

CONDENSED MATTER

Role of Magnetism in the Decomposition of α -Fe–Cu Alloy

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Recent ab initio studies of the role of magnetism in the decomposition of α -Fe–Cu alloy are analyzed. It is shown that the calculations based on effective pair potentials obtained earlier in the framework of the partial disordered-local moment model strongly overestimate the magnetic contribution. A simple model with the ab initio parametrization is formulated. It allows us to calculate the solubility limits for the bcc and fcc copper precipitates in α -Fe, which are in good qualitative agreement with the experimental data.

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On cooling from the high-temperature state, in the Fe–Cu alloy (with a low copper content of $c \sim 0.01$), a γ – α structural transformation first occurs, Cu atoms within the bcc crystal lattice are clustered, and eventually, when the precipitates attain a size of about 10 nm, the lattice transforms into the fcc type [1]. At the stage of formation of bcc–Cu nanoprecipitates, the strength and plasticity of steel become higher, and this effect is used in applications [2]. The absence of any adequate theory quantitatively describing the solubility of copper in iron has stimulated the development of models with the ab initio parametrization [3, 4]. In [4], the effective Cu–Cu pair potentials based on the partial disordered-local moment model are suggested [5], the Monte Carlo simulation of the alloy decomposition is performed using these potentials, and good agreement with the experimental data [1, 6, 7] is achieved for the calculated solubility limit. The developed technique was later used for other systems [8]. However, our further studies revealed some substantial drawbacks of this approach.

First, the Monte Carlo simulation in [4] gives the stability limit of the homogeneous state (an analog of spinodal) rather than the solubility limit itself. The correct calculation procedure for the solubility limit implies determining the residual Cu content (as the atomic fraction) in the α -Fe solid solution at achieving equilibrium with a large Cu precipitate. In [9], it was shown that the solubility limit (binodal) and the stability limit of the homogeneous state (an analog of spinodal) do not coincide in the Monte Carlo simulations. In the case under study, they differ by one or two orders of magnitude (see curves 1 and 2 in Fig. 1), so there is no agreement with experiment.

Second, the Monte Carlo simulations give the copper solubility in the alloy with the bcc lattice, whereas the experimental data [1, 6, 7] correspond to the

binodal obtained for fcc copper precipitates in the fcc host material. Taking into account the known energy difference between the bcc and fcc copper ($\phi \approx 3.3$ mRy) [10], we can find a correction factor $\sim \exp[-\phi/kT]$ (see the explanations below), which leads to the additional lowering of the copper solubility by a factor of about 1.5 within the temperature range under study.

Third, the model used in [4] is self-contradictory because the suggested effective pair potentials V_p are

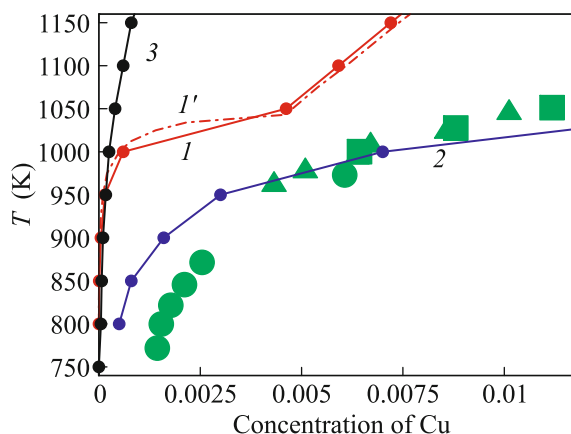


Fig. 1. (Color online) Monte Carlo results (curve 1) for the solubility limit of Cu and (curve 2) for the stability limit of the homogeneous state with the effective potential suggested in [4] at the copper content $c = 0.01$. Curve 3 describes the solubility limit of Cu in the bcc lattice taking into account the concentration dependence of the potential suggested in [4]. Curve 1' is the theoretical estimate for the solubility limit within the regular solid solution model with the corresponding potential. Circles, triangles, and squares denote the experimental data for the solubility limit for fcc copper in α -Fe [1, 6, 7].

inconsistent with the calculations of the mixing potential W_{mix} performed using the exact muffin-tin orbitals in the coherent potential approximation (EMTO–CPA). Indeed, according to the definition given in [4], $W_{\text{mix}} = 1/2 \sum_p z_p V_p$, where z_p is the coordination number and V_p is the effective Cu–Cu interaction potential at the p th coordination sphere. In the limit of low copper content, the EMTO–CPA calculation gives the values of the mixing potential in the paramagnetic (PM) and ferromagnetic (FM) states $W_{\text{mix}}^{\text{PM}} = 32$ mRy and $W_{\text{mix}}^{\text{FM}} = 50$ mRy, respectively (see Fig. 1 in [4]). However, using the potentials V_p suggested in [4], we obtain $W_{\text{mix}}^{\text{PM}} = 36$ mRy and $W_{\text{mix}}^{\text{FM}} = 86$ mRy in the same limit (see Fig. 4 in [4]). Taking into account that the difference $W_{\text{mix}}^{\text{FM}} - W_{\text{mix}}^{\text{PM}}$ characterizes the magnetic contribution to the mixing potential, we conclude that the effective potentials V_p obtained within the model [5] overestimate this contribution by a factor of 3 in comparison to the EMTO–CPA calculation.

Fourth, although the potentials V_p and the values of W_{mix} were determined in [4] taking into account their dependence on the copper content, the Monte Carlo simulation was performed using the potentials independent of the copper content. In fact, this means that the magnetic characteristics of the material were assumed to be the same both in the α -Fe host and in the bulk of nonmagnetic Cu precipitates. Since the declared aim of that study was to reveal the role of magnetism in the alloy decomposition, such approximation is inadmissible.

The above analysis shows that the Cu solubility limit in α -Fe has not been calculated in [4], whereas the coincidence of the stability limit of the homogeneous state (an analog of spinodal) with the experimentally determined solubility limit turned out to be incidental.

In [11], the Monte Carlo program for the simulations of the alloy decomposition taking into account the concentration dependence of potentials V_p was tested, but the solubility limit was not considered. At the same time, the calculations show that the inclusion of the concentration dependence of the potential only increases the deviation of the solubility limit thus calculated from its experimentally determined values (see curve 3 in Fig. 1).

The simplest model is proposed below to determine the effective pair potential applicable for the Monte Carlo simulations and to calculate the solubility limit being in a qualitative agreement with the available experimental data.

The density of internal energy in the alloy can be written including the magnetic contribution in the Heisenberg form

$$g(c) = v_{\text{PM}}(c)c^2 - J(c)Q_1(T, c)(1 - c)^2, \quad (1)$$

where c is the local copper content, $v_{\text{PM}}(c)$ is the copper mixing energy in the PM state, $Q_1 = Q(|r_i - r_j|) = \langle \sigma_i \sigma_j \rangle$ is the correlation function for nearest-neighbor spins, and $J(c) = M^2 z_1 J_1 / \Omega$ is the exchange energy (M is the magnetization, J_1 is the exchange integral, z_1 is the coordination number, and Ω is the volume per atom). The factor $(1 - c)^2$ demonstrates that the magnetic contribution to the energy comes only from iron atoms.

The effective mixing energy v_{eff} is determined from expansion of Eq. (1) in a power series of c

$$\begin{aligned} v_{\text{PM}}(c)c^2 - J(c)Q_1(c)(1 - c)^2 \\ = K_0 + K_1 c + v_{\text{eff}}(c)c^2, \end{aligned} \quad (2)$$

where $K_0 = -J_0 Q_1^0$, $K_1 = (2J_0 - J_1)Q_1^0 - J_0 \frac{dQ_1}{dc} \Big|_0$, $Q_1^0 = Q_1(c = 0)$, and the function $J(c)$ is taken in the form $J(c) = J_0 + J_1 c + J_2 c^2 + J_3 c^3$.

The energy $E_{\text{mix}}(c) = g(c) - (1 - c)E_{\text{Fe}} - cE_{\text{Cu}}$ in PM and FM states was calculated in [4]. Here, E_{Fe} and E_{Cu} are the energies of pure bcc Fe and Cu, respectively; i.e., $E_{\text{Fe}} = g(c = 0) = -J_0 Q_1^0$ and $E_{\text{Cu}} = g(c = 1) = v_{\text{PM}}(1)$. Taking into account that $Q_1^{\text{PM}} = 0$ and $Q_1^{\text{FM}} = 1$ and introducing the mixing potential $W_{\text{mix}}(c) = E_{\text{mix}}(c)/[c(1 - c)]$, we find from Eq. (1)

$$J(c) = \frac{J(0) - (W_{\text{mix}}^{\text{FM}}(c) - W_{\text{mix}}^{\text{PM}}(c))c}{(1 - c)}. \quad (3)$$

The energy $v_{\text{PM}}(c)$ in Eq. (1) is also estimated from the ab initio data for $E_{\text{mix}}^{\text{PM}}(c)$. Taking into account that $Q_1^{\text{PM}} = 0$ and substituting (1) into the definition of $E_{\text{mix}}(c)$, we obtain

$$\begin{aligned} W_{\text{mix}}^{\text{PM}}(c) &= E_{\text{mix}}^{\text{PM}}(c)/[c(1 - c)] \\ &= [-v_{\text{PM}}(1) + v_{\text{PM}}(c)c]/(1 - c). \end{aligned} \quad (4)$$

Parametrizing Eqs. (3) and (4) in terms of the EMTO–CPA calculation [4], we find $J_0 = 15.2$, $J_1 = 12.7462$, $J_2 = -1.6047$, $J_3 = 20.068$, and $v_{\text{PM}}(c) \approx 28.8$ (mRy).

The spin correlation function is determined in qualitative agreement with the theory of Oguchi [12]. For this purpose, the empirical dependence for the magnetization $m(T/T_C)$ [13] with the calculated $T_C(c)$ values is used at $T < T^*$ (where $T^* = \beta T_C$, $\beta = 0.98$,

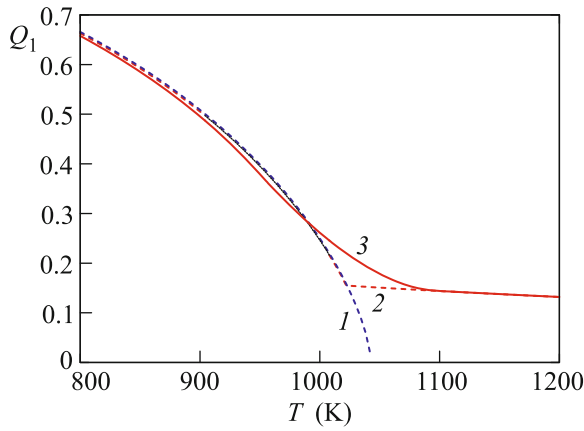


Fig. 2. (Color online) Correlation function for the nearest spins at $c = 0$ calculated by the empirical formula reported in [13] (curve 1), taking into account the short-range magnetic order by Eq. (5) (curve 2) before and (curve 3) after smoothing.

$T_C(c) = T_C(0)(1 - c)J(c)/J(0)$ is the local Curie temperature, and $T_C(0) = 1043$ K), whereas the “tail” of the short-range order with the asymptotic behavior $1/T$ is taken at $T > T^*$. The arising kink in the correlation function is smoothed using the moving average ($\Delta T = 150$ K):

$$Q_1(T) = \begin{cases} m^2(T), & \text{for } T < T^*, \\ m^2(T^*) \frac{T^*}{T}, & \text{for } T > T^*, \end{cases} \quad (5)$$

$$\tilde{Q}_1(T) = \frac{1}{\Delta T} \int_{T-\Delta T/2}^{T+\Delta T/2} Q_1(T') dT'.$$

The constructed correlation function has a qualitatively reasonable form (Fig. 2) and is sufficient for the aims of this study. A more detailed discussion of this correlation function will be presented elsewhere.

The effective Cu–Cu pair interaction potential is determined from the formula $v_{\text{eff}}(c) = (\sum_p z_p V_p^{\text{eff}}(c))/2$ taking into account only the nearest-neighbor interactions. Then, having in mind that $z_1 = 8$ (in the bcc lattice), we obtain $V_1^{\text{eff}}(c) = v_{\text{eff}}(c)/4$.

The solubility limit is theoretically estimated by the expression for the free energy density

$$f(c) = g(c) - TS, \quad (6)$$

where the entropy S is determined within the regular solid solution model [14]

$$S = -k[c \ln c + (1 - c) \ln(1 - c)]. \quad (7)$$

According to the general rule, the solubility limit is theoretically estimated by “the rule of common tangent” to the minima of the free energy [14]. Note that this implies that the coefficients J_2 and J_3 , determin-

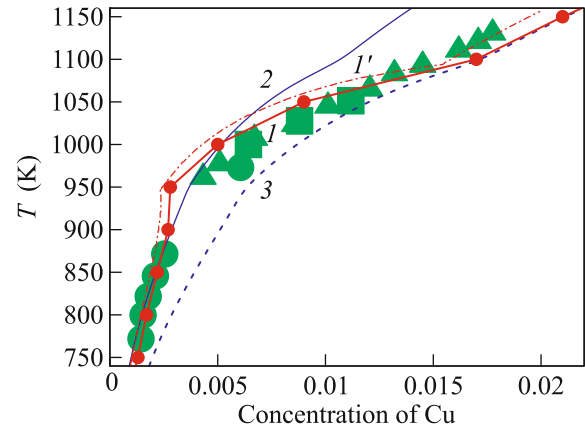


Fig. 3. (Color online) (Curve 1) Monte Carlo results for the solubility limit of Cu in the bcc lattice within the suggested model at $J_0 = 15.2$ mRy and (curve 1') its theoretical estimate. The theoretical estimate for the solubility limits for (curve 2) fcc and (curve 3) bcc copper at $J_0 = 13.2$ mRy. Circles, triangles, and squares denote the experimental data for the solubility limit of fcc copper in α -Fe [1, 6, 7].

ing the behavior of $J(c)$ at high copper contents, do not affect the solubility limit for copper in iron.

The Monte Carlo simulations were performed with the software earlier tested in [11]. Taking into account the concentration dependence of the potential, the refinement of the used procedure was performed. The copper content was calculated by averaging over the occupation numbers in the first coordination sphere around the atoms of each interacting Cu–Cu pair neighboring the sites of the initial and final configurations at the jump of atoms. Earlier in [11], a less accurate procedure was employed, in which only the concentration around the pair involved in the jump was taken into account, whereas the changes in the concentrations at the neighboring sites related to this jump were neglected. The calculations were performed for the supercell containing $90 \times 90 \times 90$ bcc unit cells. The solubility limit was calculated from the Cu content in the α -Fe-based solid solution being in equilibrium with a large Cu precipitate.

Figure 3 demonstrates the Monte Carlo results for the solubility limit (curve 1), exhibiting qualitative agreement with the available experimental data. Curve 1' corresponds to the theoretical evaluation of the binodal involving the suggested potential and exhibits good agreement with the Monte Carlo simulation results. Thus, to find the solubility limit, one can successfully use the theoretical estimate. The drawback of such calculation is that the difference between the bcc and fcc copper precipitates is still neglected, as in the earlier calculations [4, 15]. This should lead to the left shift of the solubility limit. Indeed, the calculated data (see curves 1 and 1' in Fig. 3) correspond to bcc Cu precipitates, whereas the

experiments correspond to the equilibrium of the copper solid solution in α -Fe and the fcc Cu precipitates. The energy difference between bcc and fcc Cu is about 3.3 mRy [10], and it is probably compensated by other omitted contributions or by an inaccuracy of the EMTO–CPA calculation of the exchange energy $J(c)$. From the results of [3], it follows that such compensation can be assured by the contribution of the vibrational entropy (which is disregarded here). However, according to [4], this contribution vanishes near 1000 K. The right shift of the solubility limit can also be favored by overestimating the exchange energy in pure iron. The calculation represented here (see curves 1 and 1' in Fig. 3) was performed with the value $J_0 = 15.2$ mRy, obtained from the EMTO–CPA calculation [4]. In the theory of phase transformations in carbon steel, we earlier successfully used $J_0 = 14$ mRy [16]. The recent calculation by the magnetic cluster expansion method gives $J_0 = 13.2$ mRy [17].

Curves 2 and 3 in Fig. 3 correspond to the theoretical estimate of the solubility for the cases of bcc and fcc Cu under the assumption that $J_0 = 13.2$ mRy (the other parameters remain unchanged). To estimate the solubility of fcc Cu in the range of high copper contents, an additional contribution ϕ is introduced as

$$f_{\text{Fe_in_fccCu}}(c) = -\phi + g(c) - TS, \quad (8)$$

where the energy difference between the bcc and fcc modifications of copper is $\phi \approx 3.3$ mRy (according to [10]). Then, the rule of common tangent to the minima of the free energy (under the assumption that the solubility of copper in iron is sufficiently low) allows us to relate the solubility limits for bcc and fcc Cu introducing the correction factor $\exp[-\phi/kT]$ and to estimate the solubility for fcc Cu if the corresponding estimate for bcc Cu is known. The obtained curve 2 is in qualitative agreement with the experiment. This agreement becomes worse with increasing temperature, especially at $T > T_C$. Such a behavior suggests that the deviation from the experimental data could be related to some missed contribution related to the entropy.

Thus, the effective pair potentials of Cu–Cu interaction suggested in [4] lead to an incorrect estimate for the role of magnetism in the decomposition of the Fe–Cu alloy. Instead, a simple model parametrized in terms of the EMTO–CPA calculation of the mixing potential in the para- and ferromagnetic states has been proposed [4]. This model provides qualitative

agreement with experimental data for the solubility limit.

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