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## Elastic properties of Fe–Mn random alloys studied by *ab initio* calculations

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We have studied the influence of the Mn content on the elastic properties of Fe–Mn random alloys (space group of  $Fm\bar{3}m$ ) using *ab initio* calculations. The magnetic effects in Fe–Mn alloys have a strong influence on the elastic properties, even above the Néel temperature. As the Mn content is increased from 5 to 40 at. %, the  $C_{44}$  elastic constant is unaffected, while  $C_{11}$  and  $C_{12}$  decrease. This behavior can be understood based on the magnetovolume effect which softens the lattice. Since the amplitude of local magnetic moments is less sensitive to volume conserving distortions, the softening is not present during shearing. © 2007 American Institute of Physics.

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The Fe–Mn system comprises random alloys that crystallize in the face-centered cubic (fcc) structure (space group of  $Fm\bar{3}m$ ).<sup>1</sup> The Fe–Mn alloys are antiferromagnetic with the Néel temperature of 467 K for Fe<sub>0.60</sub>Mn<sub>0.40</sub>.<sup>1</sup> There are several conflicting proposals for the noncollinear antiferromagnetic groundstate.<sup>2–4</sup> Another fascinating feature of the Fe–Mn alloys is their Invar-type behavior, giving rise to anomalous magnetization, thermal expansion, heat capacity, and elastic properties.<sup>5</sup> These random alloys are also interesting in conjunction with Mn-rich steels.<sup>6</sup> These steels exhibit high strength and exceptional plasticity due to twinning and martensitic transformation under mechanical loading.<sup>6</sup> The elastic constants have been measured only for Fe<sub>0.60</sub>Mn<sub>0.40</sub> using the ultrasonic pulse-echo-overlap technique at room temperature:  $C_{11}=170$  GPa,  $C_{12}=98$  GPa, and  $C_{44}=142$  GPa.<sup>1</sup> Hence, there are no systematic studies of the elastic properties of these Fe–Mn alloys.

In this work, we systematically study the influence of the Mn content on the elastic properties of Fe–Mn random alloys using *ab initio* calculations. It is aspired after understanding the magnetic state above the Néel temperature, and hence noncollinear effects are neglected. Fe–Mn thin films were also synthesized so as to assess the *ab initio* data. We show that magnetic effects in Fe–Mn alloys have a strong influence on the elastic properties, even above the Néel temperature. As the Mn content is increased from 5 to 40 at. %,  $C_{44}$  is unaffected, while  $C_{11}$  and  $C_{12}$  decreased by 25.6% and 39.2%, respectively. The behavior of the elastic constants can be understood based on the magnetovolume effect which softens the lattice.

The exact muffin tin orbitals (EMTO) formalism,<sup>7,8</sup> based on the Green's function<sup>9</sup> and full charge density<sup>10</sup>

techniques, was used for *ab initio* calculations in this work. The generalized gradient approximation<sup>11</sup> was applied for the density functional, and the ion cores were frozen. The integration in the Brillouin zone is done on a  $13 \times 13 \times 13$   $k$  points mesh and the total energy convergence criterion was  $10^{-7}$  Ry. The compositional and magnetic disorders were treated with the coherent potential approximation.<sup>12,13</sup> The magnetic state of Fe–Mn alloys is described here using the disordered local moment (DLM) model, which provides a reasonable approximation of the paramagnetic state above the transition temperature.<sup>14</sup> Elastic constants  $(C_{11}-C_{12})/2$  and  $C_{44}$  were obtained using the following volume conserving distortions  $D$  and  $D_{44}$  of the fcc lattice, respectively,

$$D = \begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 - \delta & 0 \\ 0 & 0 & \frac{1}{1 - \delta^2} \end{pmatrix}, \quad (1)$$

and

$$D_{44} = \begin{pmatrix} 1 & \delta_{44} & 0 \\ \delta_{44} & 1 & 0 \\ 0 & 0 & \frac{1}{1 - \delta_{44}^2} \end{pmatrix}. \quad (2)$$

The associated total energy changes are given by

$$\Delta E = V(C_{11} - C_{12})\delta^2 + O(\delta^4), \quad (3)$$

and

$$\Delta E_{44} = 2VC_{44}\delta_{44}^2 + O(\delta_{44}^4), \quad (4)$$

where  $V$  is the equilibrium volume and  $\delta$  is the distortion matrix element probed from 0 to 0.05. Elastic constants were obtained from the slope of the linear fit of  $\Delta E$  vs  $\delta^2$ , using

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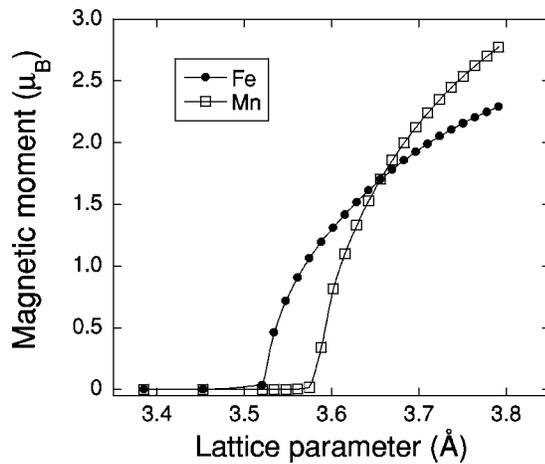


FIG. 1. Local magnetic moment vs lattice parameter for disordered local moment  $\text{Fe}_{0.60}\text{Mn}_{0.40}$  configuration.

Eqs. (3) and (4). This fitting procedure gives rise to an average error of 3%.

Since the Fe–Mn random alloy with the Mn content of 40 at. % is the most studied composition,<sup>1</sup> we start the analysis with this configuration. Figure 1 shows the average local magnetic moments of Fe and Mn for the DLM configuration as a function of lattice parameter. The same volume range is used for the calculation of bulk moduli, as discussed below. A continuous transition between the low-spin (LS) and high-spin (HS) magnetic states, i.e., nonmagnetic (NM) and DLM configurations, can be observed. In the whole range, the local magnetic moments of Fe and Mn increase from 0 to  $2.29\mu_B$  and  $2.77\mu_B$ , respectively. Furthermore, the amplitude of local magnetic moments is less sensitive to volume-conserving distortions. For the calculations of  $(C_{11}-C_{12})/2$  and  $C_{44}$ , see Eqs. (1) and (2), the local magnetic moments within the DLM model increase less than 7%, as  $\delta$  is increased from 0 to 0.05. This change is much larger for the bulk modulus calculations, which corresponds to uniform contractions or expansions of the lattice. The dependence of magnetic moments on volume is similar to their behavior in Fe–Ni Invar alloys.<sup>15</sup>

Figure 2 shows the total energy for the DLM and NM  $\text{Fe}_{0.60}\text{Mn}_{0.40}$  configurations as a function of lattice parameter. It is evident that there are fundamental differences between

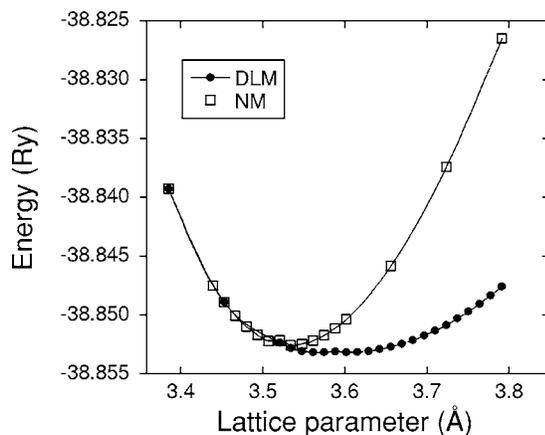


FIG. 2. Total energy vs lattice parameter for disordered local moment (DLM) and nonmagnetic (NM)  $\text{Fe}_{0.60}\text{Mn}_{0.40}$  configurations, as obtained by the EMTO code.

the binding energy vs lattice parameter behavior for these two solutions. The DLM curve intersects the NM one when magnetic moments in the system are quenched, giving rise to a two-branch shape of the binding energy curve with a continuous transition between the LS and the HS magnetic states. At the lattice parameter of  $3.604 \text{ \AA}$ , the DLM solution reaches its minimum and constitutes the global energy minimum of the system. The experimentally obtained lattice parameter for the single-crystalline  $\text{Fe}_{0.60}\text{Mn}_{0.40}$  is  $3.614 \text{ \AA}$ ,<sup>5</sup> which accounts for a 0.3% deviation from the calculated value. No experimental structural data for any other single-crystalline fcc Fe–Mn alloys are available. Furthermore, the difference between NM and DLM volume (see Fig. 2) is also an indication of the large magnetovolume effects. For the Mn-content probed, the calculated lattice parameters for the DLM configuration vary in the range of  $3.600\text{--}3.606 \text{ \AA}$ . In order to further assess the calculated lattice parameters, we have synthesized Fe–Mn thin films on Si(100) at room temperature using combinatorial setup<sup>16,17</sup> in an ultrahigh vacuum chamber. The chemical composition and structure of as-grown Fe–Mn thin films were analyzed using energy dispersive x-ray spectroscopy and x-ray diffraction with an areal detector, respectively. In the Mn-content range from 29 to 42 at. % and  $d$  spacing values from 2.075 to  $2.077 \text{ \AA}$  were measured. This is consistent with the calculated  $d$  spacing of (111) planes of fcc Fe–Mn bulk alloys.

Let us now discuss the elastic properties of  $\text{Fe}_{0.60}\text{Mn}_{0.40}$ . Strictly speaking, a determination of room temperature elastic constants in fcc Fe–Mn alloys requires a determination of the groundstate magnetic structure thereof at each composition and temperature. However, this is a challenging task, and moreover, different theoretical reports predict different groundstates.<sup>2–4</sup> At the same time, the experimental data<sup>1</sup> indicate that a change of elastic constants upon the magnetic phase transition, i.e., between 400 and 600 K, is small ( $<11\%$ ), which is within the general accuracy of calculating elastic constants by first-principles methods.<sup>18,19</sup> It is well known that the energetics of a magnetic alloy above the magnetic transition temperature is well described by the DLM model.<sup>13,20</sup> We, therefore, adopt this model for the calculations of elastic constants. Based on their relatively small variations with temperature, as mentioned above, we believe that we can still study trends of the elastic properties in fcc Fe–Mn alloys reliably as a function of composition.

For the  $\text{Fe}_{0.60}\text{Mn}_{0.40}$  alloy, the NM and DLM solutions (see Fig. 2) give rise to bulk modulus values of 266 and 114 GPa, respectively. Note that following Ref. 15, we used a cubic spline fitting procedure in order to account for the anomalous two-branch shape of the binding energy curve. Since the experimental value is 123 GPa,<sup>1</sup> the DLM configuration is closer to the measurement (7.9% deviation). It is evident that the magnetic effects in Fe–Mn alloys have a strong influence on the elastic properties, even above the Néel temperature. These effects cannot be neglected. As a matter of fact, the NM configuration overestimates the bulk modulus by a factor of  $\sim 2$ .

Let us continue the discussion of the dependence of the elastic properties on the Mn content. Figure 3 shows all elastic constants and local magnetic moments for the DLM Fe–Mn configurations as a function of the Mn content. The  $C_{44}$  values are in the range of 135–138 GPa, and are hence nearly independent of the Mn content.  $(C_{11}-C_{12})/2$  is also independent of the Mn content, while  $C_{11}$  and  $C_{12}$  exhibit

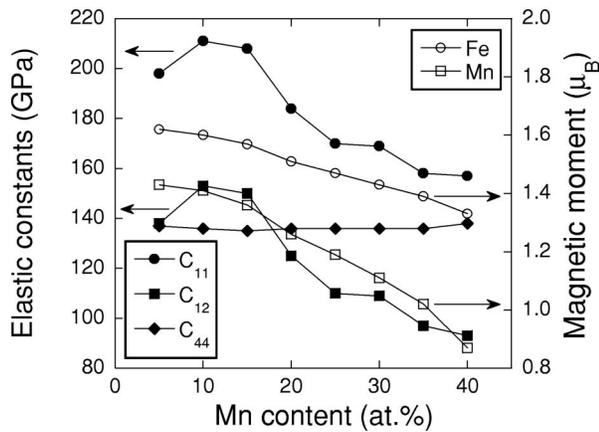


FIG. 3. Elastic constants and local magnetic moment for disordered local moment Fe–Mn configurations as a function of the Mn content.

drastically different behaviors. At a Mn content of 5 at. %, the values are 198 and 138 GPa, respectively. There is a slight increase to 211 GPa ( $C_{11}$ ) and 153 GPa ( $C_{12}$ ) as the Mn content increases to 10 at. %. Further increase of the Mn content to 40 at. % results in a drop of 25.6% and 39.2% to 157 and 93 GPa, respectively. The deviation between the calculated and experimentally obtained values<sup>1</sup> for  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  in the case of  $\text{Fe}_{0.60}\text{Mn}_{0.40}$  is 8.3%, 5.4%, and 2.9%, respectively. The local magnetic moment for Fe and Mn decreases from  $1.62\mu_B$  to  $1.33\mu_B$  and from  $1.43\mu_B$  to  $0.87\mu_B$ , respectively, as the Mn content increases from 5 to 40 at. %. This is consistent with the previous work.<sup>2</sup> The behavior of the elastic constants can be understood based on the so-called magnetovolume effect<sup>15</sup> observed in our calculations. The strong dependence of local magnetic moments on lattice parameter (or volume), as shown in Fig. 1, is known to soften the lattice.<sup>15</sup> Since the amplitude of the local magnetic moments is less sensitive to volume conserving distortions, the softening is absent in shearing, as described by  $C_{44}$  and  $(C_{11}-C_{12})/2$ , but is present as the volume changed during uniform compression for the determination of the bulk modulus. Since the bulk modulus<sup>21</sup> is defined as

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \quad (5)$$

it is expected that  $C_{11}$  and  $C_{12}$  show softening.

In conclusion, the effect of the Mn content on the elastic properties of Fe–Mn random alloys has been investigated using the EMTO formalism. We have also synthesized Fe–Mn thin films to assess our *ab initio* data. Measured and calculated  $d$  spacing values are consistent with each other. As

the Mn content is increased from 5 to 40 at. %,  $C_{44}$  is unaffected, while  $C_{11}$  and  $C_{12}$  decrease by 25.6% and 39.2%, respectively. The behavior of the elastic constants can be understood based on the magnetovolume effect. Local magnetic moments depend strongly on volume, which in turn softens the lattice. This is less present in volume conserving distortions so that the softening is absent in shearing [elastic constant  $C_{44}$  and  $(C_{11}-C_{12})/2$ ], but is readily accessible in volume affected deformations, such as bulk modulus,  $C_{11}$ , and  $C_{12}$ . It is hence evident that the magnetic effects in Fe–Mn alloys have a strong influence on the elastic properties, even above the Néel temperature.

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