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Direct laser interference patterning of nonvolatile magnetic nanostructures in Fe₆₀Al₄₀ alloy via disorder-induced ferromagnetism

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Section 1: Chemical ordering/disordering in substitutional alloys

In a system close enough to its equilibrium, the general equation for relaxation of the order parameter $\eta(\mathbf{r}, t)$ varying in space (\mathbf{r}) and time (t) reads^{1,2,3}

$$\frac{\partial \eta(\mathbf{r}, t)}{\partial t} = -\frac{\Gamma}{2\beta} \frac{\delta F}{\delta \eta(\mathbf{r})}, \quad (S1)$$

where $\beta = k_B T$, k_B is the Boltzmann constant, T is temperature in the system, Γ is the characteristic frequency of the relaxation process, and $\delta F / \delta \eta(\mathbf{r})$ is the functional derivative of the free energy of the system.

For a substitutional alloy, equation (S1) can be rewritten in a discrete approximation for chemical ordering via atomic diffusion through vacancies in the atomic lattice,

$$\frac{\partial \Delta(\mathbf{r}, t)}{\partial t} = -\frac{1}{2\beta} \sum_{\mathbf{r}'} \Gamma(\mathbf{r} - \mathbf{r}') x c_v(t) \frac{\delta \Delta F}{\delta \Delta(\mathbf{r}')}, \quad (S2)$$

which is similar to that introduced previously, for instance, in ref.⁴. The notations in equation (S2) are as follows: $\Delta(\mathbf{r}, t) = n(\mathbf{r}, t) - x$ is the modified order parameter, that is, deviation of the probability for the occupation of the site \mathbf{r} by an atom of the specific kind A from the fully disordered state in the alloy, $x = N_A / N$ the total concentration of the component A, N_A and N are respectively the number of atoms of the component A and total number of atomic sites, $c_v(t)$ the concentration of vacancies, and $\Gamma(\mathbf{r} - \mathbf{r}') x c_v$ is the probability for an atomic jump from a site \mathbf{r}' to a site \mathbf{r} per a unit of time. The Gibbs free energy of mixing in a substitutional alloy can be written as⁴

$$F = \frac{1}{2} \sum_{\mathbf{r}, \mathbf{r}'} V(\mathbf{r} - \mathbf{r}') n(\mathbf{r}) n(\mathbf{r}') + \beta \sum_{\mathbf{r}} [n(\mathbf{r}) \ln n(\mathbf{r}) + (1 - n(\mathbf{r})) \ln(1 - n(\mathbf{r}))], \quad (S3)$$

where the first term is the internal energy with $V(\mathbf{r} - \mathbf{r}')$ being the interaction potential of atoms occupying the sites \mathbf{r} and \mathbf{r}' , while the second term is the entropy of mixing. The second term is obtainable from the general Boltzmann equation $S = k_B \ln W$, where $W = N! / N_A! (N - N_A)!$. Taking in account the Stirling formula, i.e., $\ln N! \approx N \ln N - N$, after algebraic transformations the entropy in the completely disordered state can be written as

$$S_0 = -N k_B [x \ln x + (1 - x) \ln(1 - x)]. \quad (S4)$$

In the case of partially ordered alloy, i.e., when the probability for finding of an atom A in a site \mathbf{r} differs from x , equation (S4) can be rewritten as $S = -k_B \sum_{\mathbf{r}} [n \ln n + (1 - n) \ln(1 - n)]$. Then, neglecting high-power terms in the expansions of $\ln(1 + \Delta/x) = \Delta/x - \Delta^2/(2x^2) + \dots$ and $\ln[1 - \Delta/(1 - x)] \approx -\Delta/(1 - x) - \Delta^2/[2(1 - x)^2] - \dots$ and taking into account that $\sum_{\mathbf{r}} \Delta(\mathbf{r}) \equiv 0$ and $\sum_{\mathbf{r}} \Delta^3(\mathbf{r}) \equiv 0$ we obtain that the change in the Gibbs free energy is

$$\Delta F = \frac{1}{2} \sum_{\mathbf{r}, \mathbf{r}'} [V(\mathbf{r} - \mathbf{r}') + \frac{\beta}{x(1 - x)} \delta_{\mathbf{r}, \mathbf{r}'}] \Delta(\mathbf{r}) \Delta(\mathbf{r}'), \quad (S5)$$

where $\delta_{\mathbf{r}, \mathbf{r}'}$ is the Kronecker delta. The functional derivative of ΔF on $\Delta(\mathbf{r}')$ is¹

$$\frac{\delta \Delta F}{\delta \Delta(\mathbf{r}')} = \sum_{\mathbf{r}} [V(\mathbf{r} - \mathbf{r}') + \frac{\beta}{x(1 - x)} \delta_{\mathbf{r}, \mathbf{r}'}] \Delta(\mathbf{r}). \quad (S6)$$

Then, by using the convolution theorem for the Fourier transformation, equation (S2) for relaxation of the order parameter can be rewritten as an equation describing growth of concentration wave with the amplitude $A(\mathbf{k}, t)$ ¹²:

$$\frac{\partial A(\mathbf{k}, t)}{\partial t} = -\frac{x c_v(t)}{2\beta} [V(\mathbf{k}) + \frac{\beta}{x(1 - x)}] L(\mathbf{k}) A(\mathbf{k}, t), \quad (S7)$$

where $A(\mathbf{k})$, $L(\mathbf{k})$, and $V(\mathbf{k})$ are the Fourier transforms of $\Delta(\mathbf{r})$, $\Gamma(\mathbf{r} - \mathbf{r}')$, and $V(\mathbf{r} - \mathbf{r}')$.

By analyzing the stability of the system with respect to growth of concentration waves, we get that¹³

$$V(\mathbf{k}) = -\frac{k_B T_c(\mathbf{k})}{x(1 - x)}, \quad (S8)$$

where T_c is the temperature for the order-disorder transition. As a result, we obtain that

$$\frac{\partial A(\mathbf{k}, t)}{\partial t} = \frac{L[\mathbf{k}, T(t)]}{2} \frac{T_c - T(t)}{T(t)} \frac{c_v(t)}{1 - x} A(\mathbf{k}, t). \quad (S9)$$

For the body-centered cubic (bcc) lattice and $k = 2\pi/a$, where a is the lattice constant, in which each lattice point has 8 nearest neighbors, we obtain that

$$L(\mathbf{k}) = \sum_{\mathbf{R}} \Gamma(\mathbf{R}) \exp(-i\mathbf{k}\mathbf{R}) = \Gamma \sum_{\mathbf{R}} \exp[-i(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)(h\mathbf{a}_1 + n\mathbf{a}_2 + l\mathbf{a}_3)] = 8\Gamma \quad , \quad (\text{S10})$$

where $\mathbf{R} = \mathbf{r} - \mathbf{r}'$, \mathbf{a}_i ($i=1, 2, 3$) are primitive vectors of the lattice, h, n , and l are integers which are equal to either 1 or -1 , and \mathbf{b}_i are reciprocal lattice vectors, so that $\mathbf{a}_i \mathbf{b}_j = 2\pi \delta_{ij}$.

^{t1}By definition, the functional derivative $\frac{\delta \Delta F}{\delta \Delta(\mathbf{r}')}$ is a coefficient of $\delta \Delta(\mathbf{r}')$ in the relation of $\delta \Delta F = \int \frac{\delta \Delta F}{\delta \Delta(\mathbf{r}')} \delta \Delta(\mathbf{r}') d\mathbf{r}'$.

For a variation of ΔF , we have from equation (S5) that

$$\begin{aligned} \delta \Delta F &= \frac{1}{2} \sum_{\mathbf{r}, \mathbf{r}'} [V(\mathbf{r} - \mathbf{r}') + \frac{\beta}{x(1-x)} \delta_{\mathbf{r}\mathbf{r}'}] \{ \Delta(\mathbf{r}) \delta \Delta(\mathbf{r}') + \Delta(\mathbf{r}') \delta \Delta(\mathbf{r}) \} \\ &= \sum_{\mathbf{r}} \Delta(\mathbf{r}) \sum_{\mathbf{r}'} [V(\mathbf{r} - \mathbf{r}') + \frac{\beta}{x(1-x)} \delta_{\mathbf{r}\mathbf{r}'}] \delta \Delta(\mathbf{r}') \\ &\rightarrow \sum_{\mathbf{r}} \Delta(\mathbf{r}) \int_{\mathbf{r}'} [V(\mathbf{r} - \mathbf{r}') + \frac{\beta}{x(1-x)} \delta_{\mathbf{r}\mathbf{r}'}] \delta \Delta(\mathbf{r}') d\mathbf{r}' \quad . \end{aligned}$$

^{t2}Substitution of equation (S6) into equation (S2) gives that

$$\frac{\partial \Delta(\mathbf{r}, t)}{\partial t} = -\frac{xc_v}{2\beta} \sum_{\mathbf{r}'} \sum_{\mathbf{r}''} \Gamma(\mathbf{r} - \mathbf{r}') V(\mathbf{r}' - \mathbf{r}'') \Delta(\mathbf{r}'') - \frac{c_v}{2(1-x)} \sum_{\mathbf{r}'} \sum_{\mathbf{r}''} \Gamma(\mathbf{r} - \mathbf{r}') \delta_{\mathbf{r}\mathbf{r}''} \Delta(\mathbf{r}'') \quad .$$

As $\sum_{\mathbf{r}'} \Gamma(\mathbf{r} - \mathbf{r}') \delta_{\mathbf{r}\mathbf{r}''} = \Gamma(\mathbf{r} - \mathbf{r}'')$, we have that

$$\frac{\partial \Delta(\mathbf{r}, t)}{\partial t} = -\frac{xc_v}{2\beta} \sum_{\mathbf{R}} G(\mathbf{R}) \Delta(\mathbf{r} - \mathbf{R}) - \frac{c_v}{2(1-x)} \sum_{\mathbf{R}} \Gamma(\mathbf{R}) \Delta(\mathbf{r} - \mathbf{R}),$$

where $\mathbf{R} = \mathbf{r} - \mathbf{r}''$ and $G(\mathbf{r} - \mathbf{r}'') = \sum_{\mathbf{r}'} \Gamma(\mathbf{r} - \mathbf{r}') V(\mathbf{r}' - \mathbf{r}'')$.

As $\sum_{\mathbf{R}} G(\mathbf{R}) \Delta(\mathbf{r} - \mathbf{R}) = G * \Delta$ and $\sum_{\mathbf{R}} \Gamma(\mathbf{R}) \Delta(\mathbf{r} - \mathbf{R}) = \Gamma * \Delta$, that is, the convolution of two functions, we get that

$$\frac{\partial}{\partial t} \mathbb{F}[\Delta] = -\frac{xc_v}{2\beta} \mathbb{F}[G] \mathbb{F}[\Delta] - \frac{c_v}{2(1-x)} \mathbb{F}[\Gamma] \mathbb{F}[\Delta] \quad ,$$

where $\mathbb{F}[\Delta] = A(\mathbf{k})$ is the Fourier transform of $\Delta(\mathbf{r})$, \mathbf{k} is the wave vector of the concentration wave with amplitude of A , $\mathbb{F}[G]$, and $\mathbb{F}[\Gamma]$ are the Fourier transforms of $G(\mathbf{R})$ and $\Gamma(\mathbf{R})$. In order to calculate $\mathbb{F}[G]$, we note that

$$G(\mathbf{r} - \mathbf{r}'') \equiv G(\mathbf{R}) = \sum_{\mathbf{r}'} V(\mathbf{R} - (\mathbf{r} - \mathbf{r}')) \Gamma(\mathbf{r} - \mathbf{r}') = \sum_{\mathbf{R}'} V(\mathbf{R} - \mathbf{R}') \Gamma(\mathbf{R}') = V * \Gamma,$$

where $\mathbf{R}' = \mathbf{r} - \mathbf{r}'$.

^{t3}The order parameter can be represented as a plane-expansion

$$\Delta(\mathbf{r}) = \sum_{\mathbf{k}} A(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}} + A^*(\mathbf{k}) e^{-i\mathbf{k}\mathbf{r}} \quad .$$

Substituting this expansion into equation (S5) and taking in account, for simplicity, only a one concentration wave – with a wave vector \mathbf{k} , we get that

$$\begin{aligned} \Delta F &= \frac{1}{2} \sum_{\mathbf{r}, \mathbf{r}'} [V(\mathbf{r} - \mathbf{r}') + \frac{\beta}{x(1-x)} \delta_{\mathbf{r}\mathbf{r}'}] [A(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}} + A^*(\mathbf{k}) e^{-i\mathbf{k}\mathbf{r}}] [A(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}'} + A^*(\mathbf{k}) e^{-i\mathbf{k}\mathbf{r}'}] \\ &= \frac{1}{2} A^2(\mathbf{k}) \sum_{\mathbf{r}} e^{2i\mathbf{k}\mathbf{r}} \sum_{\mathbf{r}'} \left[V(\mathbf{r} - \mathbf{r}') + \frac{\beta \delta_{\mathbf{r}\mathbf{r}'}}{x(1-x)} \right] e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')} + \text{c.c.} \\ &\quad + \frac{1}{2} |A(\mathbf{k})|^2 \sum_{\mathbf{r}} \sum_{\mathbf{r}'} \left[V(\mathbf{r} - \mathbf{r}') + \frac{\beta \delta_{\mathbf{r}\mathbf{r}'}}{x(1-x)} \right] e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')} + \text{c.c.} \end{aligned}$$

We also note that

$$\sum_{\mathbf{r}'} \left[V(\mathbf{r} - \mathbf{r}') + \frac{\beta \delta_{\mathbf{r}\mathbf{r}'}}{x(1-x)} \right] e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')} = V(\mathbf{k}) + \frac{\beta}{x(1-x)} \quad .$$

As the terms with $A^2(\mathbf{k})$ and their c.c. are equal to zero because $\sum_{\mathbf{r}} e^{\pm 2i\mathbf{k}\mathbf{r}} \equiv 0$, so that the change of the Gibbs energy of mixing is

$$\Delta F = \sum_{\mathbf{k}} |A(\mathbf{k})|^2 \left[V(\mathbf{k}) + \frac{\beta}{x(1-x)} \right].$$

When $T=T_c(\mathbf{k})$, we have that $\Delta F=0$ and, finally, one obtains equation (S8).

We take into account atomic jumps from nearest lattice sites \mathbf{r}' only, which are located at a distance of $a\sqrt{3}/2$ from the site \mathbf{r} , and assume that atomic jumps have the same probability from all the nearest sites, so that $\Gamma(\mathbf{r}-\mathbf{r}') \equiv \Gamma$.

According to the Einstein relation for the Brownian motion, we have that the diffusion coefficient for the atomic jumps to nearest lattice sites in the bcc lattice is

$$D = \frac{\Gamma}{6} \left(\frac{\sqrt{3}}{2} a \right)^2.$$

Then, we have that

$$L(\mathbf{k}, t) = \frac{64D[T(t)]}{a^2},$$

where $D=D_0 \exp(-E_m/k_B T)$ is the diffusion coefficient, E_m is the activation energy for atomic diffusion (or enthalpy of vacancy migration), and D_0 is the pre-exponential factor.

Therefore, equation (S9) can be rewritten as

$$\frac{dA}{dt} - \alpha(t)A = 0, \quad (\text{S11})$$

where $\alpha=32D(t)(T_c-T)c_v(t)/[Ta^2(1-x)]$, whose solution is

$$A(t) = A(0) \exp \left[\int_{t_1}^{t_2} \alpha(t) dt \right], \quad (\text{S12})$$

where and t_1, t_2 the starting and finishing moments of ordering (disordering) at $T < T_c$ ($T > T_c$). The quantity of $c_v(t)$ can be found from the relaxation equation of the Bloch type

$$\frac{dc_v}{dt} = \frac{c_{eq}(T) - c_v}{\tau}, \quad (\text{S13})$$

where $c_{eq}(T)=\exp(-E_v/k_B T)$ is the equilibrium concentration of vacancies, E_v the enthalpy of vacancy formation, and $\tau=L^2/D$ the relaxation time, which is the characteristic time of vacancy life between its formation and annihilation at crystallite boundaries, and L the crystalline grain diameter. The solution of equation (S13) [or equation (3) in the main body] is as follows:

$$c_v(t) = \exp \left[-\frac{1}{\tau_0} \int_0^t \exp[-E_m/T(t_1)] dt_1 \right] \times \left[c_v(0) + \frac{1}{\tau_0} \int_0^t \exp \left[-\frac{E}{T(t_1)} + \frac{1}{\tau_0} \int_0^{t_1} \exp[-E_m/T(t_2)] dt_2 \right] dt_1 \right],$$

where $\tau_0=L^2/D_0$ and $E=E_m+E_v$.

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