Effect of Temperature on the Elastic Anisotropy of Pure Fe and $Fe_{0.9}Cr_{0.1}$ Random Alloy

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The elastic properties of pure iron and substitutionally disordered 10 at. % Cr Fe-Cr alloy are investigated as a function of temperature by using first-principles electronic-structure calculations by the exact muffin-tin orbitals method. The temperature effects on the elastic properties are included via the electronic, magnetic, and lattice expansion contributions. We show that the degree of magnetic order in both pure iron and $Fe_{90}Cr_{10}$ alloy mainly determines the dramatic change of the elastic anisotropy of these materials at elevated temperatures. The effect of lattice expansion is found to be secondary but also very important for quantitative modeling.

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The development of construction materials for new generations of power plants (both thermal and nuclear) is one of the most urgent tasks in materials science. Attention has recently been drawn to stainless steels [1,2]. Steels have been studied experimentally and theoretically for many decades, but tools for atomistic modeling of these inherently complex materials are at the development stage. The main complication here is magnetism of iron and of some other steel ingredients. The change of magnetic order in iron and steel with temperature is known to strongly affect their thermodynamic and kinetic properties. However, these effects are extremely difficult to model starting from first principles. Development of *ab initio* modeling techniques that can describe the properties of iron and steel at temperatures relevant for applications of these materials, not just at 0 K, is therefore a challenging scientific task of high practical importance.

In this Letter, we present a modeling approach, based on electronic-structure calculations, to describe temperature dependence of the elastic properties of iron and its alloys. Elastic properties are vital for many practical applications but are also important parameters of phenomenological models such as the phase-field method or continual dislocation theory [3]. It has been experimentally found that the elastic anisotropy of α-Fe increases by almost an order of magnitude upon the temperature change from room temperature to above the Curie point [4–6].

The temperature dependence of elastic constants in α-Fe is a vivid manifestation of the magnetic effect on the physical properties of iron and its alloys. Strictly speaking, the crystal structure of α-Fe is body-centered tetragonal [7,8] below the Curie temperature ($T_C = 1043$ K), although the tetragonality is small (10^{-5}) so that ferromagnetic iron may be considered cubic for most practical purposes. Also, its elastic anisotropy $A = C_{44}/C'$ [where $C' = (C_{11} - C_{12})/2$ is the tetragonal shear constant and C_{ij} are the three cubic elastic constants] is rather weak; see Fig. 1. It is curious that, as α-Fe becomes truly cubic in the paramagnetic phase above T_C, it simultaneously becomes strongly elastically anisotropic. The high anisotropy values are mainly due to softening of C' in the paramagnetic state of α-Fe. This softening of the crystal lattice with respect to tetragonal shear has important metallurgical implications, e.g., for the activation energy of carbon diffusion in steel [5].

The temperature dependence of the elastic constants of bcc Fe was theoretically investigated before within the single-site spin-fluctuation theory of band magnetism by Hasegawa, Finnis, and Pettifor [9]. They qualitatively reproduced the observed anomalous softening of C' close to the Curie temperature and related it to the e_g electronic states. However, their microscopic approach is based on a simplified treatment of electronic structure in the tight-binding approximation employing fitting parameters and therefore does not possess the predictive power needed for computational materials design.

Here we propose a first-principles-based modeling approach to this phenomenon and demonstrate its numerical accuracy for the case of pure iron, for which detailed experimental data exist. Using an example of a random $Fe_{90}Cr_{10}$ alloy, we show how this approach can naturally be extended to alloys.

The present modeling is based on density-functional-theory (DFT) calculations of the total energy and employs the generalized gradient approximation to the exchange-correlation potential [10]. The main body of calculations is performed by using the exact muffin-tin orbital (EMTO) method combined with the full-charge-density technique [11]. The method has been implemented within the Green's function formalism [12] and can treat chemically and/or magnetically disordered alloys in the coherent potential approximation [13]. For the case of the ferromagnetically ordered iron, we benchmark our EMTO calculations against the projector-augmented-wave (PAW) [14,15] calculations performed by using the Vienna *ab initio* simulation package (VASP) [16]. The EMTO-coherent potential

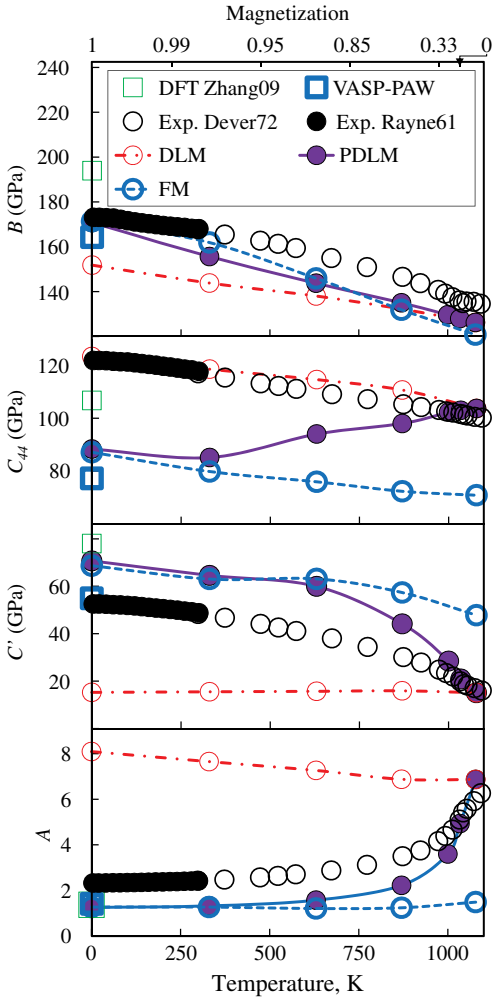

FIG. 1 (color online). Experimental and calculated elastic properties of iron as a function of temperature: bulk modulus B, shear elastic constants C_{44} and C' (all in GPa), and anisotropy constant A (dimensionless). The results are compared with the available experimental data from Refs. [4,5], as well as with theoretical results (for FM state) of Ref. [29] and of our present VASP-PAW calculations. Lattice parameter dependence on temperature is taken from Ref. [20]. The legend applies to all panels.

approximation calculations have been performed by using an orbital momentum cutoff of $l_{\max} = 3$ for partial waves. The VASP-PAW calculations have been performed by using a plane-wave cutoff energy of 350 eV. The elastic properties have been calculated according to the scheme proposed by Mehl, Klein, and Papaconstantopoulos [17], by using one isotropic (volume) strain and two volume-conserving (orthorhombic and monoclinic) strains to determine, respectively, the bulk modulus B and two shear elastic constants C' and C_{44}. Convergence of the elastic property calculations with respect to k points and other computational details has been carefully checked; see Ref. [18] for details.

To extend the modeling to finite temperatures, one has to include the thermodynamic contributions due to phonon, electronic, and magnetic degrees of freedom. At present, this task is too heavy for a fully *ab initio* treatment [19], especially taking into consideration the mutual interdependence of these contributions. A practical approach to disentangle this complicated modeling situation is to use data easily obtainable either from the literature or by direct experiments. The present model uses experimental data on the lattice parameter and the long-range magnetic order parameter (magnetization).

The model treats the temperature dependence of elastic constants as a combination of three contributions from, respectively, lattice (thermal) expansion, electronic excitations, and magnetic disorder. This approach is quite general and may be applied to a wide range of solids. For instance, in a nonmagnetic insulator, only the first contribution is substantial, and it mainly originates from phonons. To include the effect of lattice expansion, the present calculations are done at the experimental temperature-dependent lattice parameters [20]. The contribution from electronic excitations is included in the usual form of Fermi-function smearing (electronic temperature) [21,22]. In the case of iron, these two contributions exhibit a normal behavior, whereas the magnetic contribution is anomalously strong.

Thermal magnetic disorder is modeled via the partially disordered local moment (PDLM) approximation, described in detail in Ref. [23]. A partially disordered ferromagnetic state with the long-range magnetic order parameter (magnetization) m is approximated by a random alloy $\mathrm{Fe}_{1-y}{}^{\uparrow}\mathrm{Fe}_{y}{}^{\downarrow}$ such that $m = 1 - 2y$. In the completely ordered ferromagnetic (FM) state, one has $m = 1$. The disordered paramagnetic state with $m = 0$ reduces to the well-known disordered local moment (DLM) state, which for pure Fe is represented by a random $\mathrm{Fe}_{0.5}{}^{\uparrow}\mathrm{Fe}_{0.5}{}^{\downarrow}$ alloy of Fe atoms with spin up ($\uparrow$) and spin down ($\downarrow$) orientations [24]. In the present calculations, the magnetic order parameter is varied from 1 to 0 as a function of temperature according to the experimental magnetization curve measured by Crangle and Goodman [25] and represented in analytical form by Kuzmin [26]. One obvious shortcoming of the PDLM approximation is its mean-field nature; i.e., it neglects magnetic short-range order above T_C.

In Fig. 1, the results of present calculations are compared with previous theoretical and experimental data. In order to single out the effect of lattice expansion, we perform a series of calculations in the fully ordered FM state ($m = 1$). The calculated FM moduli decrease with temperature, mainly due to lattice expansion, thus exhibiting a normal softening behavior [27,28]. The present VASP-PAW results have been obtained at the extrapolated to 0 K *experimental* lattice parameter $a_{\mathrm{exp}}^{0\mathrm{K}} = 2.860$ Å [20]. We note that the EMTO and VASP-PAW elastic constants calculated at the extrapolated to 0 K lattice parameter are closer to the experimental data than the EMTO results of Ref. [29] calculated at the theoretical lattice parameter. At

the same time, our calculations at the *theoretical* lattice parameter $a_{\mathrm{calc}}^{0\mathrm{K}} = 2.837$ Å yield values $B = 194$ GPa, $C_{44} = 102$ GPa, and $C' = 78$ GPa that are very close to those obtained in Ref. [29].

When comparing with experimental data from ultrasonic measurements, such as those of Refs. [4–6], one should keep in mind that ultrasonic techniques yield adiabatic elastic moduli. The difference between isothermal and adiabatic elastic moduli cancels out for shear moduli (which are of our primary interest here) but is an increasing function of temperature for bulk and Young's moduli [28,30]. However, typical frequencies of electronic and magnetic relaxation processes in metals are much higher than the frequencies used in ultrasonic measurements, so that at any instant of time (on the phonon time scale) the system may be considered as relaxed with respect to the fast (electronic and magnetic) degrees of freedom. In order to mimic the experimental situation in the calculations, the elastic moduli should be defined as second-order derivatives (with respect to the strain) of a *partial free energy* that contains entropy contributions due to magnetic and electronic degrees of freedom but not due to phonons.

The changes of elastic moduli due to electronic temperature are calculated to be small in the paramagnetic DLM state (at $T = T_C$), typically less than 2 GPa. In the ordered FM state considered at T_C, the corresponding changes are more pronounced, about 16 GPa, but such a state is unstable at high temperatures. The results for the high-temperature DLM state ($m = 0$) are indicated in Fig. 1 by open circles with dot-dashed lines. The change with temperature exhibited by the FM and DLM curves plotted in Fig. 1 shows a combined effect of thermal expansion and electronic excitations on the elastic properties of iron in the two magnetic states. The distance between the curves gives the effect due to the change of magnetic order parameter from 1 to 0. This effect is mostly due to energy; the effect of magnetic entropy, evaluated as $S_{\mathrm{magn}} = k_{\mathrm{B}} \ln(M_S + 1)$, where k_{B} is the Boltzmann constant and M_S is the magnitude of local magnetic moment (in Bohr magnetons), on the bulk modulus is found to be about 4 GPa at the Curie temperature. Note that, if the magnetic order parameter value is fixed to either 1 or 0, the C' and A are almost insensitive to temperature up to T_C.

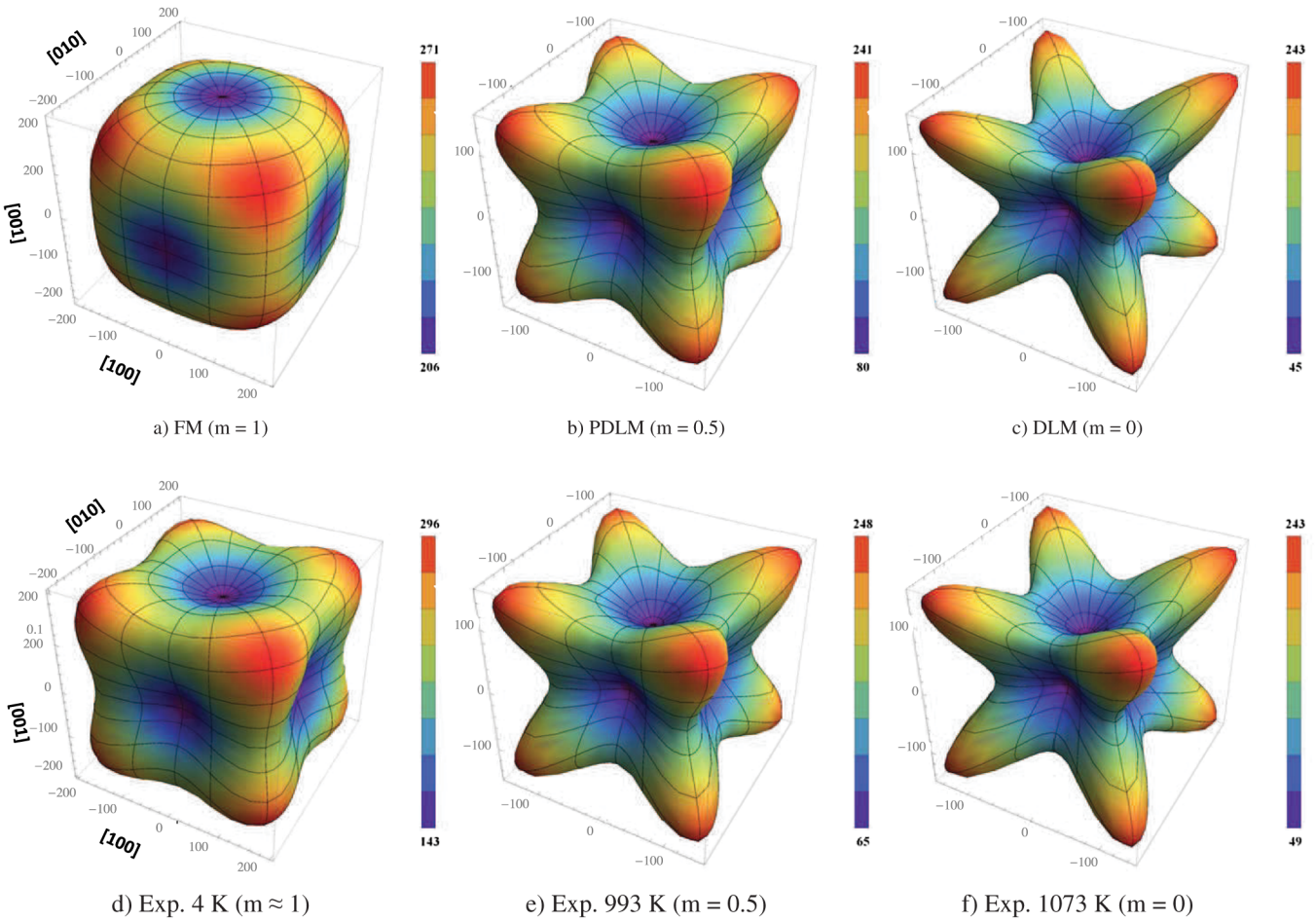

FIG. 2 (color online). Experimental [4–6] and calculated characteristic surfaces showing the Young's modulus as a function of crystallographic direction in α-Fe. The values on the color scale and on the axes are in GPa.

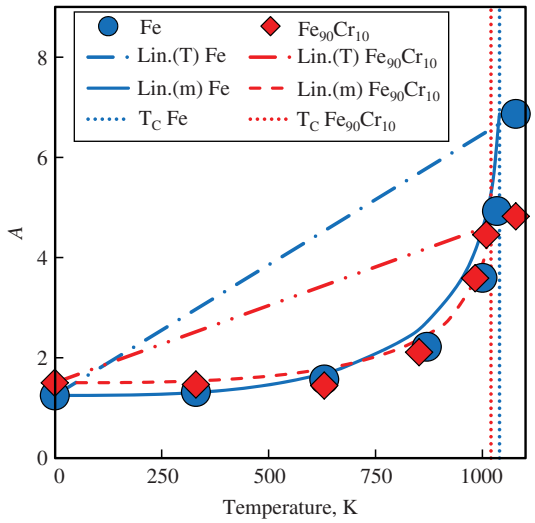

FIG. 3 (color online). Calculated elastic anisotropy constants (A) of iron and $Fe_{90}Cr_{10}$ alloy as a function of temperature. PDLM data compared to the linear interpolations between FM (0 K) and DLM (T_C) states. Lin.(T) notation in the legend stands for the linear interpolation of A as a function of temperature and Lin.(m) as a function of magnetization.

Thus, our calculations confirm that it is the change of magnetic order with temperature which produces a decisive effect on the elastic anisotropy of iron. The PDLM results (filled circles, full lines in Fig. 1) represent the prediction of our model for the elastic properties of Fe in the temperature interval $0 < T < T_C$. The model performs very well in the DLM state at $T = T_C$, where it very closely reproduces the elastic moduli and the strong elastic anisotropy of iron. At low temperatures the accuracy is worse, mainly because the C_{44} of ferromagnetic iron is underestimated in DFT calculations (the absolute error is about 30 GPa for VASP-PAW and 40 GPa for EMTO). This is a known problem of semilocal DFT functionals that may be resolved in the future by using more accurate approximations for the exchange-correlation energy. Most importantly for practical applications, the present model is able to describe the temperature dependencies of B and C' and the elastic anisotropy of pure iron. The change of the elastic anisotropy of pure iron with magnetization (temperature) is further illustrated in Fig. 2, where we plot the experimental and calculated characteristic surfaces of the Young's modulus of Fe in the FM ($m = 1$), PDLM ($m = 0.5$), and DLM ($m = 0$) states.

Finally, we apply our model to the random $Fe_{90}Cr_{10}$ alloy having a typical composition of steels considered for nuclear energy applications [1,2]. The experimental lattice parameters for the alloy are taken from Ref. [31]. The magnetization dependence on temperature for the alloy is taken in the same analytical form as for Fe [26], and the Curie temperature is taken from Ref. [32].

In Fig. 3, the calculated elastic anisotropy of $Fe_{90}Cr_{10}$ alloy is compared to that of pure iron. The lines are linear interpolations (using temperature or magnetization as the variable) between FM and DLM states. One can see that the elastic anisotropy constant in both Fe and $Fe_{90}Cr_{10}$ alloy has a very pronounced curvature reproduced by our PDLM calculations and observed in the experiments for pure iron (see Fig. 1). Figure 3 shows that at high temperatures, relevant for the manufacturing and some applications of steel, the alloy is less elastically anisotropic than pure iron, although the calculated anisotropy value is still quite high.

In summary, we have developed a microscopic finite-temperature modeling approach to calculate the elastic properties of iron and its alloys. The effect of temperature on the elastic properties of pure iron and $Fe_{90}Cr_{10}$ alloy has been investigated, and different contributions to the temperature dependence of elastic moduli have been analyzed. The degree of magnetic order is found to have a dramatic effect on the elastic anisotropy.

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