Effect of the $\alpha - \gamma$ Phase Transition on the Stability of Dislocation Loops in bcc Iron

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Body-centered-cubic iron develops an elastic instability, driven by spin fluctuations, near the $\alpha - \gamma$ phase transition temperature $T_c = 912\,^{\circ}\mathrm{C}$ that is associated with the dramatic reduction of the shear stiffness constant $c' = (c_{11} - c_{12})/2$ near T_c. This reduction of c' has a profound effect on the temperature dependence of the anisotropic elastic self-energies of dislocations in iron. It also affects the relative stability of the $a\langle 100\rangle$ and $a/2\langle 111\rangle$ prismatic edge dislocation loops formed during irradiation. The difference between the anisotropic elastic free energies provides the fundamental explanation for the observed dominant occurrence of the $a\langle 100\rangle$, as opposed to the $a/2\langle 111\rangle$, Burgers vector configurations of prismatic dislocation loops in iron and iron-based alloys at high temperatures.

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The frequent occurrence of the $a\langle 001\rangle$-type prismatic edge dislocation loops in bcc iron irradiated *at high temperatures* of the order of 550 °C was first observed by Masters [1,2]. This still remains one of the mysteries associated with radiation damage effects in iron and iron-based alloys, since the self-energy argument exploiting the theory of isotropic elasticity [3] favors dislocation loops with smaller Burgers vectors, such as $a/2\langle 111\rangle$. Recent studies of irradiated iron using *in situ* electron microscopy [4] indicate that upon heating to 300 °C, small dislocation loops spontaneously transform from the $a/2\langle 111\rangle$ to the $a\langle 001\rangle$ Burgers vector configurations. The loop transformations are not primarily driven by collisions between mobile $a/2[\bar{1}\,\bar{1}\,1]$ and $a/2[111]$ prismatic loops that could conceivably give rise to the formation of the $a[001]$ dislocation segments [1,5]. The argument that collisions between the migrating $a/2\langle 111\rangle$ loops are not responsible for formation of the $a\langle 100\rangle$ loops is supported by the fact that the $a\langle 100\rangle$ loops are almost never observed in the nonmagnetic bcc metals, where small prismatic $a/2\langle 111\rangle$ loops are just as mobile as in bcc iron. Furthermore, an entropy argument favors the $a/2\langle 111\rangle$ loop configurations at the expense of the $a\langle 100\rangle$ loops since the former, due to their higher mobility, are able to explore a greater volume of phase space per unit time.

In this Letter we show that the development of a soft elastic mode in bcc iron at elevated temperatures, driven by spin fluctuations, and leading to the bcc-fcc $\alpha - \gamma$ phase transition [6] at $T_c = 912\,^{\circ}\mathrm{C}$, is responsible for the observed anomalies in the behavior of dislocation loops. This elastic instability is associated with the dramatic reduction of the shear stiffness constant $c' = (c_{11} - c_{12})/2$ near T_c. This reduction has a profound effect on the temperature dependence of the anisotropic elastic free self-energies of dislocations in iron and, in turn, on the relative stability of the $a\langle 100\rangle$ and $a/2\langle 111\rangle$ prismatic edge dislocation loops formed during high temperature irradiation. The elastic free energy of the 001[100]-type edge dislocations actually vanishes in the limit $c' = 0$, whereas the elastic free energies of all the $a/2\langle 111\rangle$ edge dislocations remain finite.

Why is it necessary to use the full anisotropic elasticity approximation in the treatment of dislocations near the $\alpha - \gamma$ phase transition? A displacive bcc-fcc phase transition in iron is associated with the development of the (110) soft transverse acoustic phonon mode corresponding to the shear deformation of the bcc unit cell along the phase transformation pathway [6]. The only type of softening occurring in the *isotropic* elasticity approximation corresponds to the simultaneous vanishing of *two* transverse acoustic phonons at melting. A solid-to-solid transition involves only one soft phonon mode, and hence the treatment of the corresponding elastic deformations requires using full anisotropic elasticity.

The elastic free energy of a dislocation loop in a force free body of volume V is

$$F = \frac{1}{2}\int_V c_{ijkl} u_{i,j} u_{k,l} dV, \tag{1}$$

where $u_{i,j}$ is the elastic distortion field tensor of the loop at an arbitrary point in V, which excludes the nonlinear core region, c_{ijkl} is the temperature-dependent elastic stiffness tensor [7]. To evaluate this integral over the linear region V we invoke the Gauss theorem to convert the volume integral to a surface integral, one of which is over the ''core'' surface surrounding the nonlinear core, and the other is taken over the two surfaces of a cut through the linear region extending from the core surface to the external surface of the body, which is traction free. The relative displacement of the two cut surfaces defines the strength (the Burgers vector) of the dislocation. It is important to stress that both the surface integral contribution over the core surface (known as the core-traction energy) and over the two surfaces of the cut depend on the choice of the cut, but the sum of them is invariant with respect to this choice. The free energy of a loop is [8]

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$$F = \left[\oint \hat{F}(\mathbf{t})d\mathbf{t}\right]\ln(\tilde{R}/\delta) + \oint F_\delta(\mathbf{t})d\mathbf{t} + \oint F_c(\mathbf{t})d\mathbf{t}, \quad (2)$$

where $\tilde{R}$ is a measure of the effective range of the elastic field of the loop, and δ is the radius of the nonlinear dislocation core. $\hat{F}(\mathbf{t})$ is the prelogarithmic energy factor, per unit length, of a straight dislocation with orientation $\mathbf{t}$ in an infinite anisotropic medium, $F_\delta(\mathbf{t})$ is the core-traction energy per unit length, and $F_c(\mathbf{t})$ is the nonlinear core-energy term.

The energy factor $\hat{F}(\mathbf{t})$ of a straight infinite dislocation with Burgers vector $\mathbf{b}$ and orientation vector $\mathbf{t}$ is given by [8]

$$\hat{F}(\mathbf{t}) = \frac{1}{2\pi} b_i b_m n_j n_q c_{ijkl} c_{npmq} \Im\left[\sum_{\kappa=1}^{3} \kappa_p^\eta \kappa_l^\eta \frac{N_{kn}(\boldsymbol{\kappa}^\eta)}{n_s \frac{\partial D(\boldsymbol{\kappa}^\eta)}{\partial \kappa_s}}\right], \quad (3)$$

where for an edge dislocation $\boldsymbol{\kappa}^\eta = \mathbf{m} + \mathbf{n}\omega^{(\eta)}$, $\mathbf{n} = \mathbf{b}/b$, $\mathbf{m} = \mathbf{n} \times \mathbf{t}$, and $\omega^{(1)}$, $\omega^{(2)}$ and $\omega^{(3)}$ are the three complex roots of the sextic equation $S(\omega) = \det[c_{ijkl}(m_j + n_j\omega) \times (m_l + n_l\omega)] = 0$ situated in the upper half of the complex plane $\omega = \Re\omega + i\Im\omega$. $N_{ik}(\boldsymbol{\kappa})$ is the matrix adjoint to $L_{ik}(\boldsymbol{\kappa}) = c_{ijkl}\kappa_j\kappa_l$, and $D(\boldsymbol{\kappa}) = \det L_{ik}(\boldsymbol{\kappa})$.

In the anisotropic approximation the elastic self-energy of an edge dislocation varies when the dislocation line rotates around the direction of its Burgers vector $\mathbf{b}$ (or the $\mathbf{n}$ vector). Figure 1 shows the ratio of prelogarithmic factors evaluated for straight $\mathbf{b} = a[001]$ and $\mathbf{b} = a/2[111]$ edge dislocations plotted as a function of the rotation angle, around each $\mathbf{b}$ vector, between the orientation vector of the dislocation line, and one of the directions where this elastic energy is a minimum (these directions are [100] for the case of a $\mathbf{b} = a[001]$ dislocation and $[11\bar{2}]$ for the case of a $\mathbf{b} = a/2[111]$ dislocation). With the exception of tungsten, which is elastically isotropic, the curves shown in Fig. 1 systematically deviate from the isotropic elasticity limit, where the ratio of the two energies equals the square of the ratio of moduli of the two Burgers vectors $\mathbf{b}_{001}^2/\mathbf{b}_{111}^2 = 4/3$. Iron is already strongly anisotropic at room temperature, and its elastic anisotropy increases further as the temperature approaches T_c.

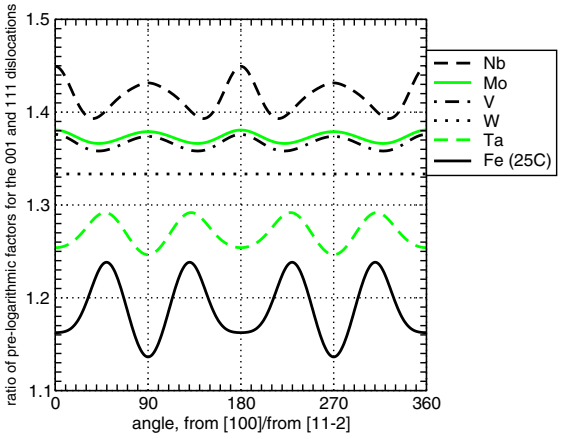

FIG. 1 (color online). The variation of the ratio of the prelogarithmic energy factors for straight edge dislocations with $\mathbf{b} = a[001]$ and $\mathbf{b} = a/2[111]$, for several bcc metals, as we rotate the dislocation line direction vector $\mathbf{t}$ around their respective Burgers vector directions. The experimental values of stiffness constants used in calculations were taken from [3].

As the value of c' falls near T_c [6] the dependence of the prelogarithmic factor (3) on the direction of the dislocation line becomes more pronounced. At room temperature the elastic self-energy of a $\mathbf{b} = a[001]$ and $\mathbf{t} = 2^{-1/2}[110]$ edge dislocation is 7% higher than the energy of the same dislocation for either the $\mathbf{t} = [100]$ or the $\mathbf{t} = [010]$ orientations. At 800 °C this difference increases to 27%. The fact that elastic anisotropy does indeed determine the morphology of dislocation structures is confirmed by experimental evidence [1,2,9] showing that all the $\mathbf{b} = a[001]$ dislocation loops formed at high temperature have a square shape with their sides parallel to the $\langle 100 \rangle$ directions.

The $\mathbf{b} = [001]$, $\mathbf{t} = [100]$, and $\mathbf{b} = a/2[111]$, $\mathbf{t} = 6^{-1/2}[11\bar{2}]$ cases correspond to the minima of elastic self-energy for the two Burgers vectors of dislocations in bcc iron. In the first case the sextic equation is analytically solvable, and the prelogarithmic factor (3) is [10]

$$\hat{F}_{001}([100]) = \frac{a^2}{4\pi}(c_{11} + c_{12})\left[\frac{c_{44}(c_{11} - c_{12})}{c_{11}(c_{11} + c_{12} + 2c_{44})}\right]^{1/2}. \quad (4)$$

A remarkable feature exhibited by this equation is that it shows that the prelogarithmic part of the elastic self-energy vanishes completely in the limit $c' \to 0$.

A solution for the $\mathbf{b} = a/2[111]$, $\mathbf{t} = 6^{-1/2}[11\bar{2}]$ dislocation is more cumbersome, and there is no explicit analytical expression for the prelogarithmic part of the elastic self-energy. Figure 2 shows that the leading prelogarithmic factors (3) in the elastic free self-energies of certain straight edge dislocations in iron strongly depend on temperature, and that the energies of both the 100[001] and the $111[11\bar{2}]$ edge dislocations decrease sharply near the temperature T_c. Self-energies of dislocations with the same Burgers vectors but different line orientations do not exhibit significant temperature dependence. Only the pure edge 100[001] dislocation has a precisely *zero* elastic energy factor at $c' = 0$.

To investigate the implications of the strong temperature dependence of dislocation self-energy factors for the relative thermal stability of dislocation loops, we also need to include the core-traction term [11], and the core energy term. The core-traction term in Eq. (2) is given by Eq. (31) of Ref. [8]. We evaluate it numerically using an approach similar to (3). The remaining anharmonic core energy term cannot be evaluated using linear elasticity and has to be treated separately. The magnitude of this term depends on the choice of the cutoff parameter δ. To estimate δ we use zero-temperature atomistic relaxations and find that for both the 111 and 001 dislocations the characteristic radius

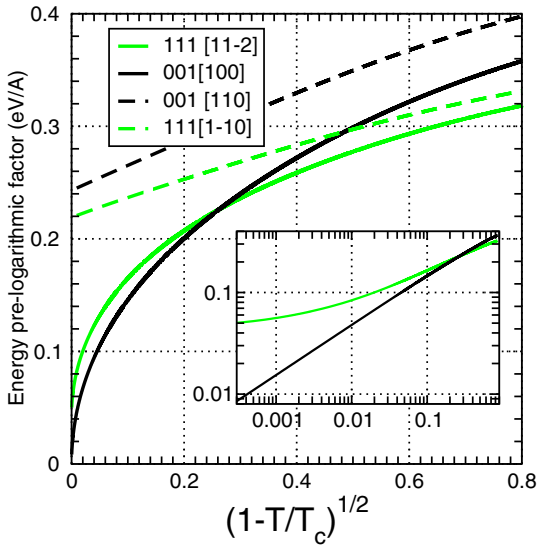

FIG. 2 (color online). The leading prelogarithmic factors (3) in the elastic free energy for straight $\mathbf{b}$, $\mathbf{t} = a/2[111]$, $[11\bar{2}]/\sqrt{6}$; [001], [100]; [001], $[110]/\sqrt{2}$ and $a/2[111]$, $[1\bar{1}0]/\sqrt{2}$ edge dislocations evaluated as a function of temperature T near the iron $\alpha - \gamma$ transition temperature T_c. Inset shows the curves for the two lowest energy dislocations on the logarithmic scale. The intersection point between the 001[100] and the $111[11\bar{2}]$ curves corresponds approximately to 820 °C. The 001[100] and the $111[1\bar{1}0]$ curves intersect at 685 °C. Elastic constants are described by smooth fits to experimental points [6,7], with $c' \approx 56.8(1 - T/T_c)^{1/2}$ GPa. The 001[100] curves follow the exact analytical solution (4).

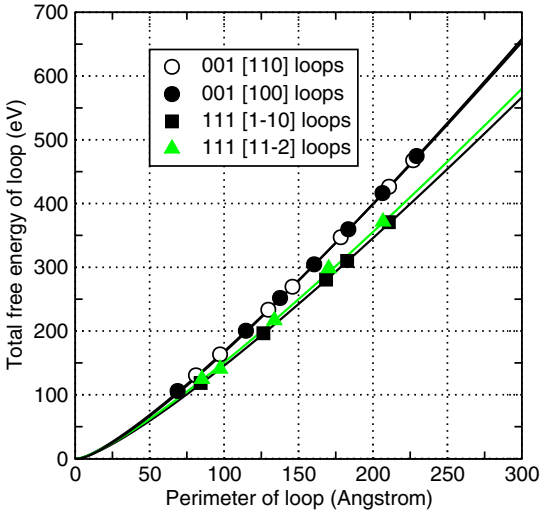

FIG. 3 (color online). The total energy of various types of dislocation loops at $T = 0$ K found using the magnetic potential [12]. The lines are given by Eq. (5) with $\hat{F}(\mathbf{t})$ and F_δ calculated using anisotropic elasticity.

of a region around the dislocation core, where linear elasticity breaks down and the level of strain exceeds ~5%, is $\delta = 0.4$ nm.

To determine a functional form for the total free energy of a dislocation loop, we have investigated appropriate hexagonal and square loops for the $a/2\langle 111\rangle$ and $a\langle 001\rangle$ Burgers vectors, respectively. The dislocation segments defining the sides of such loops for each loop shape have the same local crystallographic orientation. The free energies of dislocation loops are [8]

$$F_{\text{tot}} = P\hat{F}(\mathbf{t}) \ln\left(\frac{4R^*}{e\delta}\right) + PF_\delta + PF_c, \tag{5}$$

where P is the perimeter of the loop, $e = 2.7182\ldots$, R^* is the radius of the equivalent circular loop [3] that is a planar aggregate of the same number of point defects, and $\hat{F}(\mathbf{t})$ is the prelogarithmic factor for a straight dislocation, the segments of which form the sides of the loops. The best fit to atomistic calculations determines the magnitude of the anharmonic core term F_c, as illustrated in Fig. 3. The zero-temperature values of F_c found using Eq. (5) with the interatomic magnetic potential [12] are $F_c(111[11\bar{2}]) = 0.5(0.41)$ eV/Å, $F_c(111[1\bar{1}0]) = 0.43(0.36)$ eV/Å, $F_c(001[110]) = 0.48(0.35)$ eV/Å, and $F_c(001[100]) = 0.55(0.33)$ eV/Å. Values in brackets correspond to another choice of interatomic potential [13,14]. The zero-temperature core-traction energies are $F_\delta(111[11\bar{2}]) = 0.345$ eV/Å, $F_\delta(111[1\bar{1}0]) = 0.349$ eV/Å, $F_\delta(001[110]) = 0.390$ eV/Å, and $F_\delta(001[100]) = 0.387$ eV/Å.

To assess the temperature stability of dislocation loops we use experimental data on the temperature variation of elastic constants taken from [7] and interpolated towards T_c according to [6]. Note that elastic constants are defined in terms of second order variations with respect to a systems free energy [15] and therefore the use of experimental values as a function of temperature implicitly includes lattice entropic effects due to phonons and magnons. Thus the core-traction and anisotropic elastic free energies in Eq. (5) may be easily evaluated as a function of temperature. On the other hand the nonlinear core term, derived from empirical potentials, is a zero-temperature quantity, and for such strongly distorted regions [16] there presently exists no calculational method to determine the temperature-dependent free energy due to phonons and magnons. However, due to the close proximity of the nonlinear core and core-traction regions, it can be assumed that the entropic contribution to the dislocation-core free energy scales similarly with respect to temperature as that of the core-traction contribution. While this procedure is not exact, its possible inaccuracy is of little significance for the relative stability of the $a/2\langle 111\rangle$ and $a\langle 001\rangle$ dislocation loops in iron. This is confirmed by the fact that in the nonmagnetic bcc metals the ''anomalous'' $a\langle 001\rangle$ dislocation loops do not occur, despite that the core structures, and mobilities, of the $a/2\langle 111\rangle$-type dislocation loops in iron and other bcc metals at low temperatures are fundamentally very similar.

Figure 4 shows the ratio of the total free energies of the two types of prismatic dislocation loops most often ob-

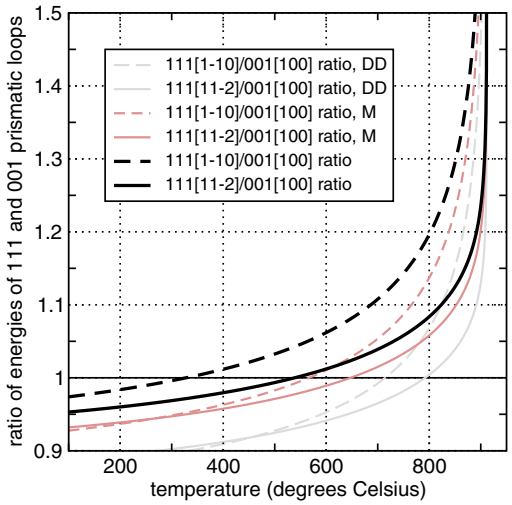

FIG. 4 (color online). The ratio of the total free energies of $P = 10$ nm prismatic dislocation loops with 111 and 001 Burgers vectors plotted as a function of temperature. The two sets of lighter lines correspond to using an F_c found using the empirical potentials for α-Fe [12–14], whereas the darker curves represent the best fit in terms of F_c to experimental observations.

served in irradiated iron. The total defect contents of both loops are the same. The hexagonal 111 loops are assumed to have the sides parallel to either $\langle 11\bar{2}\rangle$ or the $\langle 1\bar{1}0\rangle$ directions. The 001 loops are assumed to have a square shape with sides parallel to the $\langle 100\rangle$ directions, as found in experiments [1,2]. In this figure, the two sets of lightly shaded curves employ the nonlinear core energy calculated using the two empirical potentials [12,13], whereas the central darker curves represent the best fit within the uncertainty levels of F_c defined by the empirical calculation and which agrees well with experimental observations. In particular, such a fit yields $F_c(111[11\bar{2}]) = 0.46$ eV, $F_c(111[1\bar{1}0]) = 0.47$ eV and $F_c(001[100]) = 0.33$ eV all of which differ minutely from the empirical potential values. Figure 4 shows that there are always three regions of stability of dislocation loops on the temperature axis. In region 1, corresponding approximately to $T < 350\,^{\circ}$C for the case shown by darker lines, the $a/2\langle 111\rangle$ loops are unconditionally stable. In region 2 the $a/2\langle 111\rangle$ loops with sides parallel to the $\langle 1\bar{1}0\rangle$ directions are thermodynamically unstable and may reduce their energy by either altering the orientation of their sides or by transforming into the $a\langle 001\rangle$-type configurations. In region 3 ($T > 550\,^{\circ}$C) loops of the $a\langle 001\rangle$ type are unconditionally stable.

For a population of loops formed, for example, under cascade irradiation, where the stability of each loop depends on its size and on the orientation of its sides, the boundaries between regions 1, 2 and 3 become more diffuse, leading to the somewhat complex behavior observed experimentally [4]. Still, the ultimate stable high temperature configuration remains a square-shaped $a\langle 001\rangle$ loop that may be formed, for example, by the agglomeration of single interstitial atoms under electron irradiation [2]. New experimental observations [17] performed already after this Letter was submitted for publication, confirmed the formation of square-shaped $a\langle 100\rangle$ dislocation loops under cascade irradiation at 500 °C.

The present work provides a fundamental explanation of the experimental observation that in α-Fe $a\langle 001\rangle$ prismatic loops become increasingly favorable at temperatures higher than 300 °C. The above analysis also shows that the treatment of dislocations at elevated temperatures in iron and in iron-based alloys requires using full anisotropic elasticity approximation. It also indicates that a full anisotropic elasticity treatment should be required to understand the mechanical properties of other materials where similar phase transformations occur, for example, plutonium, zirconium, titanium, uranium, and many alloys.

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