

Effect of pressure on phase stability in Fe-Cr alloys

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The effect of hydrostatic pressure on the phase stability of Fe-Cr alloys has been studied using *ab initio* methods. We show that while pressure decreases the tendency toward the phase separation in the paramagnetic state of bcc alloys, in the ferromagnetic state it reduces the alloy stability at low Cr concentration and vice versa, makes the solid solution more stable at higher concentrations. This behavior of the phase stability can be predicted from the deviation of the lattice parameter from Vegard's law in bcc Fe-Cr alloys. On the atomic level, the pressure effect can be explained by the suppression of the local magnetic moments on Cr atoms, which gives rise to a decrease of the Fe-Cr magnetic exchange interaction at the first coordination shell and, as a result, to the observed variation of the ordering tendency between the Fe and Cr atoms.

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I. INTRODUCTION

The binary Fe-Cr alloys are the base for many important industrial steels. For the purpose of corrosion resistance, the alloys containing more than 10 at.% of Cr are of the greatest practical interest. However, at about 800 K, these alloys are a subject to the so-called spinodal decomposition¹⁻³ occurring for alloy concentrations close to 20 at.% of Cr and leading to the degradation of mechanical properties. Since these alloys are used, for example, in the cooling pipes of pressure vessel reactors, it is important to analyze the effect of pressure on phase stability and spinodal decomposition.

Although the reliable *ab initio* picture of the phase equilibria in Fe-Cr alloys is far from being firmly established, it is clear, that chemical interactions, driven in many cases by magnetism, play a crucial role in this system. One of the interesting features of Fe-Cr system, which is directly related to the spinodal decomposition, is the existence of the anomalous alloying behavior, when the dominating effective interaction at the first coordination shell becomes of ordering type in Fe-rich alloys. The effect was predicted theoretically by Hennion⁴ using the tight-binding generalized perturbation method (GPM),⁵ and confirmed later in the diffuse-neutron-scattering measurements of the atomic short range order (ASRO) by Mirebeau *et al.*⁶

A similar switching of the alloying type behavior at low concentrations of Cr has been found from the first-principles calculations of enthalpy of formation of random Fe-Cr alloys in the ferromagnetic state, first by Olsson *et al.*⁷ and later by a number of consequent first-principles calculations.⁸⁻¹¹ The consensus at the moment is that the origin of this effect is the magnetic behavior of Cr atoms, which acquire a magnetic moment antiparallel to that of Fe in the dilute limit due to antiferromagnetic interactions. At the same time, the magnetic exchange interaction of a couple of Cr atoms is also antiferromagnetic at the first coordination shell. Thus appearance of a couple of nearest-neighbor Cr atoms causes a frustration of the local magnetic configuration, leading to a gradual loss of magnetic moment by the Cr atoms with increasing Cr concentration and the

corresponding change in the type of the effective chemical interactions.^{9,12}

At higher Cr concentration, the interactions (on average, see Ref. 11 on the local environment effects) become of a phase-separation type leading to the corresponding change in the concentration dependence of the enthalpy of formation and, in particular, to the change of the curvature of the enthalpy of formation. The latter could be related to the spinodal decomposition. Of course, at finite temperature, one should consider the Gibbs free energy. However, if the effect is strong enough, it will also remain at least within the temperature interval where the ferromagnetic state is still stable. In this paper, we investigate the effect of pressure on the enthalpy of formation of random Fe-Cr alloys and, thereby, its possible effect on the spinodal decomposition. It is well known that pressure can strongly influence the properties of materials, including the phase stability.¹³⁻¹⁶ However, in most of previous publications the effect of pressure on Fe-Cr alloys has not been taken into account.

II. DETAILS OF CALCULATIONS

The calculations were performed using the exact muffin-tin orbital (EMTO)^{17,18} method combined with the coherent potential approximation (CPA)¹⁹⁻²¹ for the electronic structure of random alloys. The disordered local-moment model was used for the paramagnetic state.²² It is known that the generalized-gradient approximation (GGA)²³ provides better agreement between calculated and experimental equilibrium volumes, and accordingly pressure-volume relations, but leads to an overestimation of the magnetic moment of bcc Fe. Therefore the self-consistent electron densities were obtained within the local-density approximation (LDA),²⁴ and then the total energies were calculated in the GGA using full charge-density formalism. As advocated in Ref. 25, this scheme gives very accurate description of both magnetic and thermodynamic properties of transition metal alloys.

The energy integration has been carried out in the complex plane using a semielliptic contour comprising 24 energy points. The calculations were performed for a basis set including

valence s, p, d , and f orbitals, whereas the core states were recalculated at each iteration of the self-consistency loop. In our CPA calculation, we included the screening contribution to the electrostatic potential and energy to take into account the effect of charge transfer between the alloy components. We used screening constants obtained in Ref. 11. In Fe-Cr alloys, the on-site screening constants are different for the ferromagnetic (FM) and disordered local-moment (DLM) states, which we use to represent the magnetic ground state and the high-temperature paramagnetic state, respectively.^{7,8,11,12} Their values exhibit a pronounced concentration dependence in the FM state of Fe-rich alloys¹¹ because of strong correlation between the magnitude of the magnetic moment and the screening.

It has been established earlier that CPA is fully adequate for the description of configuration-averaged quantities in disordered transition metal alloys in general,²⁶ and their magnetic properties in particular, including magnetic moments and exchange interactions.^{27,28} For Fe-Cr alloys, this has been demonstrated explicitly by a comparison with the experimental concentration dependence of the net magnetization⁷ as well as with supercell calculations.^{8,11}

Details about the ground-state properties and electronic structure of random Fe-Cr alloys at ambient pressure can be found in Refs. 7,8,11, and 12.

III. THERMODYNAMIC ANALYSIS OF PRESSURE EFFECT

As suggested by Alling *et al.*¹⁶ the influence of hydrostatic pressure on phase stability in an alloy system can be predicted from a simple thermodynamic consideration by looking at deviations of the lattice parameters from Vegard's law at ambient pressure. We write the pressure derivative of the free energy of mixing

$$\Delta G = G_{\text{Fe}_{1-c}\text{Cr}_c} - (1-c)G_{\text{Fe}} - cG_{\text{Cr}}, \quad (1)$$

where G is Gibb's free energy and c denotes Cr concentration at fixed temperature.

$$\left(\frac{d\Delta G}{dp} \right)_T = \Delta V \quad (2)$$

and

$$\Delta V = V_{\text{Fe}_{1-c}\text{Cr}_c} - (1-c)V_{\text{Fe}} - cV_{\text{Cr}}, \quad (3)$$

where ΔV is the deviation of the solid solution volume from Zen's law.²⁹ From Eq. (2), we see that if $\Delta V > 0$, the pressure derivative of the free energy of mixing is positive and one should observe increasing tendency toward a phase decomposition of the alloy with increasing pressure. In the opposite case, then $\Delta V < 0$, the pressure increase should lead to reduction of the free energy of mixing and increasing stability of the alloy.

The insets in Fig. 1 show the calculated lattice parameters of Fe-Cr alloys as a function of Cr concentration for different magnetic states of the alloy together with its average value given by Vegard's law. Note that our results are similar to those obtained in Refs. 7,8, and 11, and differ by less than 1% from experimental values. The concentration dependence of the lattice parameter in the FM state exhibits oscillating behavior with positive deviations from the Vegard's (or Zen's) law

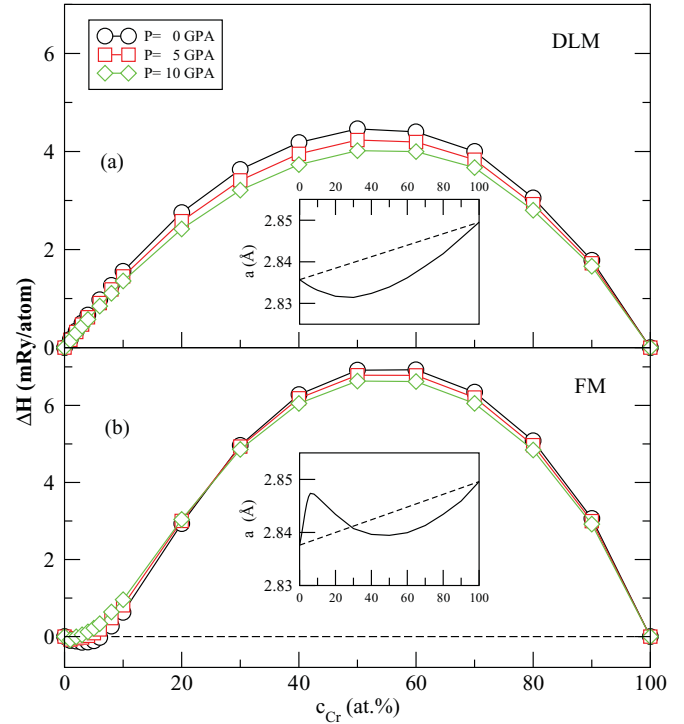


FIG. 1. (Color online) (a) Calculated mixing enthalpy of paramagnetic (DLM) and (b) ferromagnetic Fe-Cr alloys as a function of Cr concentration for different pressures between $P = 0$ and 10 GPa. The insets in upper and lower panels show the concentration dependence of the calculated lattice parameter in bcc Fe-Cr alloys in paramagnetic (DLM) and ferromagnetic states, respectively. Dashed lines correspond the lattice parameter predicted from Vegard's rule.

($\Delta V > 0$) for Fe-rich compositions and negative deviations ($\Delta V < 0$) for the intermediate and Cr-rich compositions. The lattice parameters of random Fe-Cr alloys in the DLM state are always less than the average one, given by the Vegard's law. Therefore just from Eq. (2) we predict that the pressure produces different effects on the alloy stability in the FM or DLM state; the pressure will reduce the tendency toward decomposition in the DLM state, while in the FM state it actually should promote the phase separation of Fe-rich Fe-Cr alloys.

In order to verify the prediction of the thermodynamic model, we have calculated the mixing enthalpy ΔH at different pressures for the DLM and FM states of Fe-Cr alloys. The mixing enthalpy is defined as

$$\Delta H = H_{\text{Fe}_{1-c}\text{Cr}_c} - (1-c)H_{\text{Fe}} - cH_{\text{Cr}}. \quad (4)$$

Note that the standard states of bcc Fe H_{Fe} in the FM and DLM cases are different, while the reference state of bcc Cr H_{Cr} is considered to be nonmagnetic in both cases.

Let us note that our results for ΔH at $P = 0$ GPa are in good agreement with the results obtained by Olsson *et al.*^{7,8} and Korzhavyi *et al.*¹¹ At the same time, as one can see in Fig. 1, the pressure reduces the phase-separation tendency in the whole concentration interval in the DLM state and for a wide range of compositions, in FM state. The alloy stabilization is weakened in the case of Fe-rich alloys. With increasing pressure the depth and width of the ΔH minimum in the FM state decreases. Although the enthalpy is still negative at pressures up to

10 GPa, the stability of the alloy reduces. On the other hand, positive values of ΔH for large Cr concentrations decrease, indicating decreasing tendency toward the phase separation in this concentration range with increasing pressure.

IV. CHEMICAL AND MAGNETIC INTERACTIONS

To understand the results presented in the previous section, we calculate the effective pair interactions of the Ising-type alloy Hamiltonian:²⁵

$$H_{\text{conf}} = \frac{1}{2} \sum_p V_p^{(2)} \sum_{i,j \in p} c_i c_j. \quad (5)$$

Here, $V_p^{(2)}$ are the effective pair interactions (EPI) for coordination shell p , c_i are the occupation numbers taking on values 1 or 0 if Fe or Cr atoms occupy a site i , respectively, and the Fe concentration in the alloy is c . The EPI characterize the tendency of an alloy toward ordering or phase separation: positive EPI at a given coordination shell correspond to the ordering at this coordination shell, while a negative EPI indicate a tendency toward clustering.

In Fe-Cr alloys, the effective interactions strongly depend on Cr concentration and the global magnetic state at ambient pressure.^{4,6,12} In the present work, the effective pair interactions have been determined in the FM state by the screened generalized perturbation method (SGPM).^{30,31} In Fig. 2(a), we show the EPI at the first coordination shell at ambient pressure and at $P = 10$ GPa. One can see that pressure reduces $V_1^{(2)}$ (open circles and triangles) at low Cr concentration and

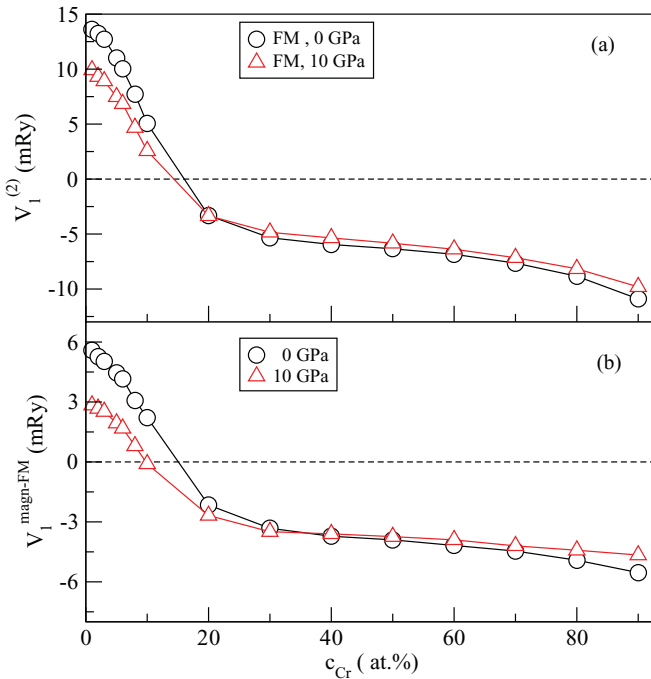


FIG. 2. (Color online) The concentration dependence of the effective pair interactions of the Ising Hamiltonian (Eq. (5)) (a) in FM state at $P = 0$ GPa and $P = 10$ GPa in random Fe-Cr alloys. The (b) shows the magnetic interactions $V_1^{\text{magn-FM}}$ (Eq. (11)) as function of Cr concentration for pressures 0 GPa and 10 GPa.

increases them at a Cr concentration higher than 20 at.% in the FM state. This means that the pressure destabilizes alloy formation in the FM state at low Cr concentration and, vice versa, makes the solid solution more stable at higher Cr concentrations. As has been discussed above, the calculated mixing enthalpy shows exactly the same behavior.

As has been noted by Ruban *et al.*,¹² the concentration dependence of the EPI at the first coordination shell almost exactly follows the concentration dependence of the nearest-neighbor Fe-Cr magnetic exchange interaction. Their explicit connection in fact can be easily demonstrated within a simple phenomenological model based on Heisenberg Hamiltonian for magnetic degrees of freedom, which has been frequently used in the past³²⁻³⁹ to elucidate the magnetic contribution to the ordering behavior of alloys. If the chemical and magnetic exchange interactions in an alloy $A_c B_{1-c}$ do not depend on the atomic and magnetic configuration, the Hamiltonian combining both degrees of freedom can be written as

$$H_{\text{alloy}} = \frac{1}{2} \sum_p \sum_{i,j \in p} [(v_p^{AA} - 2J_p^{AA} \mathbf{e}_i^A \mathbf{e}_j^A) c_i c_j + 2(v_p^{AB} - 2J_p^{AB} \mathbf{e}_i^A \mathbf{e}_j^B) c_i (1 - c_j) + (v_p^{BB} - 2J_p^{BB} \mathbf{e}_i^B \mathbf{e}_j^B) (1 - c_i) (1 - c_j)], \quad (6)$$

where v_p^{XY} are the chemical interatomic potentials between X and Y alloy species at the p th coordination shell, J_p^{AB} is the magnetic exchange interaction parameter of the classical Heisenberg Hamiltonian ($H_{\text{magn}} = -\sum_p \sum_{i,j \in p} J_p \mathbf{e}_i \mathbf{e}_j$), and \mathbf{e}_i^X is the direction of the spin of atom X at site i .

Omitting in Eq. (6) the part that does not depend on alloy configuration, this Hamiltonian is reduced to the form of the above written configurational Hamiltonian (5):

$$H_{\text{conf}} = \frac{1}{2} \sum_p \sum_{i,j \in p} V_p^{\text{mod}} c_i c_j, \quad (7)$$

where the whole effective interaction of this model can be presented as a sum of the chemical and magnetic parts:

$$V_p^{\text{mod}} = V_p^{\text{chem}} + V_p^{\text{magn}}. \quad (8)$$

The chemical part is formally defined in the usual way:

$$V_p^{\text{chem}} = v_p^{AA} + v_p^{BB} - 2v_p^{AB}, \quad (9)$$

but its meaning will be clear after the definition of the magnetic part, which is

$$V_p^{\text{magn}} = -2(J_p^{AA} \mathbf{e}_i^A \mathbf{e}_j^A - 2J_p^{AB} \mathbf{e}_i^A \mathbf{e}_j^B + J_p^{BB} \mathbf{e}_i^B \mathbf{e}_j^B). \quad (10)$$

The magnetic contribution depends on the magnetic state through the direction of the magnetic moments of particular atoms at particular sites. In the ground-state magnetic configuration, for instance, in the FM state, it is well determined since the orientations of the spins are fixed. However, it is not the case of the paramagnetic state, in which the directions of magnetic moments fluctuate with high frequency, much higher than atomic jumps due to diffusion equilibrating atomic alloy configuration. The latter means that one should consider

the average magnetic configuration in order to determine the contribution of the magnetic interactions to the total effective interaction.

In particular, in the paramagnetic or DLM state the orientations of the spins are totally uncorrelated on different sites, which means that average products $\langle e_i^X e_j^Y \rangle = 0$, and thus $V_p^{\text{magn-DLM}} = 0$, i.e., the magnetic exchange interactions do not contribute to the total effective interactions: $V_p^{\text{chem}} = V_p^{\text{mod-DLM}}$. This defines the ‘‘chemical’’ contribution in this particular model. As has been demonstrated in Ref. 11, the nearest-neighbor interaction in the DLM state $V_1^{\text{magn-DLM}}$ is practically independent of concentration; our calculations have shown that they also do not depend on pressure. Therefore we focus our attention only on the magnetic interactions. In the FM state of Fe-rich Fe-Cr alloys, they are

$$V_p^{\text{magn-FM}} = -2(J_p^{\text{FeFe}} + 2J_p^{\text{FeCr}} + J_p^{\text{CrCr}}), \quad (11)$$

where we have taken into consideration the antiparallel alignment of Cr magnetic moment with respect to that of Fe.

Figure 2(b) shows the $V_1^{\text{magn-FM}}$ obtained using Eq. (11) at $P = 0$ and 10 GPa. It is clear that the change of $V_1^{\text{magn-FM}}$ with concentration is almost identical to that of the EPI at the first coordination shell at different pressures, which includes both magnetic and chemical interactions. The components of the magnetic part of the effective interaction in the FM state given by Eq. (11) are shown in Fig. 3. One can see that the main ordering contribution at the first coordination shell (with positive sign) comes from Cr-Cr and Fe-Cr magnetic interactions, while the strong ferromagnetic interaction between Fe atoms

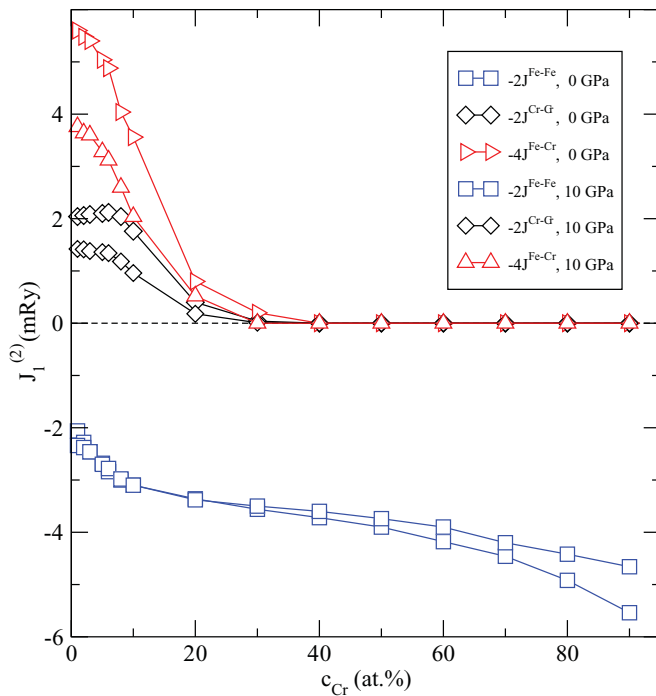


FIG. 3. (Color online) The concentration dependence of nearest-neighbor Fe-Fe ($J^{\text{Fe-Fe}}$), Fe-Cr (J^{FeCr}), and Cr-Cr (J^{CrCr}) exchange interactions of the Heisenberg Hamiltonian with expansion coefficients (for the ground magnetic state) of $V_1^{(2)}$ in the FM state at $P = 0$ and 10 GPa in random Fe-Cr alloys.

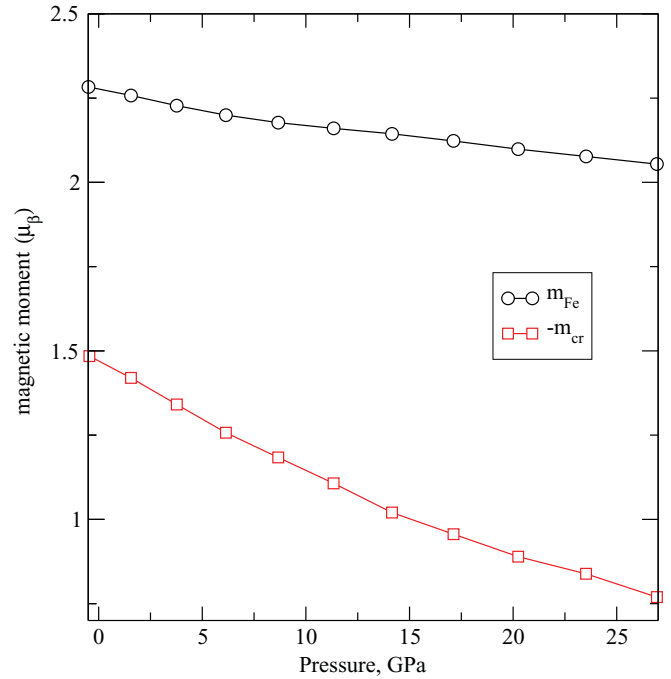


FIG. 4. (Color online) The pressure dependence of local magnetic moments on Fe and Cr atoms in the FM $\text{Fe}_{0.97}\text{Cr}_{0.03}$ alloy.

at the first coordination shell promotes the phase separation. Thus it is energetically favorable for Cr and Fe atoms to be nearest neighbors.

One can also now clearly see why at the ambient pressure, the effective pair interactions at the first coordination shell as a function of concentration closely follow the Fe-Cr magnetic exchange interaction mentioned in Ref. 12. In this case, the Fe-Fe and Cr-Cr magnetic exchange interactions compensate each other to a large degree, leaving basically only one Fe-Cr exchange interaction contribution in Eq. (11). However, this picture is no more valid at elevated pressure, which reduces the Fe-Cr and Cr-Cr exchange interactions leaving the Fe-Fe exchange interaction practically unchanged. This is so, since the pressure strongly affects the local magnetic moment of Cr, while the magnetic moment of Fe is affected very little.

This can be clearly seen in Fig. 4, where we show the magnitude of Fe and Cr local magnetic moments in $\text{Fe}_{0.97}\text{Cr}_{0.03}$ alloy as a function of pressure. One can see that the magnetic moment of Fe decreases by only about 4% at 10 GPa, while the Cr magnetic moment is reduced by more than 25%. This means that the contribution from Fe-Fe exchange interactions becomes dominating at high pressure, which increases the phase-separation tendency.

V. SPINODAL DECOMPOSITION AND STRUCTURAL STABILITY

The stability of alloy against the phase separation is determined by the balance between the Gibbs free energy of alloy and the competing phases. However, even if the Gibbs free energy of an alloy is higher than that of competing phases, the alloy can still be in a metastable phase due to, for instance, a high barrier for the phase transformation. It can be stable against composition (or atomic configuration) fluctuations on

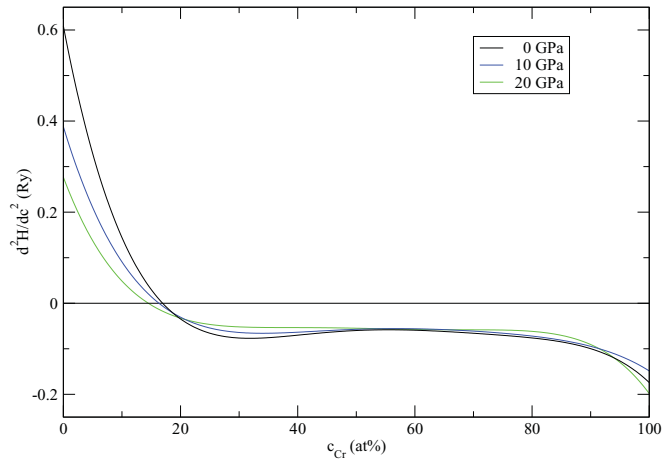


FIG. 5. (Color online) The concentration dependence of the second derivatives of the mixing enthalpy for pressures $P = 0, 10,$ and 20 GPa.

the local scale. In the macroscopic limit, the metastability requires that the second derivative of the Gibbs free energy has to be positive ($d^2G/dc^2 > 0$).

When the second derivative is negative, any fluctuation of the composition should initiate the phase separation. At the boundary between these two limits, where the second derivative of the Gibbs free energy is zero, an alloy undergoes the so-called spinodal decomposition. Thus the knowledge of this boundary is very important in providing (meta)stable alloys for industrial applications. In general, the spinodal boundary is a function of temperature. However, at low temperatures, the mixing enthalpy gives dominating contribution to the Gibbs free energy and thus it can be used to check the effect of the pressure on the qualitative level.

In Fig. 5, we plot the second derivative of the mixing enthalpy as a function of Cr concentration at different pressures. The predicted limit for spinodal decomposition at $P = 0$ GPa is about 17 at.%. The calculated data are in good agreement with the results obtained in Ref. 7 and with Mössbauer spectroscopy measurements.⁴⁰ From Fig. 5, one can see that at pressure $P = 20$ GPa the concentration of Cr corresponding to the onset of spinodal decomposition decreases from 17 to 14 at.%. Thus when pressure increases, the concentration boundary on the Fe-rich side of the phase diagram at $T = 0$ K shifts to the left, i.e., a region of spinodal decomposition becomes wider.

Finally, in Fig. 6, we represent the structural enthalpy differences $\Delta H = H_{\text{fcc}} - H_{\text{bcc}}$ in random Fe-Cr alloys as a function of Cr concentration at $P = 0$ and 10 GPa. We consider both the FM and PM states of bcc iron and only the PM state of fcc iron (γ phase). The latter restriction is reasonable due to low Néel temperature of fcc Fe. We can see that at ambient pressure, bcc FM alloys are more stable as compared to fcc DLM alloys in the whole concentration range, while the bcc structure in the DLM state becomes less stable with respect to PM fcc alloys at low Cr concentration. These results are in qualitative agreement with the available Fe-Cr phase diagram¹ and a theoretical study considering the α - γ phase transition in this alloys.⁴¹ With increasing pressure, the FM bcc phase (at $P = 10$ GPa) is still more stable than the PM fcc structure

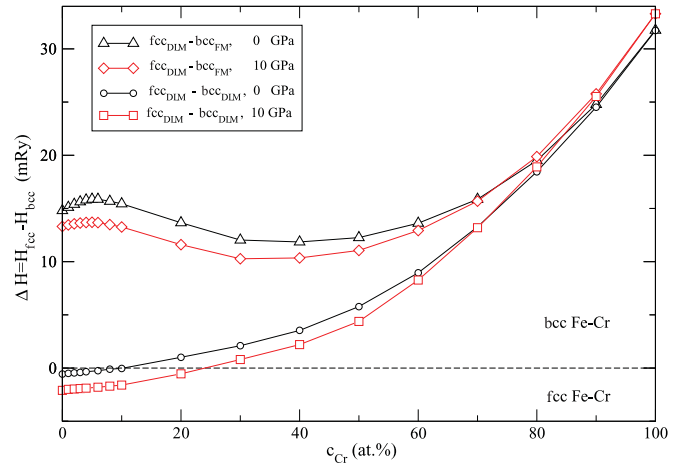


FIG. 6. (Color online) Calculated structural enthalpy differences ΔH in random Fe-Cr alloys as a function of Cr concentration at $P = 0$ GPa and $P = 10$ GPa.

but the stability of the FM bcc phase decreases, whereas the paramagnetic fcc phase becomes more stable compared to the PM bcc alloys in the Fe-rich part of the phase diagram. This means that applied pressure should extend the range of existence of the γ phase. Note, however, that the hpc phase was not considered in this study.

VI. CONCLUSIONS

Using the EMTO-CPA method, we have studied the effect of hydrostatic pressure on the phase stability of Fe-Cr alloys in the FM state and the PM state described within the DLM model. We find that in the PM state, the pressure decreases the tendency toward phase separation, while it promotes the phase separation in the Fe-rich alloys in the FM state. To analyze the effect of pressure on the phase stability, we use a simplified model in which the effective pair interactions are split into chemical and magnetic terms. This model shows that the effect of pressure on the phase stability in this system comes mostly through the decrease of the magnetic moment on Cr, and consequently, Fe-Cr exchange interaction, which dictates the anomalous stability of the alloy at ambient conditions. We predict that the region of spinodal decomposition should become wider with increasing pressure. Further, our calculations show that under pressure, the paramagnetic fcc phase becomes more stable compared to the PM bcc alloys in the Fe-rich part of the phase diagram.

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