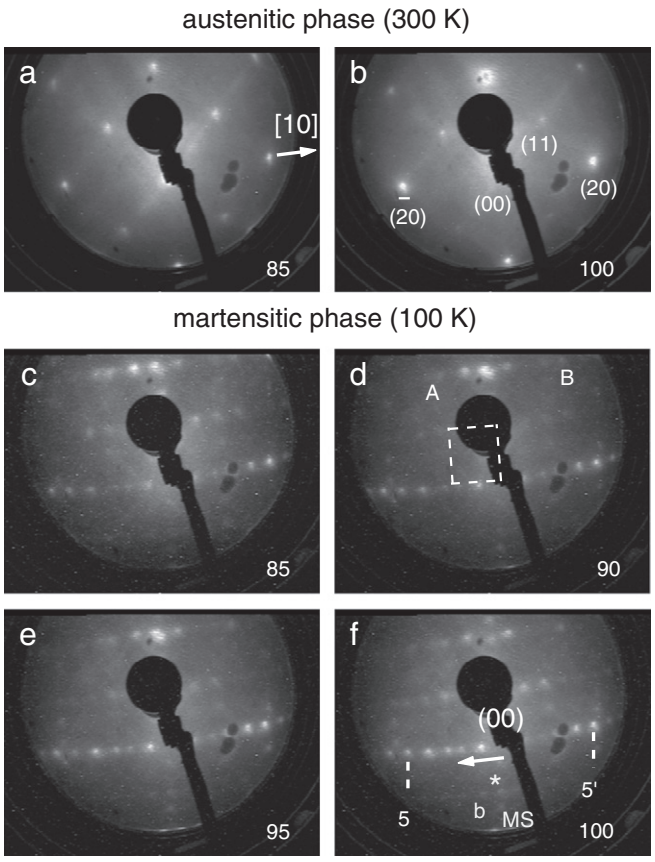

Fig. 1. Low energy electron diffraction (LEED) patterns of $Ni_2MnGa(100)$ in (a–b) the austenite phase at room temperature and in (c–f) the martensite phase at 100 K. The electron beam energies (E_p) in eV are shown in the bottom right corners. The first Brillouin zone(white dashed square) and the direction AB along [10] outside first Brillouin zone are shown in (d). In (f), dashed lines indicate the 5 and 5′ spots and the white arrow represents b^*_{MS}.

3. Results and discussion

3.1. LEED of stoichiometric $Ni_2MnGa(100)$ in martensite phase

Ni_2MnGa is in the austenite phase at room temperature since its M_s (martensitic start temperature) is 206.5 K. Thus, the (100) surface exhibits a four-fold LEED pattern (Fig. 1(a–b)), as reported earlier [11,12]. A spectacular modification of the LEED pattern occurs in the martensite phase with the appearance of an array of satellite spots corresponding to each of the spots in the austenite phase. These spots are observed over the range $85<E_p<120$ eV in the [10] direction (Fig. 1(c–f)). In the corresponding intensity profiles shown in Fig. 2, the spots appearing along $(00)\rightarrow(\bar{2}0)$ are marked as 1–5, where 1 is closest to the (00) spot. Similarly, spots that appear along $(00)\rightarrow(20)$ are designated by numbers 1′–5′. The intensity profiles in Fig. 2(b) show that all the satellite spots move toward the (00) spot as E_p increases. Comparison of the profiles shows that 5 and 5′ spots in the martensite phase nearly coincide with $(\bar{2}0)$ and (20) spots in the austenite phase, indicating that these are the fundamental reflections in the martensite phase (Fig. 2(a)). As mentioned in the previous section, to compare with the bulk, note that the direction of compression (vertical i.e. [01]) corresponds to the shorter c axis of the bulk martensite phase with respect to the b.c.t. cell in the austenite phase. The b axis of the bulk is along [10], and this is the direction in which the modulation appears in the bulk.

To understand the origin of the satellite spots in the martensite phase, we first examine their separations. If the four spots (1–4) between the fundamental reflections (00) and spot 5 are equispaced, this would mean a five times increase of the surface unit cell in the real space. However, detailed analysis of the line profiles brings forth an interesting result that the satellite spots are not equispaced. This is observed in all the profiles shown in Fig. 2(b): the separation between spots 2 and 3 is clearly smaller than the separation between other spots. This indicates that the surface structure is not simple and generally unequal separation of the diffraction spots is indicative of a modulated structure. The theoretical formulation of Bragg reflections from modulated structures shows that the scattering vectors are $g\pm nq$, where g is a reciprocal lattice vector, q is the modulation wave vector and n is an integer [16]. Thus, each fundamental spot of the basic structure given by g is surrounded by a series of equally spaced satellite reflections of diminishing intensity at distances $\pm nq$. The intensity of the satellite reflections is less if the deviation of atom positions from the basic structure is small, and all the satellites might not be observed [16]. Unequal separation is observed between satellite reflections corresponding to the different fundamental reflections when the basis vector (g_p) of the reciprocal lattice is not an integral multiple of q, indicating presence of modulation. If q/g_p is rational (irrational), the nature of the modulation is commensurate (incommensurate).

To quantify the spot separations, we have considered 37 profiles for averaging, including those shown in Fig. 2(b). The separations are obtained as a fraction of the basis vector of the reciprocal lattice in the non-modulated martensite phase [17]: b^*_{MS} ($=g_{10}$) obtained as half of the separation between spot 5 and (00) (Fig. 1(f)). The spot separations turn out to be $0\rightarrow1$: 0.413 ± 0.002; $1\rightarrow2$: 0.421 ± 0.002; $2\rightarrow3$: 0.287 ± 0.001; $3\rightarrow4$: 0.430 ± 0.003 and $4\rightarrow5$: 0.431 ± 0.002, where the error is given by the standard deviation divided by