Journal of Magnetism and Magnetic Materials 453 (2018) 67–77

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Research articles

Lattice dynamics, elasticity and magnetic abnormality in ordered crystalline alloys Fe_3Pt at high pressures

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ARTICLE INFO

Article history:
Received 22 March 2017
Received in revised form 5 September 2017
Accepted 2 January 2018
Available online 6 January 2018

Keywords:
Ferromagnetic collapse critical pressure
Soft mode phase transitions
Lattice dynamics
Elastic modulus
Magnetism
Crystalline Invar alloy Fe_3Pt

ABSTRACT

The ordered crystalline Invar alloy Fe_3Pt is in a special magnetic critical state, under which the lattice dynamic stability of the system is extremely sensitive to external pressures. We studied the pressure dependence of enthalpy and magnetism of Fe_3Pt in different crystalline alloys by using the first-principles projector augmented-wave method based on the density functional theory. Results show that the *P*4/*mbm* structure is the ground state structure and is more stable relative to other structures at pressures below 18.54 GPa. The total magnetic moments of $L1_2$, *I*4/*mmm* and DO_{22} structures decrease rapidly with pressure and oscillate near the ferromagnetic collapse critical pressure. At the pressure of 43 GPa, the ferrimagnetic property in DO_{22} structure becomes apparently strengthened and its volume increases rapidly. The lattice dynamics calculation for $L1_2$ structures at high pressures shows that the spontaneous magnetization of the system in ferromagnetic states induces the softening of the transverse acoustic phonon TA1 (M), and there exists a strong spontaneous volume magnetostriction at pressures below 26.95 GPa. Especially, the lattice dynamics stability is sensitive to pressure, in the pressure range between the ferromagnetic collapse critical pressure (41.9 GPa) and the magnetism completely disappearing pressure (57.25 GPa), and near the pressure of phase transition from $L1_2$ to *P*4/*mbm* structure (27.27 GPa). Moreover, the instability of magnetic structure leads to a prominent elastic modulus oscillation, and the spin polarizability of electrons near the Fermi level is very sensitive to pressures in that the pressure range. The pressure induces the stability of the phonon spectra of the system at pressures above 57.25 GPa.

1. Introduction

Both of Fe-rich alloys Fe-Pt and Fe-Ni exhibit Invar effect, but Fe-Pt alloys are different in some physical properties from Fe-Ni alloys [1]. In Fe-Ni Invar alloys, the deviation of the concentration dependence of the lattice constant and magnetic moment from the Vegard law and the Slater-Pauling curve is observed, while no such deviations occur in Fe-Pt Invar alloys. In addition, in Fe-Ni Invar alloys, both magnetic atoms (Fe, Ni) have contributions to the magnetism of the system, and the itinerant nature of the valence electrons makes a major contribution. However, the magnetism is mainly induced by Fe atoms in Fe-Pt Invar alloys, Pt atoms exhibit paramagnetic properties, and the magnetism of system mainly relates to the localization of valence electrons.

The specific heat of Invar alloys is expressed as $C_P = \gamma T + \beta T^3 + \delta T^{3/2}$. The first item γT is the electronic contribution to the specific heat, where the coefficient $\gamma = \frac{1}{3}\pi^2 k_B^2 N(E_F)$ increases significantly near the Invar composition, which indicates that the ground state structure of Invar alloys is unstable. In general, the structural stabilization is closely related to the electronic density of states $N(E_F)$ in the position of the Fermi level (E_F) for binary alloys [2], that is, if the E_F falls on the valley which separates bonding states from the antibonding/nonbonding states (namely $N(E_F)$ value is very small), the ground state structure is more stable, while the ground state structure might be unstable if the E_F lies at the peak position (In the case of metastable phases or martensitic transformation in materials, structural stability does not comply with the above correlation criterion [3,4]). The second term βT^3 of the above specific heat expression is the lattice dynamical contribution to the specific heat. Wassermann et al. [5] have measured the specific heat of Fe-Pt Invar alloys using a quasi-adiabatic method at low temperatures and revealed that the coefficient

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https://doi.org/10.1016/j.jmmm.2018.01.008
0304-8853/

$\beta = \frac{12}{5}\pi^4 N k_B (1/\Theta_D)^3$ increases near the Invar composition. This indicates that the Debye temperature Θ_D of materials decreases as the Invar effect becomes lower. Therefore, it is necessary to study the Invar effect of the Fe-Pt crystalline alloys from lattice dynamics. Endoh, Tajima and Ishikawa et al. [6–9] have reported the measurements on the temperature dependence of phonon dispersion in ordered Fe-Pt and Fe-Ni Invar alloys by inelastic neutron scattering, and found obvious softening of the phonons below the Curie temperature T_c, which corresponds to the elastic softening of Invar alloys. Endoh et al. [6–8] have proposed that the phonon softening of Invar alloys results from the enhancement of electron-phonon coupling caused by the high density of the states of d electrons near the Fermi level. The third item $\delta T^{3/2}$ of the above specific heat expression is associated with the excitation of spin waves, in which the coefficient is $\delta = 0.113 k_B^{5/2} D^{-3/2}$. Ishikawa et al. [9] have found the abnormal behavior of the spin wave stiffness coefficient, that is $D_s \neq D_m$, where D_s is the spin wave stiffness coefficient determined by neutron scattering, and D_s is the one as deduced from the temperature dependence of the magnetization for crystalline ferromagnetic Invar alloys, while in non-Invar alloys $D_s = D_m$. Xianyu et al. [10,11] have measured the generalized phonon density of states (PDOS) of the amorphous $Fe_{86}Co_4Zr_{10}$ Invar alloy by inelastic neutron scattering, and found that the PDOS in the low-energy region becomes soft below the Curie temperature. They explained this phenomenon by the electron-phonon interaction, and proposed that the phonon excitation may cause "magnetic moment effect" that hints the existence of "magnon-phonon interaction". In addition, Wiele et al. [12] have investigated the PDOS of Invar alloy $Fe_{72}Pt_{28}$ and its changes with temperatures, and found the softening phenomenon of the transverse acoustic phonon $TA_{[110]}$ mode near 7.5 meV.

In $Fe_{64}Ni_{36}$, $Fe_{72}Pt_{28}$ and other Invar alloys, the spin state transitions from a high-spin ferromagnetic state (the γ_2 state possess big volume and magnetic moment) at low pressure to a low-spin anti-ferromagnetic state (the γ_1 state possess small volume and magnetic moment) at intermediate pressure (5 GPa < P < 15 GPa) , and eventually to an nonmagnetic state with magnetic moment on iron collapsed at higher pressure (P > 15 GPa) were examined by the high-pressure X-ray diffraction, X-ray emission spectroscopy, as well as the ultrasonic measurement. The above observations support the 2γ-state hypothesis [1,13–16], and are consistent with the results obtained by Magnetic circular two color absorption spectrum (XMCD).

The work of Gruner et al. [17] in 2010 caught our attention. They have investigated the structural stability and lattice dynamics of ordered crystalline Fe_3(Ni, Pd, Pt) alloys under the normal pressure by using first principles based on density functional theory (DFT). However, they did not further investigate the lattice dynamics or other properties of the ferromagnetic ordered crystalline Fe_3-Pt alloy at high pressures. Therefore, in this paper, some physical properties of ferromagnetic ordered Fe_3Pt crystalline alloys have been systematically studied using DFT under high pressures, which is helpful to reveal the origin of the Invar effect of the Fe_3Pt crystalline alloy.

2. Computational details

The calculations were performed by using a first-principles plane-wave pseudo potential method based on DFT, implemented in the Vienna Ab initio Simulation Package (VASP) [18,19]. For the exchange correlation function of electrons, we used the Perdew-Burke-Ernzerhof (PBE) scheme of the generalized gradient approximation (GGA) [20]. The interaction between core and valence electrons was described by using the projected augmented wave (PAW) [21]. For Fe and Pt atoms, the valence electron configurations were set to be $3d^74s^1$ and $5d^9\,6s^1$, respectively. The relaxation of atoms used the method of first-ordered Methfessel-Paxton smearing method and the width of the smearing was 0.2 eV. The total energy was calculated by the linear tetrahedron method with BlÖchl corrections [22] to obtain higher accuracy. Spin polarization was considered in all calculations. The self-consistent convergence criteria of the energy for the relaxation of electrons and ions are 1×10^{-6} and 1×10^{-4} eV, and the forces convergence criterion was 1×10^{-7} eV/Å. The phonon dispersion relations were calculated by the supercell calculation method with a $3 \times 3 \times 3$ supercell, implemented in the PHONOPY [23] code, and a k mesh of $2 \times 2 \times 2$ is based on Monkhorst-Pack scheme.

For the phonon dispersion curves of the $L1_2$-Fe_3Pt alloy with the space group of $Pm\bar{3}m$ at 0 GPa, the imaginary frequency of the transverse acoustic phonon TA1 near symmetry point M (0.5 0.5 0) in the Brillouin zone (BZ) is treated by PHONOPY code, and the details were as follows. With respect to the supercell of $2 \times 2 \times 1$ (lattice constant $a = b = a_0 = 7.4810$ Å), we moved Fe atoms in the plane XY (namely plane [1 0 0]-[0 1 0]) along the direction of polarization vector corresponding with the imaginary frequency. When the movement reaches at $0.02159a_0$, the structure with the lowest total free energy was found, which corresponded to the tetragonal structure with the space group of $P4/mbm$.

The BZ was sampled by the Monkhorst-Pack scheme, and the integral grid was $12 \times 12 \times 12$ for $L1_2$-Fe_3Pt and $I4/mmm$-Fe_3Pt, $10 \times 10 \times 10$ for DO_3-Fe_3Pt ($Fm\bar{3}m$) and $L2_1$-Fe_3Pt ($Fm\bar{3}m$), $8 \times 8 \times 10$ for DO_{22}-Fe_3Pt ($I4/mmm$), and $8 \times 8 \times 11$ for $P4/mbm$-Fe_3Pt. The structures can be obtained in the way of replacing Al atoms or Mn atoms by Pt atoms, and other positions are replaced by Fe atoms in the face-centered cubic $L2_1$-Cu_2MnAl crystalline alloy. The cutoff energy for the plane-wave basis was tested with the convergence accuracy less than 2×10^{-3} eV, and was taken as 600 eV. The crystal structures information of different ordered crystalline alloys Fe_3Pt after optimization were listed in Table 1. It can be seen that our calculation results were in good agreement with the previous work [24–27], which indicated our calculations were reliable.

3. Results and discussion

Fig. 1(a) and (b) shows that the imaginary frequencies appear in phonon spectra at the main high-symmetry point M and the lines Z, Σ, Λ, T, S of BZ for crystalline ferromagnetic (considering the spin polarization of electrons) alloy $L1_2$-Fe_3Pt at 0 GPa, and the hybridization occurs between high-frequency optical phonons and low-frequency phonons. The analysis of phonon polarization vectors shows that the imaginary frequencies come from the transverse acoustic phonons, the twofold degenerate transverse acoustic (TA1, 2) phonon appears small imaginary frequency in line Λ (line G-R), and the imaginary frequency of acoustic phonon (TA1) at the point M is mainly caused by the relative vibration among Fe atoms at face centers (perpendicular to the crystal orientation [0 0 1] and across the plane (0, 0.5, 0.5)). In Fig. 1(c) and (d), all phonon spectra exhibit positive frequencies, which indicates the dynamical stability of $L1_2$-Fe_3Pt lattices without considering the electron spin polarization, and there is a clear gap between high-frequency optical phonons and low-frequency phonons. For the phonon density of states in Fig. 1(d), we find the contribution to the phonon density of states of low-frequency region (frequencies below 1.5 THz) mainly comes from the acoustic phonons. Acoustic phonons show the vibration information of the centroid of primitive cells. Since the atomic weight of Pt atoms is about 3.5 times larger than that of Fe atoms, so the main contribution to the phonon density of states of this region (frequencies below 1.5 THz)