

Basic and Applied Research of Transition-metal Based Magnetic Materials

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Various transition-metal magnetic materials have been investigated from basic and practical viewpoints. The concentration dependence of the Néel temperature T_N of Cr-based alloys is complicated. Cr-Si and Cr-Fe antiferromagnetic alloys show Invar characteristics in the ternary alloys. Fe-based amorphous alloys exhibit weak ferromagnetic properties, resulting in remarkable magnetovolume effects. The icosahedral quasicrystals containing Mn show a spin-glass behavior, in a similar manner as those of amorphous counterparts. Itinerant-electron metamagnetic transition occurs in $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$, accompanied by many drastic change in magnetic and elastic properties. These drastic changes are practically useful in the field magnetic refrigeration and linear magnetostriction. The magnitude of T_N of Mn-based γ -phase is increased by addition of Ir, Ru, Rh and the spin structures change, depending on temperature and composition. Several kinds of L1₀-type Mn alloys have a high value of T_N with a large magnetocrystalline anisotropy. The shift of the exchange-bias field for the collinear spin structure in L1₀-type phase is induced by spin frustration. L2₁- and B2-type Co₂CrGa metallurgical stable alloys exhibit a high spin polarization. Several kinds of L2₁-type and B2-type alloys show a large ferromagnetic shape memory effect associated with twin-boundary motions.

Key words: antiferromagnetic Invar alloy, weak ferromagnetic Fe-based amorphous alloy, quasicrystalline alloy, spin-glass, itinerant-electron metamagnetic transition, magnetic refrigerant, giant magnetostriction, exchange-bias field, half-metallicity, ferromagnetic shape memory alloy

1. Introduction

In the present article, I introduce my several research subjects for the MSJ Award 2016. I have engaged in basic and applied research for a variety of transition-metal magnetic materials during several decades. Listed below are our main subjects: antiferromagnetism and Invar characteristics of Cr-based alloys, weak ferromagnetic Fe-based amorphous alloys, Hall resistivity of amorphous alloys, comparison between magnetic properties in quasicrystalline and amorphous states of Al-based Mn alloys, perpendicular magnetic anisotropy of Tb-Fe bulk amorphous alloys, random magnetic anisotropy and coercive field of Fe-rare earth amorphous alloys, giant magnetoresistance effect in Cu-Co granular alloys, linear magnetostriction of Fe-Pd and Fe-Ga alloys,

itinerant-electron metamagnetism of Laves phase compounds and NaZn_{13} -type compounds exhibiting large magnetocaloric effects (MCE), spin fluctuations in β -Mn alloys, antiferromagnetism, magnetocrystalline anisotropy and exchange coupling in Mn alloys, magnetocrystalline anisotropy in Fe-Pd and Fe-Pt alloys, half-metallicity and magnetic-field induced shape memory effect in Heusler type alloys. These achievements have been contributed to publish several kinds of international monographs¹⁻⁸⁾. I present the results for the selected topics given in Fig. 1. The neighboring research fields in the figure share technical, magnetic and physical common terms, providing research continuity.

2. Explanation of main topics

2.1 Antiferromagnetism and Invar characteristics of Cr-based alloys.

Cr with a bcc structure orders antiferromagnetically in a spin-density-wave (SDW) structure below $T_N = 311$ K, showing a prototypical itinerant antiferromagnet. It has been pointed out that pure Cr indicates a weak first-order transition at T_N . Cr-based alloys exhibit three distinct ordered phases transverse SDW (AF₁), longitudinal SDW (AF₂), and commensurate SDW (AF₀). The magnetic phase diagrams for Cr-based alloys have been studied as functions of concentration, pressure, temperature, and magnetic field⁹⁾.

We investigated magnetic properties of a number of Cr-based alloys. The transition metals at the right of Cr in the periodic table, except for ferromagnetic

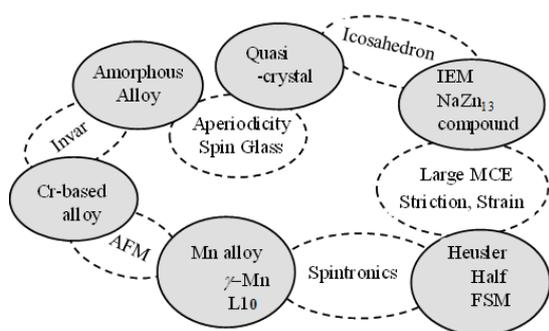


Fig.1 Correlation chart between several kinds of research topics in magnetism and magnetic materials.

elements Fe, Co and Ni, and paramagnetic Pd, increase T_N . While the transition metals at the left of Cr in the periodic table decrease T_N . For non-transition metal additions, such as Al (above 2%), Ga (above 1%), Ge, Sn, As and Sb increase T_N , although Si decreases it¹⁰.

The wave vector, Q , of the SDW is along one of the cube axes and is incommensurate with the periodicity of the lattice. The wavelength of the SDW is about 25 unit cells at room temperature and is temperature dependent. The $\langle 100 \rangle$ cross sections of the Fermi surface centered at Γ and H are the inter-sections of the octahedrons; the former is the electron octahedron and the latter the hole octahedron. The antiferromagnetic state is stabilized by the nesting due to the coulomb interaction between the Γ and H surfaces. When the SDW is shifted in the direction of $\langle 100 \rangle$, the wave vector Q is given as

$$Q_{\pm} = \frac{2\pi}{a}(1 \pm \delta), \quad (1)$$

where a is the lattice constant and δ is the nesting parameter^{11,12}. The value of δ increases with the introduction of the transition metals at the left of Cr in the periodic table, as for V and Ti, for example. Meanwhile, δ decreases and vanishes for certain concentration of metals, as with the introduction of 3d-metal impurities like Mn, Fe, Re, changing SDW to AF₀, i.e., $\delta = 0$.

The Néel temperature T_N , which is an experimental measure of stability of the SDW, is given by an equation of the form

$$T_N = T_0 \exp\left(-\frac{1}{\lambda}\right), \quad (2)$$

where T_0 is a function which depends on the band structure and

$$\lambda = \frac{\gamma^2 V(0)(k_c)^2}{2\pi^2 v}. \quad (3)$$

Here γ is the mean overlap matrix element for electrons in the same band, $V(0)$ the average screened Coulomb potential, k_c the wave vector in the first Brillouin zone and v is the arithmetic mean of the Fermi velocities in two bands. It is considered to be senseless to predict T_N from Eq. (2) because of the exponential dependence on some of the quantities involved¹¹. In such complicated circumstances, it is considered to be practically useful that Cr-Fe¹³) and Cr-Si¹⁴) alloys exhibit a strong first-order magnetic phase transition, accompanied by a large spontaneous volume magnetostriction below T_N in the AF₀ structure.

Before LCD (liquid crystal display), CRT (cathode ray tube display) had been used for long time. The CRT has an Invar alloy as a shadow mask. However, conventional Invar alloys are ferromagnetic, and then remanent magnetization and geomagnetism involve color drifts offensive to the eye. Therefore, development of non-ferromagnetic Invar alloys was a pressing issue at that time. The Invar characteristics, that is, a very low

thermal expansion is associated with the cancelation of the phonon part of thermal expansion by the spontaneous volume magnetostriction. Reducing the steep volume change by addition of the third element to Cr-Fe and Cr-Si binary alloys, Invar characteristics was obtained below T_N . Practically, we require to set Invar characteristics in the vicinity of room temperature. By changing the electron concentration, the value of T_N is tunable. From these data, we can make suitable non-ferromagnetic (\equiv antiferromagnetic) Invar alloys.

Figure 2 shows the thermal expansion curves of Cr-Fe-Mn alloys¹⁵). For comparison, we present the thermal expansion curve of a conventional Invar alloy

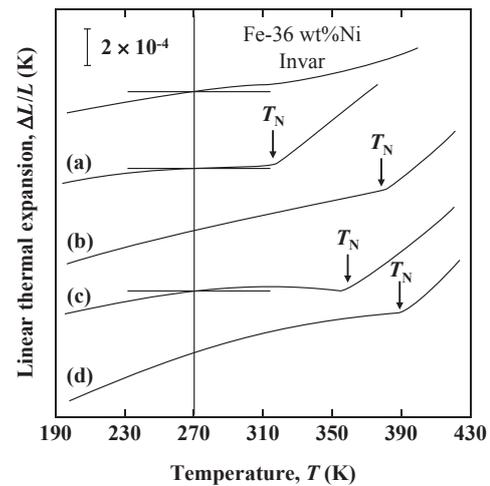


Fig. 2 Thermal expansion curves of Cr-Fe-Mn antiferromagnetic alloys, together with the curve of conventional Invar alloy (Fe-36 wt% Ni)¹⁵.

(a) Cr-5.5%Fe-0.5%Mn, (b) Cr-25.5%Fe-1.0%Mn, (c) Cr-4.3%Fe-0.5%Mn, (d) Cr-4.2%Fe-1.0%Mn.

(Fe-36%wt%Ni). It is clear that the curves of Cr-Fe-Mn alloys exhibit an excellent Invar characteristics. On the basis of data accumulation, we developed many kinds of Cr-Fe and Cr-Si based antiferromagnetic Invar-type ternary alloys^{10,16,17}). Figure 3 lists the possible combinations of elements, which are selected from the right upper grey area. In the figure, the dot-dashed line divides the border above which the Néel temperature T_N of Cr increases and below which it

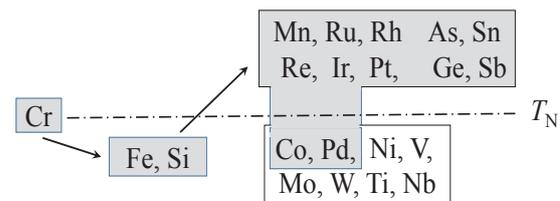


Fig.3 Combination of elements for Cr-based antiferromagnetic Invar-type ternary alloys^{10,16,17}.

decreases. What should be noted is that Co and Pd decrease T_N of Cr, yet increase T_N of Cr–Fe and Cr–Si alloys, exhibiting Invar characteristics around room temperature^{1,10}.

2.2. Weak ferromagnetic Fe-based amorphous alloys

2.2.1 Large magnetovolume and magnetoelastic properties of Fe-based amorphous alloys

Amorphous magnetic alloys provide many peculiar properties because of loss of lattice periodicity. Various amorphous alloys have been prepared by melt-quenching in a ribbon state and sputtering in a film state. Fe–metalloid systems in the equilibrium phase diagram have a relatively low eutectic point, showing an excellent forming-ability of amorphous ribbons. The striking aspect is that the number of nearest-neighbor atom in transition metal–metalloid systems is estimated to be about 13, being very close to that of the fcc lattice. Concentration dependence of the magnetic moment per Fe atom for amorphous Fe–B alloys is not monotonic and a maximum occurs around 14 at% boron¹⁸, but then the Curie temperature T_C decreases with a decrease in the boron content. Such peculiar concentration dependences are similar to those of Fe–Ni fcc alloys which are classified as weak ferromagnets with an incomplete filling of up-spin band, resulting in Invar effects such as a low thermal expansion and a strong pressure effect on the Curie temperature T_C .

On thermal expansion curves of amorphous Fe–B and Fe–P alloys, a large anomaly due to a remarkable spontaneous volume magnetostriction is observed in a wide temperature range below the Curie temperature T_C ¹⁸. For Fe₈₃B₁₇ alloy, the value of the spontaneous volume magnetostriction ω_s estimated from the thermal expansion curve is about 1×10^{-2} , being of the same of magnitude as that of crystalline Fe–Ni Invar alloys. In addition, the pressure coefficient of the Curie temperature, $\partial T_C / \partial P$, is very large negative; the largest negative value is of about -7 K/kbar, corresponding to that of Fe₇₁Ni₂₉ crystalline fcc alloy. According to Wohlfarth's theory on very weak itinerant ferromagnetism¹⁹, the pressure effect on T_C is given by

$$\frac{\partial T_C}{\partial P} = -\frac{A}{T_C}, \quad (4)$$

where the parameter A is proportional to the density of states, compressibility, effective degeneracy temperature and the Bohr magneton. The data of Fe–Ni crystalline Invar alloys are in line with $A = 2050$ K²/kbar, and these of Fe–B amorphous alloys fit approximately with $A = 3500$ K²/kbar. The compressibility κ calculated from the shear modulus and Young's modulus for Fe–B alloys is larger than that of Fe–Ni crystalline Invar alloys. That is, the value of the former is larger than that of the latter value by a factor of about 1.7²⁰. This result is qualitatively consistent with Wohlfarth's theory because the value of A in Eq. (4) is proportional to κ .

Hitherto we have demonstrated that the magnetic properties of Fe–B amorphous Invar alloys are very similar to those of Fe–Ni crystalline Invar alloys. It has been well that Invar behavior of Fe–Ni crystalline alloys is very complicated at lower Ni concentrations because of the occurrence of a martensitic transformation. On the other hand, the magnetic properties of amorphous alloys are studied without taking such a complicated effect into consideration, because amorphous alloys involve no martensitic transformation. Accordingly, these results exclude a conventional explanation of the origin of Invar effects associated with the pre-martensitic transformation.

It is notable point that Fe–B amorphous alloys also exhibit a remarkably large ΔE effect defined as $\Delta E/E_0$ with $\Delta E = E_s - E_0$, where E_s and E_0 are Young's moduli in saturating field and in zero magnetic field, respectively. This effect is responsible for the Elinvar characteristics²¹. The temperature coefficient of the delay time t of delay lines is expressed as

$$t = -\frac{1}{2}(\alpha + e), \quad (5)$$

where α and e are the temperature coefficients of thermal expansion and Young's modulus, respectively. Fe–B amorphous alloys indicate a very small temperature coefficient of the delay time, because they have the Invar and Elinvar characteristics at the same temperature, in contrast to Fe–Ni crystalline Invar alloys which exhibit a large value of e at room temperature.

2.2.2 Forming-ability and weak ferromagnetism and spin-glass behavior of E–Fe alloy systems

There are several kinds of electron theories for forming-ability of amorphous films. According to Moruzzi et al, theory²², a high Fermi level state density means a lack of structural stability, resulting in an amorphous state. In the case of early transition metal (E)–Fe systems, the larger the atomic size difference becomes, the higher the Fermi level becomes²³. We systematically investigated the lower limit of solute elements vs. the size difference ratio between Fe and the solute element. It was pointed out that the lower limit of forming-ability of amorphous films depends not only on the size difference ratio but also on the valence difference between E and Fe^{3,24}. That is, the lower limit shifts to lower concentration ranges with increasing values of the size and valence differences. The energy separation in the density of state is roughly proportional to the valence difference and leads to the gradual formation of a well-defined gap for compounds²²; namely, split-band state densities are formed by constituents with large valence differences, leading to the stabilization of an amorphous phase. Therefore, the effect of the size difference on the forming-ability is explained by the theory proposed by Moruzzi et al.

In Friedel's model²⁵ which is valid in the strong

ferromagnetic situation, the charge displaced by the early transition metal atom is related to the magnetization change by the simple formula $10-\Delta z$, where Δz is the host-solute valence difference. If the assumptions underlying this simple relation were obeyed over the entire concentration range, then the concentration dependence of the average moment $\bar{\mu}$ is defined as

$$\bar{\mu} = \mu_0 - x(10 - \Delta z), \quad (6)$$

where x is the atom fraction and μ_0 is the host moment at $x=0$. Friedel's formula Eq. (6) follows from the assumption that the repulsive solute potential displaces precisely five majority-spin states from below to above the Fermi level E_F . Implicit in the Friedel formula, therefore, is the assumption that the state density immediately above the d -bands of the paramagnetic host is negligible; this assumption is a necessary condition for strong magnetism. Figure 4 displays the concentration dependence of the mean magnetic moment $\bar{\mu}$ of $E_x\text{Fe}_{1-x}$ with $E = \text{Lu, Y, Th, Hf, Zr, Ti, Ta, Nb, V}$ ²⁶. The value of $\bar{\mu}$ becomes larger as the differences of the atomic size and the valence between E and Fe increases. Such a systematic tendency is explained from the band calculation²³. In the figure, three dotted straight lines indicate the expected line from Friedel's model which is valid for strong ferromagnets. Since the observed values are smaller than the expected values of dotted straight lines, $E_x\text{Fe}_{1-x}$ amorphous systems are regarded as weak ferromagnets which have holes in both d -bands.

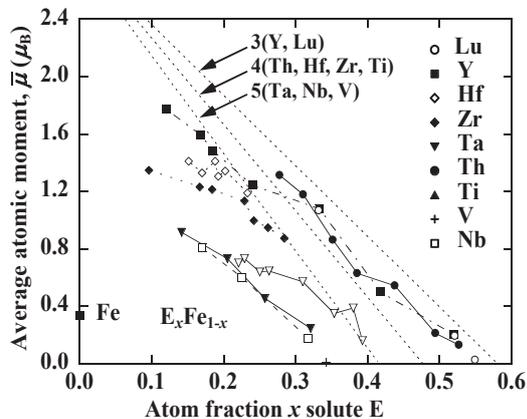


Fig.4 Average low temperature magnetic moment $\bar{\mu}$ of amorphous Fe alloys with many kinds of early transition metal solutes (E) as a function of atomic fraction x ²⁶.

The Curie temperature T_C of $E_x\text{Fe}_{1-x}$ amorphous films with $E=\text{La, Lu, Ce, Hf}$ and Zr exhibits a broad maximum at $x=0.2$ and the ferromagnetic state disappears around $x=0.1$, resulting in a spin-glass state below about 110 K^{3,27}. This spin-glass state is caused by spin frustrations in the magnetically concentrated $E_x\text{Fe}_{1-x}$

amorphous alloys. It is meaningful to note that the nearest neighbor distance of Fe , $d_{\text{Fe-Fe}}$, is about 2.5 \AA ²⁸, very close to the critical distance of ferromagnetic and antiferromagnetic interactions.

2.3 Comparison between magnetic properties in quasicrystalline and amorphous states of Al-based Mn alloys

Electron diffraction studies revealed that Al-Mn quenched alloys exhibit sharp spots with five-fold symmetry axes²⁹. This discovery contradicts a well-known crystallographic theorem which states that five-fold symmetry axes can never appear in substances having a truly long-range periodicity. A quasiperiodic crystal, or quasicrystal, is a structure that is ordered but not periodic. A quasicrystalline pattern can continuously fill all available space, but it lacks translational symmetry. While crystals, according to the classical crystallographic restriction theorem, can possess only two, three, four, and six-fold rotational symmetries, the Bragg diffraction pattern of quasicrystals shows sharp peaks with other symmetry orders, for instance five-fold.

It has been pointed out that computer simulations of the supercooled Lennard Jones pair potential suggest the existence of bond orientation order in liquids³⁰. Because icosahedral clusters which are composed of 13 atoms have a significantly lower energy compared with that of nuclei of fcc and hcp crystals, icosahedra should be prevalent in liquids near the melting temperature^{31,32}. It has been remarked that an amorphous Lennard-Jones packing has about 32% of its atoms on icosahedral sites³³, and the scattering patterns observed in several amorphous alloys are quite similar to those from icosahedral clusters. The sign of the exchange interaction oscillates between positive and negative depending on the Mn-Mn distance. It is therefore interesting to study the magnetic properties of quasicrystalline and amorphous alloys containing Mn.

We investigated magnetic properties of Al-Cu-TM and Al-Pd-TM (TM: transition metal) quasicrystalline alloys^{4,34}. The difference between the quasicrystalline alloys and their amorphous counterparts for magnetic properties was confirmed in Al-Cu-Mn and Al-Pd-Mn alloy systems in contrast to Al-Mn alloy system.

The magnetization is much smaller than the value expected from the effective magnetic moment P_{eff} (μ_B), indicating that the magnitude of magnetic moment is not uniform, depending on the Mn sites in the quasicrystalline phase. From many kinds of experiments, it was confirmed that there are magnetic and non-magnetic Mn atoms. The Curie constant C is written as

$$C = \frac{N\mu_B^2 \langle P_c \rangle (\langle P_c \rangle + 2)}{3k_B}, \quad (7)$$

where N is the atomic number³⁵. The average local

Table 1 The ratio of magnetic Mn atoms, X_m/X , the effective magnetic moment P_{eff} , the spin freezing temperature T_f for Al₈₅Mn₁₅, Al₆₅Cu₂₀Mn₁₅ and Al₆₅Pd₂₀Mn₁₅ alloys in icosahedral quasi-crystalline (Q) and amorphous (A) states^{34,36}.

Alloy	X_m/X (%)	$P_{\text{eff}} (\mu_B)$	T_f (K)
Q-Al ₈₅ Mn ₁₅	~9*	0.59	–
A-Al ₈₅ Mn ₁₅	~9*	0.59	–
Q-Al ₆₅ Cu ₂₀ Mn ₁₅	8.9	1.56	6.1
A-Al ₆₅ Cu ₂₀ Mn ₁₅	18.7	2.24	8.1
Q-Al ₆₅ Pd ₂₀ Mn ₁₅	9.3	2.25	10.0
A-Al ₆₅ Pd ₂₀ Mn ₁₅	18.7	2.54	13.9

*: extrapolated from the high Mn concentration range

magnetic moment per Mn atom, $\langle P_c \rangle$, which corresponds to the saturation magnetization is deduced from the Curie constant by assuming g factor to be 2. Using the values of the Curie constant, C , and the saturation magnetization per Mn atom, M_s , one can evaluate the atomic fraction, X_m from the following relations³⁵:

$$M_s \left(\frac{X}{X_m} M_s + 2\mu_B \right) = \frac{3k_B C}{N}. \quad (8)$$

Comparing with the same magnitude of $P_{\text{eff}} (\mu_B)$, the composition of Mn for Al–Mn is much higher than that for the other two alloy systems, suggesting that the formation of the localized magnetic moment in Al–Mn is much difficult than in the latter systems. The value of $P_{\text{eff}} (\mu_B)$ of Al–Mn in the amorphous (A) and quasicrystalline (Q) states is the same each other. However, the difference between the amorphous (A) and quasicrystalline (Q) states for Al–Cu–Mn and Al–Pd–Mn alloy systems is distinct as seen from Table 1³⁴. Note that the latter two alloy systems contain Cu or Pd in which the localized magnetic moment is easily established. In Table 1, the ratios of magnetic Mn atoms X_m/X in Al–Cu–Mn and Al–Pd–Mn quasicrystalline alloys are about one half that of the amorphous counterparts, although there is no essential distinction in Al–Mn alloy systems^{34,36}. The spin-glass behavior has been confirmed in both Al–Cu–Mn and Al–Pd–Mn alloy systems even below 15 %Mn, although Al–Mn alloys exhibit the spin-glass behavior above 20 %Mn. In addition, it is a noteworthy fact that Al₇₀Pd₁₅Mn₁₅ quasicrystalline alloy has a giant magnetic moment in a similar manner as Pd–Mn crystalline dilute alloys. The difference between the A- and Q-state of the spin-glass freezing temperature T_f , and the ratio of magnetic Mn atom as well, arises from the looser packing structure of the A-state, resulting in a larger Mn–Mn distance.

2.4 Itinerant-electron metamagnetism of NaZn₁₃-type compounds

2.4.1 Giant magnetocaloric and magnetostriction of La(Fe_xSi_{1-x})₁₃ system

The itinerant-electron metamagnetic (IEM) transition is the field-induced first-order transition from the paramagnetic (PM) to the ferromagnetic (FM) state in the itinerant-electron system. Wohlfarth and Rhodes³⁷ first discussed it on a phenomenological Landau theory. The relation between the magnetic free energy $F(M)$ and the magnetization M is given as

$$F(M) = \frac{1}{2}aM^2 + \frac{1}{4}bM^4 + \frac{1}{6}cM^6, \quad (9)$$

where the Landau expansion coefficients a , b and c are related to the $3d$ -electron band structures at the Fermi level E_F . The conditions of $a > 0$, $b < 0$, and $c > 0$ with $3/16 < ac/b^2 < 9/20$ are essential for the metamagnetic transition. The IEM transition is related to the onset of the exchange splitting in the band structure by applying magnetic field. This metamagnetic transition is termed 'Itinerant-electron metamagnetism (IEM)', different from a conventional metamagnetism in the localized electron system, where the metamagnetic transition (MT) takes place from the AFM to the FM state. We experimentally confirmed for the first time by using pulsed ultra-high magnetic fields that the values of the critical field for the metamagnetic transition of exchange-enhanced para-magnets YCo₂ and LuCo₂ Laves phase compounds are 69 and 71 T, respectively³⁸. These values are relatively smaller than the theoretical values, which is reasonably explained by taking into magnetovolume effect. Furthermore, the IEM transition phase diagrams of quasi-binary systems of Y(Co_{1-x}M_x)₂ and Lu(Co_{1-x}M_x)₂ (M: Al, Ga, Si)³⁹ are consistent with the theoretical phase diagram obtained by taking into the effect of spin fluctuations⁴⁰.

La(Fe_xAl_{1-x})₁₃ compounds crystallize in the cubic NaZn₁₃-type structure composed of icosahedral clusters referred in Section 2.3 with two crystallographic sites: 8b and 96i. The 8b site at the center of the icosahedral cluster is occupied by Fe^I atom only. The 96i sites at the apex of the icosahedron are randomly occupied by Fe^{II} atoms and Al atoms⁴¹. In these compounds, the high coordination numbers of Fe atoms and the shortest Fe–Fe interatomic distance of $d_{\text{Fe-Fe}} \approx 2.5 \text{ \AA}$ are realized. Such a densely packed structure with Fe atoms results in a variety of magnetic states with a different volume related to the itinerancy of Fe $3d$ -electron⁴². Note that the icosahedra exist even in La(Fe_xAl_{1-x})₁₃ in the amorphous state⁵. Furthermore, we demonstrated that La(Fe_xSi_{1-x})₁₃ compounds exhibit the IEM transition⁴³. The IEM transition is accompanied by drastic changes in magnetic and elastic properties due to the first-order phase transition. These changes are very attractive from the practical point of view. The cubic NaZn₁₃-type

La(Fe_xSi_{1-x})₁₃ compounds (space group Fm $\bar{3}c$) have a ferromagnetic ground state. In the concentration 0.86 ≤ x ≤ 0.90, the field-induced first-order magnetic transition between the ferromagnetic (FM) and paramagnetic (PM) states, that is, the itinerant-electron metamagnetic (IEM) transition, takes place above the Curie temperature T_C . We have pointed out that this IEM transition causes a large isothermal magnetic entropy change ΔS_m and a large adiabatic temperature change ΔT_{ad} ⁴⁴.

In principle, the magnetic cooling system is equivalent to conventional gas cooling systems. That is, thermodynamic parameters V (volume) corresponds to $-M$ (magnetization) and P (pressure) is changed by H (magnetic field). Therefore, the Maxwell relation is given by the following expression:

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H, \quad (10)$$

and hence the isothermal magnetic entropy change ΔS_m is expressed as

$$\Delta S_m = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \quad (11)$$

From Eq. (11), it is expected that the magnitude of ΔS_m becomes very large when the magnetic transition is of first-order. Be aware that the magnetization change at the first-order transition is ideally discontinuous, and then the value of $\partial M/\partial T$ does not exist. Under such a condition, ΔS_m should be calculated by the Clausius-Clapeyron equation given by the following equation:

$$\left|\frac{\Delta T}{\Delta H_c}\right| = \left|\frac{\Delta M}{\Delta S}\right|, \quad (12)$$

where ΔM is the difference between magnetization before and after the discontinuity for a given T , ΔH_c is the shift of critical field from ΔT and ΔS is the difference between the entropies of the two phases. In experiments, however, a complete discontinuous magnetization data at the first-order transition temperature is scarcely obtained due to frozen disorders⁴⁵. Figure 5 illustrates the temperature dependence of ΔS_m in the magnetic field change from 0 to 5 T ($\mu_0\Delta H = 5$ T) obtained by using Eq. (11) for La(Fe_{0.88}Si_{0.12})₁₃ compound⁴⁴. The value of $\partial M/\partial T$ exhibits a large value around T_C because of the thermal-induced first-order transition, and T_C is increased by the magnetic field, keeping a large value of $\partial M/\partial T$. Consequently, ΔS_m in $\mu_0\Delta H = 5$ T indicates a negative maximum value of 22.3 J/kgK at $T_C = 195$ K. Note that the magnitude of ΔS_m obtained from Eq.(11) is comparable with that calculated from Eq. (12). The adiabatic temperature change ΔT_{ad} is obtained from

$$\begin{aligned} \Delta T_{ad} &= - \int_0^H \frac{T}{C_H} \left(\frac{\partial M}{\partial T}\right)_H dH \\ &= [T(S)_H - T(S)_0]_S \cong \frac{T}{C_t} \Delta S_m, \end{aligned} \quad (13)$$

where $C_H = T(\partial S/\partial T)_H$ and C_t are the heat capacity in the

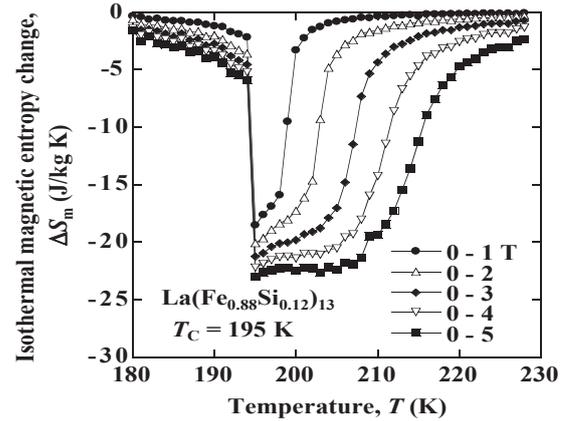


Fig. 5 Temperature dependence of the isothermal magnetic entropy change ΔS_m for La(Fe_{0.88}Si_{0.12})₁₃ compound⁴⁴.

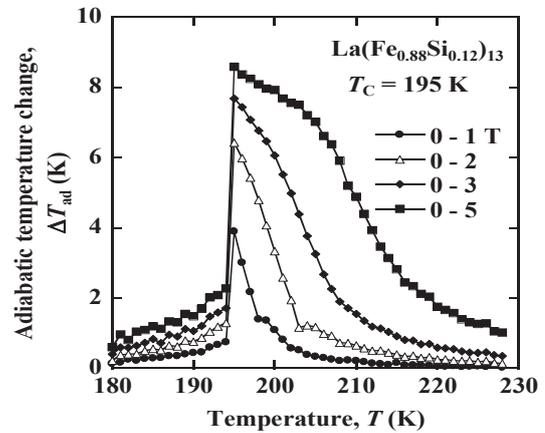


Fig. 6 Temperature dependence of the adiabatic temperature change ΔT_{ad} for La(Fe_{0.88}Si_{0.12})₁₃ compound⁴⁴.

magnetic field and the total heat capacity, respectively. Figure 6 shows the temperature dependence of ΔT_{ad} in $\mu_0\Delta H = 1-5$ T for La(Fe_{0.88}Si_{0.12})₁₃ compound⁴⁴. The value of ΔT_{ad} exhibits a large peak above T_C and the maximum value of ΔT_{ad} is 8.6 K in $\mu_0\Delta H = 5$ T at 195 K.

The value of T_C of La(Fe_xSi_{1-x})₁₃ compounds is increased significantly by hydrogen absorption, accompanied by a marked volume expansion⁴⁴. The cubic NaZn₁₃-type structure is kept after hydrogen absorption. Furthermore, the thermomagnetization curves still exhibit a significant magnetization change around T_C , because the thermal-induced first-order transition is maintained after hydrogen absorption⁴⁴. The magnitude of $\partial M/\partial T$ around $T_C = 323$ K for the compound with hydrogen concentration $y = 1.5$ is almost the same as that of the compound with $y = 0.0$ and $T_C = 195$ K. After annealing at about 400 K, T_C is hardly changed, and hence the desorption of the hydrogen for La(Fe_{0.88}Si_{0.12})₁₃H_y compounds scarcely proceeds below 400 K, because T_C is significantly sensitive to y .

Furthermore, tuning T_C by adjusting constituent elements, we can set up magnetic refrigerator systems in a wide working temperature range from 60 to 340 K⁴⁶. From these data, it is concluded that $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ and their modified compounds are promising magnetic refrigerants.

2.4.2 Isotropic volume magnetostriction

It has been pointed out theoretically that the onset of the magnetic moment accompanied by the IEM transition results in a volume change due to the magnetovolume effect. For $x=0.88$, the magnetic moment caused by the IEM transition exceeds $1 \mu_B$ and results in a huge positive volume magnetostriction of about 1.5% just above T_C ⁴⁷. The volume magnetostriction ω_s of the IEM transition is due to the onset of magnetic moment caused by exchange splitting of $3d$ -electron bands and given as⁴⁸

$$\omega_s(T) = \kappa C_{mv} \{M(T)^2 + \xi_p(T)^2\}, \quad (14)$$

where κ is the compressibility and C_{mv} is the magnetovolume coupling constant. The mean square amplitude of spin fluctuation is given by $\xi_p(T)^2$. The origin of the huge magnetostriction in $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ compounds is correlated with electronic state of $3d$ -electrons of Fe, different from the single-ion magnetoelastic coupling in TbFe_2 -based magnetostrictive materials. Therefore, it is expected that $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}$ compounds are candidates as new-type high performance magnetostrictive materials. It is notable that the transition field of the IEM transition at T_C equals zero and increases with temperature.

The maximum value of thermal expansivity, $\Delta L/L$, of $\text{La}(\text{Fe}_{0.88}\text{Si}_{0.12})_{13}$ compound greatly exceeds the value of $\Delta L/L$ of the polycrystalline TbFe_2 compound. As is well known, TbFe_2 -based magnetostrictive materials exhibit a large $\lambda_{//} - \lambda_{\perp}$, while the volume change $\lambda_{//} + 2\lambda_{\perp}$ is nearly zero and the magnetostrictive properties are anisotropic. These anisotropic magnetostrictive properties of TbFe_2 compound are mainly originated from the rotation of the localized magnetic moment of Tb. The polarization of $3d$ -electron bands causes a volume change proportional to the square of the local magnetization as given Eq. (14) and not only $\lambda_{//} - \lambda_{\perp}$ but also $\lambda_{//} + 2\lambda_{\perp}$ has finite values. A spontaneous volume change of 1.2 % occurs sharply at T_C and the value of three times of $\Delta L/L$ is very close to that of the volume change at T_C . Therefore, these results indicate that the volume magnetostriction is due to the transition from the PM phase with a small volume to the FM phase with a large volume and its volume change is almost isotropic⁴⁷. Such isotropic magnetostrictive properties are very attractive compared to those of TbFe_2 -based anisotropic magnetostrictive materials, because a huge magnetostriction can be obtained even in a poly-crystalline state. Accordingly, no crystallographic texture control such as directional solidification is essential. It is necessary to adjust the Curie

temperature in order to obtain a huge magnetostriction in low fields around room temperature. It is notable that an isotropic giant linear magnetostriction due to the IEM transition for $\text{La}(\text{Fe}_x\text{Si}_{1-x})_{13}\text{H}_y$ compounds is also observed in the vicinity of room temperature⁴⁹.

2.5 Antiferromagnetism, magnetocrystalline anisotropy and exchange coupling in Mn alloys

2.5.1 Mn rich disordered (γ -Mn) and ordered L_{12} alloys

Practically, the giant magnetoresistance (GMR) and tunnel magnetoresistance (TMR) are very important for electronic and magnetic devices such as magnetic recording heads and magnetic random access memory (MRAM) cells. There are many systems having a complex (non-collinear) spin structure, depending on the d -electron number and the crystal structure associated with the geometrical frustration of magnetic moments. Exchange-biasing characteristics and the blocking temperature are closely correlated with the spin structures and the magnitude of the Néel temperature T_N .

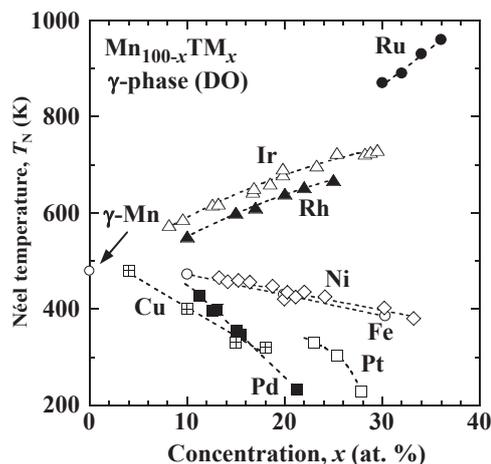


Fig. 7 Concentration dependence of the Néel temperature, T_N , for the disordered γ (fcc)-phase $\text{Mn}_{100-x}\text{TM}_x$ alloys (TM=Ir, Ru, Rh, Ni, Fe, Pt, Pd and Cu)^{7,8,50}.

The γ (fcc)-phase disordered (DO) Mn-based alloys are stabilized by several kinds of additional elements in analogy with Fe-based γ -phase alloys. The concentration dependence of T_N of $\text{Mn}_{100-x}\text{TM}_x$ γ -phase disordered alloy systems (TM: Transition Metal) is gathered in Fig. 7^{7,8,50}. The value of γ -Mn pure metal is added in the same figure, for comparison. The lower the electron concentration, and also the larger the atomic size of additive elements such as Ru, Rh and Ir, the higher the Néel temperature T_N becomes. What has to be noticed is that the magnitude of for the disordered γ -phase Mn–Rh and Mn–Ir alloys is lower by 150–200 K than that for ordered L_{12} -type ($\equiv \text{Cu}_3\text{Au}$ -type) counterparts, depending on the alloying element and its composition.

In the 1Q and 2Q SDW structures in γ (fcc)-phase disordered Mn-based alloys, the magnetic moment points to the parallel and the perpendicular to the c -axis, respectively. Take heed that the angles θ and ϕ are defined individually for each site. When ϕ is settled at 45 degrees, $\theta=0$, $\theta=90$ and $\theta=\cos^{-1}(1/\sqrt{3})=54.7$ degrees correspond to the so-called 1Q, 2Q and 3Q SDW structures (see the top panel of Fig. 9), respectively, which are labeled multiple-Q SDW structures. In the γ -phase disordered Mn alloys, the 1Q, 2Q and 3Q SDW structures are observed by changing temperature and/or composition^{7,8,50}.

2.5.2 L1₀-type Mn alloys and exchange coupling

In the vicinity of the equiatomic concentration, Mn forms alloys with Ni, Pd, Pt, Rh and Ir in a wide range of concentration. The crystal structure of these alloys is a B2 (CsCl)-type cubic phase at high temperatures and transforms into an L1₀ (CuAu-1)-type tetragonal phase with a diffusionless martensitic transformation process at low temperatures^{8,50}. The L1₀-type phase has a collinear antiferromagnetic structure (AF-1) and MnNi, MnPd and MnPt equiatomic alloys indicate a very high Néel temperature T_N of about 1100, 780 and 970 K, respectively^{8,50}. Due to such a high stability of antiferromagnetism, especially, MnPt alloy has been investigated intensively from the viewpoint of practical applications as antiferromagnetic pinning layers of GMR and TMR devices. Moreover, the linearized muffin-tin orbitals (LMTO) band calculations including the spin-orbit interaction were performed for MnPt in order to investigate the magnetocrystalline anisotropy energy (MAE) because it plays an important role in the exchange-bias field in spin valves. By using the force theorem, the MAE is obtained from the following expression:

$$\Delta E_{\text{MAE}} = E[100] - E[001], \quad (15)$$

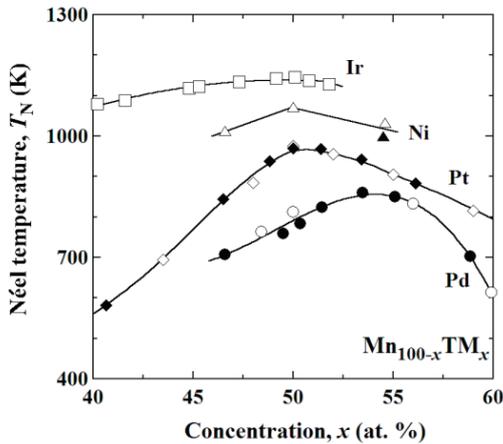


Fig. 8 Concentration dependence of the Néel temperature, T_N , for the L1₀-type Mn_{100-x}TM_x alloys (TM: Ir, Ni, Pt and Pd)^{7,8,50}.

where $E[l]$ is the sum of the eigenvalues of the Kohn–Sham equation⁵² when the magnetic moment is parallel to the crystal axis $[l]$ in the L1₀-type structure. The magnetocrystalline anisotropy constant of MnPt equiatomic alloy is calculated to be about $1.39 \times 10^6 \text{ Jm}^{-3}$, larger in magnitude with the positive sign larger than that with the negative sign of MnNi equiatomic alloy⁵¹. Plotted in Fig. 8 is the concentration dependence of T_N of L1₀-type ordered MnIr, MnNi, MnPt and MnPd alloys^{8,50}. The MnIr alloy system exhibits the highest value of T_N in the whole concentration range. In addition, attention should be paid to that the concentration dependence of T_N for this alloy system is not so sensitive, compared with that of the others of L1₂-type ordered alloy systems.

The relationship between the spin structure and the magnetization loop is provided in Fig. 9⁵³. The top panel represents the magnetic primitive cells constituted of four atoms in the γ (fcc)-phase structure. The presence of non-magnetic atoms changes the number of interacting spins at the nearest neighboring atomic sites, causing the spin frustration in the γ -phase disordered alloy system. This spin frustration lowers the energy of the 3Q spin structure, compared with that of the collinear spin structure⁵⁴. The initial spin configuration is assumed to be in the 1Q structure, and hence the final solution is obtained to be the 3Q spin structure in the case of the disordered alloy with 75% magnetic atoms and 25% non-magnetic atoms. The spin configuration of the ordered AFM layer having the L1₀-type lattice structure was also calculated by using the Monte Carlo method. Two magnetic and two non-magnetic atoms are included in the magnetic unit cell. The spin correlation angle between the nearest neighboring spins indicates 180 degrees and it corresponds to the AF-1 spin structure, being a typical collinear spin structure of AFM alloys.

The magnetization process in an external field was calculated by adding the FM layer to such AFM layers. The motion equation of spins was solved directly within the framework of the classical Heisenberg model⁵³.

$$\mathcal{H} = -\sum_{(i,j)} J_{1ij} (\mathbf{S}_i \cdot \mathbf{S}_j) - \sum_{(i,k)} J_{2ik} (\mathbf{S}_i \cdot \mathbf{S}_k) - \sum_i D_i (\mathbf{S}_i \cdot \mathbf{n}_i)^2 - g\mu_B \sum_i (\mathbf{S}_i \cdot \mathbf{H}_{\text{app}}), \quad (16)$$

where the unit vector \mathbf{S}_i denotes the spin at the i th atom, and the summation is made over all possible spin pairs by using the exchange constants, J_1 and J_2 . The indices j and k respectively represent the first and second nearest neighboring spins for i th atom. The summations for j and k are firstly carried out with fixed i , and later on, the summation for i is carried out on all atoms. The spin pairs $\langle i, j \rangle$ and $\langle i, k \rangle$ represent the summations by such the procedure. The third and fourth terms in Eq. (1) describe the magnetic anisotropy energy and the Zeeman energy, respectively. The g -factor is given by g , D_i , and the unit vector \mathbf{n}_i , respectively stand for the anisotropy applied field is

given by \mathbf{H}_{app} . The magnetic easy axis \mathbf{n} and the applied field \mathbf{H}_{app} point to the [011] and the [211] directions, respectively. As seen from the figure, the AFM/FM bilayer with the 1Q, 2Q or AF-1 structures only displays the coercivity in the magnetization loop without any shift. That is, only the 3Q structure can realize the loop shift caused by the unidirectional exchange-bias field⁵³. At first glance, the above-mentioned model seems to be invalid for the formation of unidirectional exchange-bias field in the collinear systems. As a

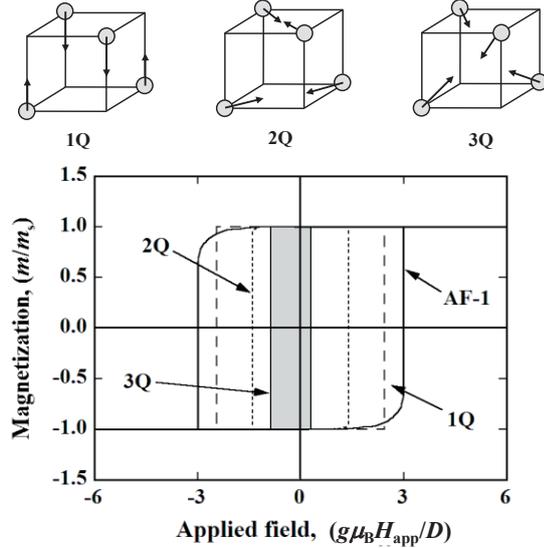


Fig. 9 Spin structures in the magnetic primitive cell of the γ (fcc)-phase lattice and magnetization loops of the AFM/FM bilayer for 1Q, 2Q, 3Q and AF-1 spin structures⁵³.

solution to explain existing experimental data, we need to introduce the frustrated spins due to the interfacial roughness and defects into the ordered L1₀-type AFM layer. In consequence, the calculated magnetization loop is actually shifted by the unidirectional exchange-bias field even in the ordered L1₀-type alloys.

2.6 Half-metallicity and field induced shape memory effect in Heusler alloys

2.6.1 Half metal Heusler alloys

The magnetic tunnel junctions (MTJs) are required for spintronic devices such as magnetic random access memories and magnetic sensors. Half-metallic ferromagnets (HMFs) with a high spin polarization ratio P have intensively been investigated as spintronic devices because MTJs using the HMFs are expected to exhibit a large value of TMR as given by the following expression:

$$TMR = \frac{2P_1 P_2}{1 - P_1 P_2}, \quad (17)$$

where P_1 and P_2 are the spin polarization ratio of electrodes⁵⁵. The spin polarization ratio P is obtained from the following expression⁵⁶:

$$P(\%) = \frac{|N_{\uparrow}(E_F) - N_{\downarrow}(E_F)|}{N_{\uparrow}(E_F) + N_{\downarrow}(E_F)} \times 100, \quad (18)$$

where $N_{\uparrow}(E_F)$ and $N_{\downarrow}(E_F)$ denote the density of states (DOS) at the Fermi level E_F in the majority and the minority spin states, respectively. In the band structure of half-metallic compounds the minority band is semiconducting with a gap at E_F , leading to 100% spin polarization at E_F .

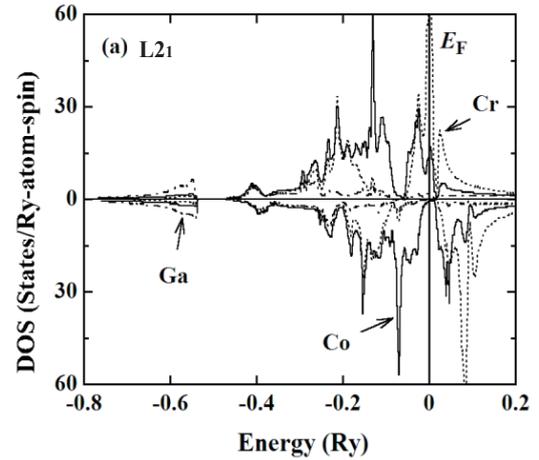


Fig. 10 Density of states of the Co₂CrGa alloy with the L2₁-type structure. The upper and lower curves in each panel correspond to the majority and the minority spin states, respectively⁵⁷.

The DOS calculated by the LMTO method in the atomic sphere approximation (ASA) for the L2₁ and B2-type (= high temperature phase of L2₁) structures of Co₂CrGa alloy are sketched in Figs. 10 and 11, respectively⁵⁷. For the calculations of B2-type structure, the coherent potential approximation (CPA) method was cooperated. The upper and lower curves in each figure refer to the majority and minority spin states, respectively. The DOS of the L2₁-type structure in Fig. 10 exhibits a half-metal-type electronic structure. As shown in Fig. 11, the DOS of B2-type is almost half-metal type and exhibits a high spin polarization. By using J_0 regarded as the effective exchange constant, T_C^{cal} is calculated from the following equation within the mean-field approximation for spin systems⁵⁷.

$$T_C^{\text{cal}} = \frac{2J_0}{3k_B}, \quad (19)$$

where k_B is the Boltzmann constant.

The calculated magnetic moment of each atom M^{cal} (μ_B/atom), the calculated total magnetic moment $M_{\text{tot}}^{\text{cal}}$ ($\mu_B/\text{f.u.}$), the calculated spin polarization P (%), the

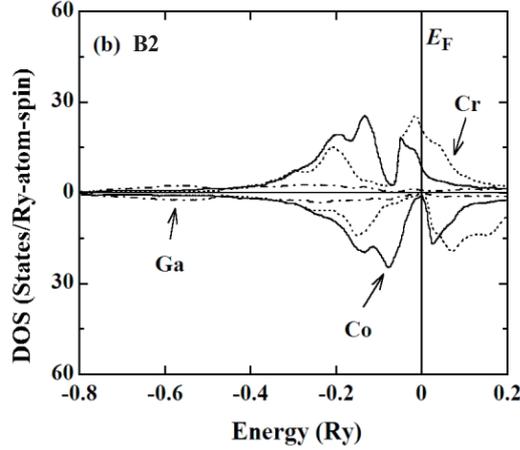


Fig. 11 Density of states of the Co_2CrGa alloy with the B2-type structure. The upper and lower curves in each panel correspond to the majority and the minority spin states, respectively⁵⁷.

saturation magnetic moment at 4.2 K M_s ($\mu_B/\text{f.u.}$), the experimental Curie temperature T_C^{exp} (K), and the calculated Curie temperature T_C^{cal} (K) obtained in the molecular field approximation scheme for Co_2CrGa

alloys with the L2₁ and B2-type structures are listed in Table 2⁵⁷. The saturation magnetic moment M_s at 4.2 K is $3.01\mu_B/\text{f.u.}$, being consistent to the theoretical value and the generalized Slater-Pauling line given by

$$M_t = Z_t - 24, \quad (20)$$

where M_t and Z_t are, respectively, the total values of magnetic moment and valence electron numbers in the unit cell. Furthermore, it is clear from the theoretical calculations that the band structure of B2-type structure also exhibits a half-metal type and the calculated Curie temperature T_C is about 100 K lower than that of the L2₁-type structure. Metallurgically, it is noteworthy to note that the L2₁-type phase of Co_2CrGa is much more stable, compared with that of $\text{Co}_2\text{Cr}_{1-x}\text{Fe}_x\text{Al}$ ⁵⁸. In $\text{Co}_2\text{Cr}_{1-x}\text{Fe}_x\text{Al}$ alloy system, the systematic theoretical calculations have been carried out, and pointed out that the disordering between the Al and the (Cr, Fe) sites scarcely degrades the spin polarization⁵⁸. Conversely, the disordering between the Co and the (Cr, Fe) sites brings about a significant reduction of the spin polarization⁵⁸. In fact, a spinodal decomposition inevitably takes places in Co_2CrAl alloy, resulting in reductions of the saturation magnetic moment and the Curie temperature⁵⁹.

Table 2 The calculated magnetic moment of each atom M^{cal} (μ_B/atom), the total magnetic moment $M_{\text{tot}}^{\text{cal}}$ ($\mu_B/\text{f.u.}$), the spin polarization P (%), the saturation magnetic moment M_s ($\mu_B/\text{f.u.}$) at 4.2 K, calculated and experimental Curie temperatures T_C^{cal} and T_C^{exp} (K) of Co_2CrGa alloys for the L2₁ and B2-type structures⁵⁷.

Structure	$M_{\text{Co}}^{\text{cal}}$ (μ_B/atom)	$M_{\text{Cr}}^{\text{cal}}$ (μ_B/atom)	$M_{\text{Ga}}^{\text{cal}}$ (μ_B/atom)	$M_{\text{tot}}^{\text{cal}}$ ($\mu_B/\text{f.u.}$)	M_s^{exp} ($\mu_B/\text{f.u.}$)	P (%)	T_C^{cal} (K)	T_C^{exp} (K)
L2 ₁	0.90	1.28	-0.07	3.01	3.01	95	419	495
B2	0.82	1.44	-0.06	3.03	–	84	295	–

2.6.2 Ferromagnetic shape memory alloys

Field-induced strains in ferromagnetic shape memory alloys (FSMAs) attract a great deal of attention as smart materials. Because FSMAs exhibit both a reversible martensitic transformation and ferromagnetism, one can control the shape memory effect by applying magnetic field in addition to conventional controls by temperature and stress. Field-induced strain in ferromagnetic shape memory alloys is due to twin-boundary motion and the strain is tied to the crystallography, not the direction of magnetization. That is, it is possible to rotate the direction of magnetization with no FSMA strain, only conventional magnetostriction, in FSMAs of relatively weak anisotropy. In magnetostrictive materials, on the other hand, field-induced strain is a result of magnetization rotation relative to the crystallography;

the strain is tied to the direction of magnetization, not the lattice.

In the martensite phase of FSMAs, the giant magnetic-field-induced strains (MFIS) have been observed in Ni_2MnGa Heusler alloy⁶⁰. This phenomenon is concerned with the rearrangement of twin variants. The MFIS depend on the crystallographic orientation, because twin-boundary motions are closely related with both the magnetocrystalline anisotropy and the Zeeman energies^{60,61}. The martensitic transformation takes place from a L2₁ (cubic) parent phase to a D0₂₂ (tetragonal) martensite phase. When the martensitic transformation occurs, some variants are introduced in consequence of the minimum elastic energy. Furthermore, microscopic magnetic domains exist in martensite twin variants so as to reduce the magnetic dipole energy. The magnetic domains not

parallel to the direction of applied magnetic field H are diminished on applying H , and then magnetization M changes direction to the magnetic field direction. The twin variants rearrange and twin boundary is moved in connection with the rotational magnetization, accompanied by macroscopic strains, when the magnetocrystalline anisotropy energy is larger than the driving energy to rearrange the twin variants.

In order to satisfy the condition for the variant rearrangement by applying magnetic field, the magnetic shear stress τ_{mag} should be larger than the mechanical shear stress τ_{req} required for the variant rearrangement. Stated differently, the following criterion should be satisfied

$$\frac{|K_u|}{s} = \tau_{\text{mag}} > \tau_{\text{req}}, \quad (21)$$

where K_u is the magnetic anisotropy constant⁶². The value of τ_{mag} is expressed as $|K_u|/s$, s is the corresponding twinning shear calculated by using the lattice parameter ratio c/a of the L1₀-type martensite phase. The twinning plane is $\{101\}_p$ for Co–Ni–Ga system, therefore the twinning shear s is expressed as

$$s = \frac{\{1 - (c/a)^2\}}{(c/a)}. \quad (22)$$

When the magnitude of shear stress becomes $\tau_{\text{mag}} < \tau_{\text{req}}$, the condition given by Eq. (21) is not satisfied. As a result, one can obtain no MFIS. In other words, a high twinning stress is required to induce the twinning transformation in the L1₀ structure. Therefore, we need a static applied twinning stress σ_{tw} to assist τ_{mag} . We have developed a new group of FSMAs in the Co–Ni–Al B2-based alloy system^{63,64}, which is characterized by good ductility and a wide range of transition temperatures. Because the composition range of these FSMAs is located near the B2+ γ two-phase region, these alloys are amenable to the introduction of the γ -phase by proper choice of composition and heat treatment temperature. The hot-workability and room temperature ductility of these alloys are significantly improved by the introduction of the γ -phase, which is a good advantage for practical applications⁶². The structure of parent phases, the lattice constant ratio c/a of martensite phases and the value of strain of the FSMs mentioned above are summarized in Table 3.

Table 3 The crystalline structure, the lattice constant ratio c/a , the value of strain of several kinds of L2₁- and B2-type ferromagnetic shape memory alloys^{62,65-67}.

Alloy	Structure	c/a	Strain (%)	Remark	Reference
Ni ₄₉ Fe ₁₈ Ga ₂₇ Co ₆	L2 ₁	1.20	-8.5	SA	65
Ni _{49.5} Fe _{14.5} Mn _{4.0} Ga _{26.0} Co _{6.0}	L2 ₁		-11.3	SA	66
Co _{47.5} Ni _{22.5} Ga _{30.0}	B2	1.18	-7.6	SA	67
Co ₄₁ Ni ₃₂ Al ₂₇	B2+ γ	1.16	-3.3	SA, ductile,	62

SA: stress assisted

3. Closing remarks

Important recent progress has been made in the theoretical and experimental fields given in Fig.1. It has been pointed out that the nesting of Fermi surfaces for electron-hole pairs in Cr is associated with the superconductivity for electron-electron pairs, and mathematically the nesting model is identical to the BCS model for superconductivity. The coexistence of SDW and superconductivity in various compound systems have been reported. Therefore, the discussion on the relation between SDW and superconductivity would become active⁶⁸. The concentration dependence of Cr-based alloys is in diverse ways, depending on additives. The formation of local moments such as Fe, Co, or Ni, might strongly modify the behavior of Cr and decreases T_N ⁹. However, strange that Cr-Fe-Co ternary alloys increase T_N as discussed in connection with Fig. 3.

Since the discovery of giant magnetoresistance in

multilayers of Fe/Cr, great effort has been done in understanding the magnetic coupling through chromium antiferromagnetic layers⁶⁹. Many data are very intricate because the SDW state depends on many factors such as temperature, film thickness, interface exchange coupling, hybridization with the adjacent layers and interface roughness.

A finite-temperature theory of magnetism that takes into account the fluctuations of local magnetic moments due to structural disorder has been discussed on the basis of the functional-integral method with the method of the distribution function⁷⁰. The results of numerical calculations point that amorphous iron forms an itinerant-electron spin-glass at low temperatures because of the nonlinear magnetic coupling between Fe local moments and the local environment effect on the amplitude of the Fe local moment due to the structural disorder. It should be emphasized that the calculated spin-glass freezing temperature (≈ 120 K) is in good

agreement with our data on Fe-rich amorphous alloys^{3,27}.

Magnetic properties of three dimensional Al-based icosahedral quasicrystals are presented in Section 2.3. Two dimensional decagonal, octagonal and dodecagonal alloys have also been known as quasicrystals. However, up to the present date, no practical magnetic quasicrystals have been reported, although some two dimensional quasicrystals exhibit excellent photonic properties⁷¹. Since quasicrystals are in both covalent and metallic states without lattice periodicity, fundamental properties of these quasicrystals have attracted much attention in the fields of strongly correlated electron and frustration systems.

Imry and Wortis discussed the broadening of the first-order transition due to local fluctuations caused by an intrinsic frozen disorder⁴⁵. The extent of broadening is affected by the size of frozen correlated region measured by the coherence length, accompanied by a spatial distribution of the phase transition field and temperature. Such frozen disorders are easily caused in multi-component materials. Therefore, the Maxwell relation is valid to calculate ΔS_m for metamagnetic La(Fe_xSi_{1-x})₁₃. In fact, its magnitude obtained from the Maxwell relation is comparable to that from the Clausius–Clapeyron equation. This model would also explain the Invar characteristics given Figs. 2 and 3 as a complete rounding of the first-order transition of Cr-Fe and Cr-Si alloys by addition of the third element.

Antiferromagnetic spintronics has become an active field of research. Park et al. have demonstrated a large spin-valve-like signal in a NiFe/Mn₈₀Ir₂₀/MgO/Pt stack with an antiferromagnet on one side and a nonmagnetic metal on the other side of the tunnel barrier. Ferromagnetic moments in NiFe are reversed by external fields of approximately 50 mT or less, and the exchange-spring effect of NiFe on Mn₈₀Ir₂₀ γ -phase alloy (see Fig. 7) induces rotation of antiferromagnetic moments, which is detected by the measured tunneling anisotropic magnetoresistance. Their work demonstrates a spintronic element whose transport characteristics are governed by an antiferromagnet⁷².

There are four kinds of Heusler-type alloys, i.e., XYZ (C1_b), X₂YZ (L2₁), inverse Heusler and quaternary Heusler and a number of half metal Heusler alloys have been reported. The structural stability comes to attention from practical viewpoints. The *sp*-elements are not responsible for the existence of the minority gap; whereas, they are nevertheless very important for the physical properties of Heusler alloys because hybridizations of *d-ps* electrons contribute to the bonding state⁷³. Therefore, studies on the chemical orbital Hamiltonian population are considered to be important.

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