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

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

where $\beta = k_B T$, Γ is the characteristic frequency of the relaxation process, $F(r)$ the local free energy of the system, and $\delta F / \delta \eta$ the functional derivative of the free energy.

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,

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

which is similar to that introduced previously, for instance, in Ref.⁴. The notations in equation (S2) are as follows: $\Delta(r, t) = \eta(r, t) - x$ is the deviation of the probability for the occupation of the site 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 vacancy concentration, and $\Gamma(r-r') x c_v$ is the probability for a jump of an atom A from a site r' to a site r per a unit of time. The Gibbs free energy of mixing for the subsystem A in a substitutional alloy can be written as⁴

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

where the first term is the energy of the subsystem A in which $V(r-r')$ is interaction potential of atoms of the component A occupying the sites r and 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 r differs from x , equation (S4) can be rewritten as $S = -k_B \sum_r [\eta \ln \eta + (1-\eta) \ln(1-\eta)]$. 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 $\sum_r \Delta(r) \equiv 0$ and $\sum_r \Delta^3(r) \equiv 0$, we obtain the change of the free energy

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

where $\delta_{rr'}$ is the Kronecker delta. The functional derivative of ΔF on $\Delta(r')$ is^{†1}

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

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 $A(k, t)$ ^{†2}:

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

where $A(k)$, $L(k)$, and $V(k)$ are the Fourier transforms of $\Delta(r)$, $\Gamma(r)$, and $V(r)$, respectively.

^{†1} By definition, the functional derivative $\delta \Delta F / \delta \Delta(r')$ is a coefficient of $\delta \Delta(r')$ in the relation of $\delta \Delta F = \int \frac{\delta \Delta F}{\delta \Delta(r')} \delta \Delta(r') dr'$. For a variation of ΔF , we have from equation (S5) that

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

^{†2} Substitution of equation (S6) into equation (S2) gives that

$$\begin{aligned}\frac{\partial \Delta(r, t)}{\partial t} &= -\frac{xc_v}{2\beta} \sum_{r'} \sum_{r''} \Gamma(r-r') V(r'-r'') \Delta(r'') - \frac{c_v}{2(1-x)} \sum_{r'} \sum_{r''} \Gamma(r-r') \delta_{r'r''} \Delta(r'') . \\ \sum_{r'} \Gamma(r-r') V(r'-r'') &= W(r-r''); \quad \sum_{r'} \Gamma(r-r') \delta_{r'r''} = \Gamma(r-r'') \\ \frac{\partial \Delta(r, t)}{\partial t} &= -\frac{xc_v}{2\beta} \sum_R W(R) \Delta(r-R) - \frac{c_v}{2(1-x)} \sum_R \Gamma(R) \Delta(r-R),\end{aligned}$$

where $R=r-r''$. As $\sum_R W(R) \Delta(r-R) = W * \Delta$ and $\sum_R \Gamma(R) \Delta(r-R) = \Gamma * \Delta$, that is, the convolutions of two functions, using the convolution theorem for the Fourier transformation, we get that

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

where $F[\Delta] = A(k)$, k is the wave vector of the concentration wave with amplitude of A , $F[W]$, and $F[\Gamma]$ are the Fourier transforms as well. In order to calculate $F[W]$, we note that

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

where $R'=r-r''$.

By analyzing the stability of the system with respect to growth of concentration waves, we get ^{†3}

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

where T_c is the temperature for the order-disorder transition, which depends on k . Then we get

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

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

$$L(k) = \sum_r \Gamma(r) \exp(-ikr) = \Gamma \sum_r \exp[-i(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)(x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3)] = 8\Gamma, \quad (S10)$$

where \mathbf{a}_i ($i=1, 2, 3$) are primitive vectors of the lattice, x, y , and z are integers, and \mathbf{b}_i are reciprocal lattice vectors, so that $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$. We assume that the atomic jumps to different nearest lattice sites have the same probability, and so, $\Gamma(r) \equiv \Gamma$.

^{†3} The order parameter can be represented as a plane-wave expansion $\Delta(r) = \sum_k A(k) e^{ikr} + A^*(k) e^{-ikr}$.

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

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

$$\text{We also have that } \sum_{r'} [V(r-r') + \frac{\beta \delta_{rr'}}{x(1-x)}] e^{ik(r-r')} = V(k) + \frac{\beta}{x(1-x)}.$$

As the terms with $A^2(k)$ and c.c. are equal to zero because $\sum_r e^{\pm 2ikr} = 0$, so that we have the change of the Gibbs energy of mixing as follows

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

When the temperature T is equal to the critical temperature $T_c(k)$ of the order-disorder transition, we get $\Delta F=0$ and thus equation (S8).

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

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

where $D = D_0 \exp(-E_m/k_B T)$ is the diffusion coefficient, E_m the activation energy for atomic diffusion (or enthalpy of vacancy migration), and D_0 the pre-exponential factor. Therefore, equation (S9) can be rewritten as

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

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

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

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

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

where $c_{eq}(T) = \exp(-E_v/k_B T)$ is the equilibrium vacancy concentration, 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 (2) 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 $E = E_m + E_v$.

References

1. Metiu H, Kitahara K, Ross J. Stochastic theory of the kinetics of phase transitions. *J Chem Phys*, **64**, 292–299 (1976).
2. Salje E. Kinetic rate laws as derived from order parameter theory I: Theoretical concepts. *Phys Chem Min*, **15**, 336–348 (1998).
3. Martin G. Relaxation rate of conserved and non conserved order parameters in replacive transitions. *Phys Rev B* **50**, 12362–12366 (1994).
4. Khachaturyan A G. Ordering in substitutional and interstitial solid solutions. *Prog Mater Sci* **22**, 1–150 (1978).