The Critical Role of Long-Range Strain-Induced Interactions in Stabilizing Zener Ordering

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As a fundamental theory of structural transformations, the Zener ordering of interstitials in a body-centered cubic host lattice, which was established more than half a century ago, has been challenged by recent first-principles investigations. In this Letter, we rigorously prove the existence of Zener ordering via Monte Carlo simulations with complete interstitial interactions and demonstrate the critical role of long-range *indirect* strain-induced interactions in stabilizing Zener ordering. These insights improve our understanding of the self-induced collective ordering of point defects in a host lattice and elucidate the fundamental physics of order-disorder phase transitions in alloys.

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Structural phase transitions constitute a key topic in condensed matter physics.[1–7] The solution of interstitials in a host lattice may result in a random distribution of solutes at the possible interstitial sites and may also trigger the formation of short- or long-range ordered phases (for example, Refs. [8,9]), with significant effects on the physical properties of the materials.[10] For long-range ordering, an archetypal example is the Zener ordering of interstitials in a body-centered cubic (bcc) lattice,[11,12] which has direct relevance for the technologically important interstitial alloy Fe-C.

The octahedral interstitial sites in a bcc lattice may be categorized into three sublattices characterized by the corresponding tetragonal deformation variants ([100], [010], and [001]) (see Refs. [2,13,14]). If the lattice was to be subjected to a tensile stress along, for instance, the [001] direction, interstitials would preferentially occupy the [001] sublattice, reducing the elastic energy. A remarkable feature of this type of behavior is that even in the absence of an external stress, interstitials still favor an occupation of only one sublattice, which is triggered by their interactions. Such self-induced preferential occupation of interstitials in a bcc lattice was first proposed by Zener[11,12] and later named Zener ordering.

Figure 1 illustrates the Zener ordering in the prototype system, an Fe-C alloy, expressed as the dependence of the c/a ratio on the C concentration at room temperature. In the regime of a high concentration of C, the system is stable as a body-centered tetragonal (bct) ordered phase, for which the c/a ratio has a linear dependence on the concentration of C because of the preferential occupation of C atoms on one of the three sublattices. In contrast, in the regime of a low concentration of C, the interstitial C atoms are randomly distributed among the three sublattices in the disordered phase, which leads to a bcc crystal structure and, thus, a c/a ratio of 1. A critical concentration of C is reached at a point between these two regimes; above the critical concentration, the system undergoes a disorder → order transition.

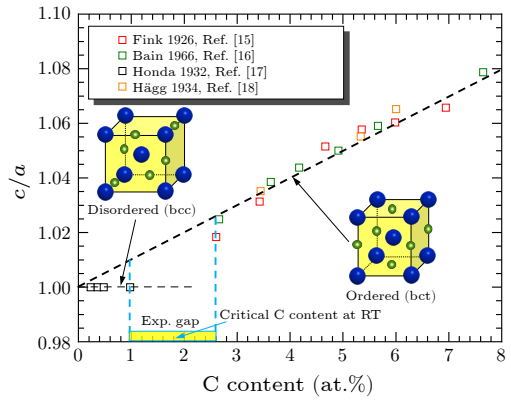

Fig. 1. Dependence of the c/a ratio of the Fe-C solid-solution phase on C content, at room temperature (RT). The experimental data were sourced from Refs. [15–18]. The crystal structures of the ordered (bct) and disordered (bcc) phases are also schematically visualized. Blue spheres represent Fe atoms, whereas green spheres denote C atoms. The yellow bar indicates the experimental gap of the critical C content at RT, above which the disorder → order transition occurs.

After Zener ordering was proposed, a few theoretical approaches were developed to provide a quantitative description of such ordering, ranging from initial empirical modeling[11,12,19] to first-principles calculations.[14,20,21] Initially, Zener[11,12] and Fisher[19] developed empirical

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approaches to estimate the interstitial interactions and the critical temperature of the order → disorder transition as a function of C concentration. Subsequently, Khachaturyan [22–26] established microscopic elasticity theory (MET) to calculate the strain-induced interaction between two interstitials in reciprocal space using lattice constants and the dynamical matrix as input. Using this approach, they confirmed the presence of Zener ordering from the eigenvectors of the interaction matrix and derived the critical temperature based on a mean-field approximation. This approach has been widely used and has been further improved through better parametrization from experiments, [27–29] atomistic simulations, [30] and density functional theory (DFT) computations. [20] In addition, Zener ordering has been analyzed using molecular dynamics simulations [31,32] and CALPHAD modeling. [33,34] However, there is considerable scatter in the critical temperatures derived from the various approaches presented in the literature. The state-of-the-art approach for analyzing order → disorder transitions in alloys is the use of Monte Carlo (MC) simulations incorporating an Ising-type Hamiltonian based on pair interactions, computed using either empirical potentials or DFT. This approach was recently implemented by Ruban, [21] who concluded that there was no profound energetic preference for C to occupy only one sublattice. Ruban further concluded that Zener ordering did not exist and that the sublattice preference of C in bcc Fe basically resulted from the crystallography associated with the fcc → bcc Fe transition.

In summary, both the empirical approaches and MET were indirect and yielded varying results. However, the most recent MC approach by Ruban [21] based on DFT calculations of interstitial configurational energetics did challenge the validity of Zener ordering. This was a significant and controversial finding, and if confirmed, it would call for a reconsideration of many fundamentals of interstitial ordering. In response, the aim of the present study was to perform an independent and rigorous analysis of Zener ordering in Fe-C alloys by conducting MC simulations using directly-calculated configurational energetics instead of being limited to pair interactions with a finite real-space range. The computations presented in this study clearly prove the existence of Zener ordering and demonstrate the decisive role of small ($\ll 0.1$ eV) but infinitely-long-range strain-induced interactions in stabilizing the Zener ordering, which were not included in the cited study. [21]

In common MC simulations with the Ising-type Hamiltonian, long-range strain-induced interactions are neglected on the basis of the assumption that these interactions are sufficiently small and have a limited contribution to the order → disorder transition. This assumption holds for many material systems, but as shown below, it is not applicable to the current problem, particularly when investigating ordering at dilute concentrations of interstitials. To include the complete set of interactions between interstitials during an MC simulation, every sampled configuration must be fully relaxed (with respect to cell shape, volume, and atomic positions). This is computationally infeasible for current DFT calculations; thus, there is a need for Ising parametrization. Computation is still feasible for Embedded Atom Method (EAM) potentials when using a reasonable supercell size. Accordingly, we performed MC simulations based on energetics from a carefully selected EAM potential [35] for the Fe-C system.

The accuracy and reliability of the selected EAM potential were benchmarked using DFT, as detailed in the Supplemental Material. A $5\times5\times5$ supercell was employed. Affordable computational costs and reasonable size were taken into consideration, such that the energies of a number of representative configurations could still be benchmarked using DFT. Supercell size tests indicated that the critical temperatures converged to a maximum error of ±5 K. We used an isothermal-isobaric (NPT) ensemble, and the simulated C concentrations ranged from 1.2 to 3.5 at.%. For each MC step, n C atoms were randomly selected and moved to n other, unoccupied octahedral interstitial sites (n was a random integer between 1 and half of the total number of C atoms). Subsequently, the configuration was fully relaxed by the EAM potential to obtain its energy and we followed the standard Metropolis MC algorithm to determine the acceptance of the sampled configuration. For each value of C concentration at each temperature, 10^5 configurations were sampled and ten independent runs were performed to obtain statistical averages and standard deviations.

The order parameter θ is defined as the following combination of three sublattice order parameters: [36]

$$\theta = \frac{\sqrt{6}}{3}\sqrt{\langle\theta_1\rangle^2 + \langle\theta_2\rangle^2 + \langle\theta_3\rangle^2}, \tag{1}$$

where $\langle\,\rangle$ denotes an ensemble average, and θ_1, θ_2, and θ_3 are three sublattice order parameters, given by

$$\theta_1 = x_1 - \frac{x_2 + x_3}{2},\quad \theta_2 = x_2 - \frac{x_3 + x_1}{2},\quad \theta_3 = x_3 - \frac{x_1 + x_2}{2}, \tag{2}$$

where x_i (i = 1, 2, 3) is the fraction of interstitials occupying sublattice i. Although there are other definitions of the order parameter θ, the choice of definition does not affect our final results. Furthermore, the definition of the order parameter employed in this study has already been proven as reliable. [14]

Figure 2 presents the computed order parameter θ as a function of temperature and C concentration. At all concentrations, there is a clear transition from an ordered to a disordered state with increasing temperature. For comparison, we also performed MC simulations for a particular C concentration (1.2 at.%), relaxing only the atomic positions. In this case, because the cell was fixed, long-range strain-induced interactions were suppressed. Consequently, the order → disorder transition vanished (see the red open circles in Fig. 2). This result explains why the order → disorder transition could not be captured in the previous MC simulation using the simplified Hamiltonian, and also demonstrates the crucial role of the long-range interactions mediated by strains in the Fe lattice in stabilizing the Zener ordering.

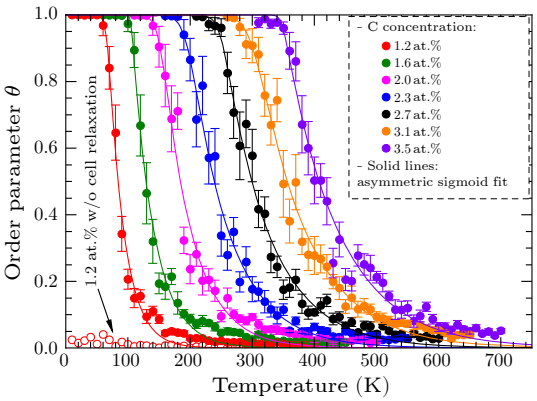

Fig. 2. Order parameter as a function of temperature and C concentration. The error bars are defined as one standard deviation of ten independent runs.

To determine the critical temperatures at different C concentrations quantitatively, we used the following asymmetric sigmoid function[37] to fit the data from MC simulations, as shown in Fig. 2:

$$\theta = \frac{1}{[1+(2^{1/A_3}-1)e^{A_1(T-A_2)}]^{A_3}}, \tag{3}$$

where A_1, A_2, and A_3 are fitting parameters. After fitting, the critical temperature T_c can be determined directly by equating the second derivative of θ to zero, with the following result:

$$T_c = \frac{1}{A_1}\ln\frac{2^{1/A_3}-1}{A_3} + A_2. \tag{4}$$

The derived critical temperatures as a function of the C concentration are shown in Fig. 3, together with results from previous studies in the literature. It can be seen that, compared to the present MC results, most of the previous studies overestimated the critical temperature. An early report by Zener[12] and the first study using MET[22] show relatively good agreement with the results of the present study. The agreement is ascribed to the fact that in those prior studies, only strain-induced interactions were considered – although only empirical approaches were available at that time. Subsequent studies made significant efforts to include short-range chemical interactions as well, which led to remarkable overestimations. The most severe case was that reported by Khachaturyan in 1983,[25] in which an empirical potential formula was used to estimate the short-range repulsion. Moreover, it was reported in Ref. [30] that in the absence of considering the short-range chemical interactions, the dispersion of the total interactions in reciprocal space predicted the disordered state to be more stable. The problem with that approach or, in general, the MET approach, stems from the inclusion of short-range interactions. First, MET as a harmonic theory cannot quantitatively capture short-range strain-induced interactions without additional anharmonic corrections, owing to the large displacements ($> 10\%$) of the nearest-neighbor host atoms around the interstitials. Second, as indicated in Ref. [21], Zener ordering is a theory that applies to dilute interstitial concentrations, where large short-range chemical and strain-induced interactions are not decisive. Most of the previous approaches using MET overestimated the importance of short-range interactions.

For the critical C concentration at room temperature, only a single experimental data point was reported by Xiao *et al.*.[28] This data point has frequently been used to validate the accuracy of theoretical predictions. As depicted by the yellow bars in Figs. 1 and 3, there is an experimental gap for the critical C content at room temperature. The critical C content at room temperature (2.34 at.%) derived from the present MC simulations almost captures the upper limit of the experimental gap. Recently, we have shown that there might also be competition between C ordering and segregation to extended defects;[14] this further complicates an exact comparison with experimental data. Furthermore, because Zener ordering results in a tetragonal deformation of the bcc lattice, the critical temperature (or C content) is sensitive to external stresses. Accordingly, experimental results are often not obtained under stress-free conditions (see Ref. [38]). Therefore, we believe that it is not constructive to focus on an explicit comparison of

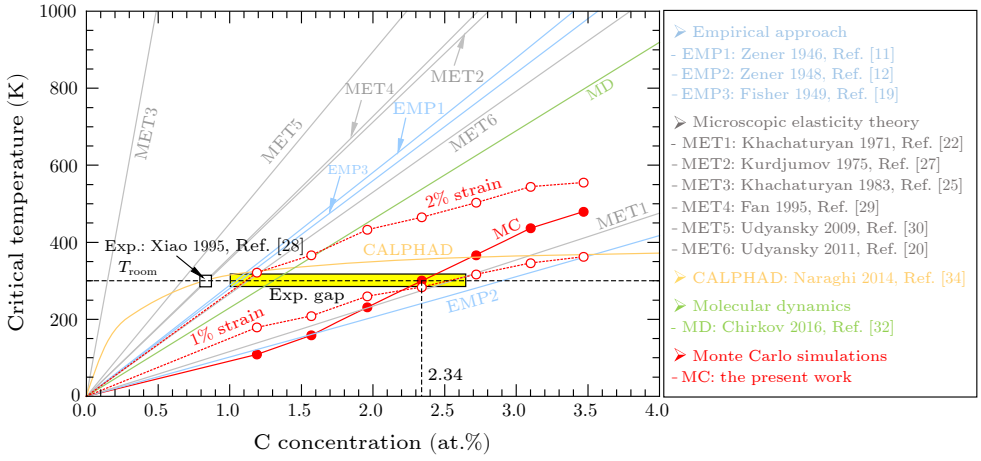

Fig. 3. Critical temperature of the order → disorder transition as a function of C concentration derived from various approaches in the literature[11,12,19,20,22,25,27,29,30,32,34] and from Monte Carlo simulations in the present study. The open square shows the experimental data point measured by Xiao *et al.*.[28] The yellow bar presents the experimental gap of the critical C content at room temperature derived from the datasets shown in Fig. 1.

the calculated results with the limited experimental data; instead, it is more important to rigorously investigate possible factors that could impact the order → disorder transition, such as residual stresses in the material samples. In what follows, we explicitly examine the effect of (intentional or unintentional) strain on the critical concentration and temperature of the order → disorder transition.

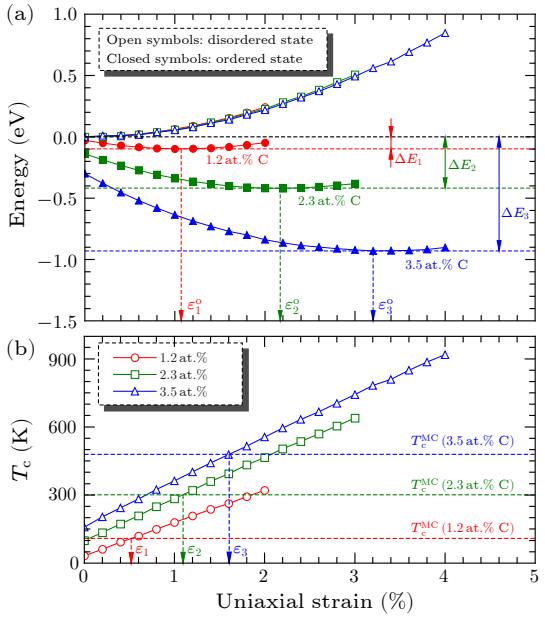

Fig. 4. (a) Effect of uniaxial strain on the energies of the disordered and ordered states. (b) Effect of uniaxial strain on the critical temperature (T_c) of the order → disorder transition computed from Eq. (5). Each data point in panel (a) is an average of the energies (full relaxations with fixed c/a ratios) of 10^5 randomly generated configurations of the corresponding state. ΔE_1, ΔE_2, and ΔE_3 show the energy differences between the minima of the disordered and ordered states for three C concentrations, respectively. Notably, in panel (a) the ordered state is still energetically more favorable than the disordered state, even at zero strain. This occurs because we have relaxed the volume but kept the cubic shape for strain zero, which is different from the situation of the red open circles in Fig. 2, where only atomic positions have been relaxed. All energies in panel (a) are aligned using the energy minimum of the corresponding disordered state for each C concentration as reference.

Figure 4(a) shows the energies of the disordered and ordered states as a function of uniaxial tensile strain, at three representative C concentrations. The energy of the disordered state gradually increases with increasing tensile strain because the disordered state favors a cubic symmetry. Moreover, for the disordered state, the reliance on tensile strain depends weakly on the C concentration. In contrast, for the ordered state, the energy first decreases and then increases with tensile strain. This occurs because for the ordered state at each C concentration, there is an optimum tensile strain [as denoted by ε_1^o, ε_2^o, and ε_3^o in Fig. 4(a)], which corresponds to the tetragonality of the fully ordered phase at a particular C concentration [see Fig. 1]. The driving force for the order → disorder transition is the energy difference between the minima of the disordered and ordered states as a function of the C content [denoted by ΔE_1, ΔE_2, and ΔE_3 in Fig. 4(a)].

Because the configurational entropy, to first order, does not depend on the applied strain, the strain dependence of the critical temperature at each C concentration is dominated by the energy difference between the disordered and ordered states at different strains. Consequently, we quantitatively evaluated the impact of the strain on the critical temperature by applying the following rescaling:

$$T_c(x_C, \varepsilon) = \frac{\Delta E(x_C, \varepsilon)}{\Delta E^{MC}(x_C)} T_c^{MC}(x_C), \tag{5}$$

where x_C is the C concentration and ε is the applied uniaxial tensile strain. $\Delta E(x_C, \varepsilon)$ and $\Delta E^{MC}(x_C)$ are the energy differences between the disordered and ordered states for a strain ε and under fully stress-free conditions (in the context of our MC simulations), respectively. $T_c^{MC}(x_C)$ is the critical temperature at x_C derived from the MC simulations.

Figure 4(b) shows the effect of uniaxial strain on the critical temperature obtained from Eq. (5). There is a critical uniaxial strain [for example, ε_1, ε_2, and ε_3 in Fig. 4(b)] for each C concentration that enables the same critical temperature as that of the strain-free system (T_c^{MC}), although the critical temperature increases with increasing uniaxial strain. This indicates that, compared to the stress-free reference system, the critical temperature is not always increased by the presence of a uniaxial strain but might even be reduced if the strain is smaller than the critical strain for a specific C concentration.

The critical temperatures at 1% and 2% uniaxial tensile strains for different C concentrations [based on the results from Eq. (5)] are shown in Fig. 3 using red dotted lines. The 1% strain only slightly increases the critical temperatures for C concentrations lower than ∼2.3 at.%. At higher C concentrations, the critical temperature is reduced by ∼120 K at a C concentration of 3.5 at.%. The critical C concentration at room temperature increases slightly to ∼2.5 at.%, which approaches the upper limit of the experimental gap. However, a strain of 2% significantly increases the critical temperatures for the entire C content range considered here. Consequently, the critical C concentration at room temperature is reduced to ∼1 at.%, which is close to the lower limit of the experimental gap. Therefore, we have demonstrated the crucial effect of strain on the critical temperature (or C concentration), while also suggesting the need for more precise experimental measurements.

In summary, we have revisited the Zener ordering of interstitials in a bcc host lattice, illustrated using the technologically important Fe-C system. Using precise MC simulations, we have provided direct and clear evidence for the existence of Zener ordering. We have highlighted a long-standing overestimation of the importance of large short-range interactions and an underestimation of the significance of long-range strain-induced interactions in previous studies, even though the individual effects were small. These insights improve our understanding of the

self-induced ordering of point defects in a host lattice, which is not only relevant for Fe-C alloys but also for other interstitials (for example, N and O) and other bcc materials (for example, W, Ti, Zr, V, and Mo). Moreover, the present work reveals a limitation of the commonly performed MC simulations using an Ising-type Hamiltonian when the configurations of dilute interstitial atoms are influenced or even dominated by long-range strains mediated by interstitials in the host lattice.

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