OVERVIEW

Magnetism, Electronic Structure and Thermal Properties of $(a_{1-x}b_x)_{77}B_{13}Si_{10}$ ($a, b = \text{Ti-Cu}$) Pseudo-Binary 3d-Transition Metal Amorphous Alloys

By U. Mizutani*, M. Hasegawa*†, K. Fukamichi**,
T. Goto*** and T. Matsuda****

More than 100 3d-intertransition metal pseudo-binary amorphous alloys have been fabricated from 20 alloy systems expressed in the form of $(a_{1-x}b_x)_{77}B_{13}Si_{10}$ with a and b any combinations of 3d-transition metal elements from Ti to Cu. A magnetic phase diagram was constructed by analyzing dc and ac magnetic susceptibility data measured in the range 4.2–300 K. Utilizing the magnetic phase diagram thus obtained as a guide, we could determine a full spectrum of the density of states variation at the Fermi level in the 3d-transition metal amorphous phase throughout the electron concentrations from 4 to 11. Similarly, spectra of the saturation magnetization and the crystallization temperature were determined. Magnetism, the electronic structure and the thermal properties in the present $[a-b]$ amorphous alloys are discussed in relation to the available data in the corresponding crystalline alloys.

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I. Introduction

Both magnetic and electronic structures in the series of the 3d-transition metal alloys have been extensively studied in the past, particularly for the crystalline phases existent in the equilibrium phase diagrams. The Slater-Pauling curve, representing the behavior of the saturation magnetization as a function of the average valence electrons per atom, is well known. More recently, such studies have been

extended to the non-equilibrium amorphous alloys with the hope that (1) a direct comparison with the crystalline counterparts will shed some light on the effect of the randomness on the physical properties and (2) the phase diagram limitation can be lifted under the extremely high cooling conditions. Indeed, a single phase region characterized by the amorphous state is often made much wider than that with the equilibrium crystalline phases. The 3d-intertransition metal amorphous alloys have been fabricated by adding some metalloid elements like B, Si and P and their magnetic properties have been studied by various investigators⁽¹⁾⁻⁽⁶⁾.

Mizutani and his coworkers⁽⁷⁾⁻⁽¹²⁾ concentrated on the construction of the magnetic phase diagram for 3d-transition metal pseudo-binary amorphous alloys expressed in the form of $(a_{1-x}b_x)_{77}B_{13}Si_{10}$ with a, b any combination of 3d-transition metal elements from Ti to Cu and studied the density of states variation at the Fermi level through the measurements of low-temperature specific heat.

* Department of Crystalline Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan.

** Department of Materials Science, Tohoku University, Sendai 980, Japan.

*** The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 196, Japan.

**** Department of Physics, Aichi University of Education, Kariya-shi, Aichi 448, Japan.

† Present address: Department of Materials Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan.

Hereafter we may refer to these alloys as an abbreviated form [a-b] without explicitly showing the glass former elements $B_{13}Si_{10}$. At the early stage of this work, the Fe-based alloy systems have been most thoroughly studied⁽⁷⁾⁻⁽⁹⁾. Later, their studies have been extended to Co-based alloys⁽¹⁰⁾. Non-magnetic [Ni-Cu] alloy system has been also studied⁽¹¹⁾. More recently we have made further attempts to fabricate as many [a-b] amorphous alloys as possible and, particularly, could circumvent the difficulty in obtaining melt-spun amorphous alloys in the [Cr-V] system by employing the sputtering technique⁽¹²⁾. Hence, we consider it to be timely at this stage to survey the magnetic and electronic states in all [a-b] pseudobinary amorphous alloys so far studied. Included are the results on the crystallization temperature, from which we discuss the bonding nature in relation to the band structure derived.

II. Experimental Details

Most of amorphous alloys were produced by using a single-roll spinning wheel apparatus operated in a reduced pressure of Ar gas. The liquid quenching method turned out to be unsuccessful for the alloys composed of combinations of early transition metals. However, [Cr-V] alloys could be vitrified by the high-rate DC sputtering technique. The formation of the amorphous phase was identified using the X-ray diffraction with Cu $K\alpha$ radiation. Figure 1 summarizes an amorphous single phase region obtained by either liquid quenching or sputtering techniques in totally 20 [a-b] alloy systems.

The low-temperature specific heats were measured in the temperature range 1.5–6 K. The dc magnetic susceptibilities were measured in the range 4.2–300 K. The ac magnetic susceptibilities were also measured with the field amplitude 10 Oe and the frequency 80 Hz. The differential thermal analysis (DTA) with the heating rate of 0.167 K/s (10 K/min) was employed to determine the crystallization temperature.

Fig. 1 Composition range for the formation of an amorphous single phase in $(a_{1-x}b_x)_{77}B_{13}Si_{10}$ ($a, b = \text{Ti-Cu}$) alloy systems. The 3d-elements a and b are placed at left and right corners in each rectangle. Regions marked by and represent the amorphous single phase regions obtained by the liquid quenching and sputtering techniques, respectively. A blank region indicates the range, where an amorphous single phase could not be achieved by the present liquid quenching.

III. Results

1. Magnetic phase diagram

The magnetic phase diagram was constructed for each alloy system [a-b] through the measurements of both dc and ac magnetic susceptibilities. The presence or absence of the hysteresis of the dc magnetization under zero-field and field cooling was also checked to confirm the spin-glass state. Typical examples are shown in Fig. 2, where the magnetization in the ac magnetic field or the dc magnetic susceptibility is plotted against the temperature for

Fig. 2 (a) ac magnetization and (b) dc magnetic susceptibility as a function of temperature for amorphous $[\text{Co}_{1-x}\text{Ni}_x]$ alloys.

various $[\text{Co}_{1-x}\text{Ni}_x]$ alloys. A rapid increase in magnetization with lowering temperature signals the onset of the ferromagnetism and is identified as the Curie temperature T_c .

A decrease in magnetization with further lowering temperature is evident in alloys with $x = 0.75$ and 0.80 . This indicates that the ferromagnetism becomes unstable and that the spin-glass state emerges at lower temperatures. The spin-glass state appearing via ferromagnetism is often called the re-entrant spin-glass state. When x reaches 0.85 , the ac magnetization exhibits only a sharp cusp. This is typical of the transition from the paramagnetism to the ordinary spin-glass state. The spin-freezing temperature T_f was carefully determined from the cusp in the ac magnetic susceptibility or the temperature at the onset of the dc magnetization hysteresis mentioned above. As shown in Fig. 2(b), the

temperature-dependent paramagnetism persists down to the lowest temperature of 4.2 K when x increases beyond 0.9 . However, $[\text{Ni}]$ or $\text{Ni}_{77}\text{B}_{13}\text{Si}_{10}$ shows only a negligibly small temperature-dependence of the magnetic susceptibility over a whole temperature range. Hence, we treat $[\text{Ni}]$ as being non-magnetic, in contrast to the fcc Ni. The addition of the glass former elements B and Si certainly suppressed the occurrence of the ferromagnetism in $[\text{Ni}]$. The magnetic phase diagram can be constructed by tracing the composition dependence of both the Curie-temperature and the spin freezing temperature for each alloy system.

Figures 3–13 illustrate the magnetic phase diagrams for [a–b] pseudobinary amorphous alloy systems so far studied by various investigators^{(4)–(12)}. The $[\text{Ti-V}]$, $[\text{Cr-V}]$, $[\text{Ni-V}]$ and $[\text{Ni-Cu}]$ alloy systems exhibit the temperature independent paramagnetism over a whole composition range and, hence, are safely regarded as being non-magnetic. On the other hand, an amorphous single phase region obtained by the liquid quenching in $[\text{Fe-Ti}]$, $[\text{Fe-Cu}]$, $[\text{Co-Ti}]$ and $[\text{Co-Cu}]$ is so limited that only ferromagnetism is observed. Hence, these magnetic phase diagrams are so trivial that their display is omitted.

The paramagnetic effective moment p_{eff} is calculated for the paramagnetic alloys, for which the magnetic susceptibility follows well the Curie-Weiss law down to the lowest temperatures without any transition to the spin-glass state:

$$\chi = \chi_0 + C/(T + \theta_p), \quad (1)$$

and

$$p_{\text{eff}} = (3k_B C / N\mu_B^2)^{1/2}, \quad (2)$$

where χ_0 is the temperature independent contribution, θ_p is the Curie-Weiss temperature, N is the number of magnetic atoms per mol, k_B is the Boltzmann constant and μ_B is the Bohr magneton. Such temperature-dependent paramagnetism is found in $[\text{Fe-Cr}]$, $[\text{Co-Ni}]$, $[\text{Co-Cr}]$, $[\text{Co-V}]$ and $[\text{Ni-Cr}]$. The value of p_{eff} is plotted in the respective magnetic phase diagrams.

The ferromagnetism is stable over a whole

Fig. 3

Fig. 4

Fig. 3 Magnetic phase diagram ($\blacksquare^{(4)}$) and the linearly temperature dependent specific heat coefficient γ_{exp} ($\circ^{(7)}$) for amorphous [Fe-Co] alloys. F and P denote the ferro- and paramagnetic regions, respectively.

Fig. 4 Magnetic phase diagram ($\bullet^{(12)}$, $\blacksquare^{(5)}$) and the linearly temperature dependent specific heat coefficient γ_{exp} ($\circ^{(7)}$) for amorphous [Fe-Ni] alloys. A region with dotted screen indicates the magnetic contribution to γ_{exp} . SG denotes the spin-glass region. See Fig. 3 for the symbols F and P.

composition range only in [Fe-Co]. The spin-glass state appears in many alloy systems like [Fe-Ni], [Co-Ni], [Fe-Mn] and so on. As noted above, the magnetic state between the amorphous [Ni] and the fcc Ni is strikingly different. Such difference in magnetism is found in Mn and Cr: [Mn] is the spin-glass and [Cr] is non-magnetic in contrast to the appearance of the antiferromagnetism in their crystalline state.

A particular attention may be focused on the magnetic phase denoted as "M" in the $[\text{Co}_{1-x}\text{Mn}_x]$ alloy system. The ac magnetization in the range $0.4 \leq x \leq 0.8$ shows a sharp cusp below about 60 K, indicating the existence of the spin-glass state at lower temperatures. However, the magnetization at higher temperatures does not follow a Curie-Weiss type decrease but, instead, increases with increasing temperature. Even a broad maximum has been observed at about 150 K for the

Fig. 5

Fig. 6

Fig. 5 Magnetic phase diagram ($\bullet^{(9)}$, $\blacksquare^{(6)}$) and the linearly temperature dependent specific heat coefficient γ_{exp} ($\circ^{(9)}$) for amorphous [Fe-Mn] alloys. See the earlier Figures for the symbols.

Fig. 6 Magnetic phase diagram ($\bullet$, $\circ^{(9)(12)}$, $\blacksquare^{(5)}$) and the linearly temperature dependent specific heat coefficient γ_{exp} ($\circ^{(9)(12)}$) for amorphous [Fe-Cr] alloys. A open circle in the magnetic phase diagram represents the paramagnetic effective moment deduced from the Curie-Weiss law. See the earlier Figures for other symbols.

$[\text{Co}_{0.3}\text{Mn}_{0.7}]$ alloy. The dc magnetization was also measured under the zero-field and field cooling for these alloys through this critical temperature range. The hysteresis appeared only below the spin-freezing temperature deduced from the above mentioned cusp in the ac magnetization. No anomalous behavior was found in the vicinity of the broad maximum in the ac magnetization. The magnetic state in the temperature range intervened by these two maxima is, hence, temporarily denoted as "M" in the magnetic phase diagram. A further study is needed to clarify the magnetic state "M". All relevant magnetic data are summarized in Table 1.

2. Low-temperature specific heat

The low-temperature specific heat was measured in the range 1.5–6 K. The results

Fig. 7

Fig. 8

Fig. 7 Magnetic phase diagram ($\bullet^{(12)}$, $\blacksquare^{(6)}$) for amorphous [Fe-V] alloys. See the earlier Figures for symbols.

Fig. 8 Magnetic phase diagram ($\bullet$, $\circ^{(12)}$) and the linearly temperature dependent specific heat coefficient γ_{exp} ($\circ^{(7)}$) for amorphous [Co-Ni] alloys. See the earlier Figures for symbols.

should reflect the magnetic state near 4.2 K, which can be read from the magnetic phase diagram at the lowest temperature range. The low-temperature specific heat in this temperature range is generally written in the form:

$$C = \gamma T + \alpha T^3 + C_m, \quad (3)$$

where γ and α are the electronic and lattice specific heat coefficients and C_m represents the magnetic specific heat. The C_m is obviously absent for the non-magnetic alloys.

The magnetic specific heat C_m for the ferromagnetic alloys is generally well described in terms of the spin wave excitations and can be independently evaluated from the temperature dependence of the saturation magnetization at low temperatures⁽¹³⁾. The ferromagnetic Co-rich alloys exhibit the T^{-2} -type specific heat arising from the interaction of ^{59}Co nuclei with the internal magnetic field H_{int} ⁽¹³⁾. This is observed as an upturn in the C/T versus T^2 plot and can be again isolated from the total by the least-squares fitting. Therefore, the electronic specific heat coefficient γ can be reliably deduc-

Fig. 9

Fig. 10

Fig. 9 Magnetic phase diagram ($\bullet^{(10)}$) and the linearly temperature dependent specific heat coefficient γ_{exp} ($\circ^{(10)}$) for amorphous [Co-Mn] alloys. See the text for the magnetic state denoted as M. See the earlier Figures for other symbols.

Fig. 10 Magnetic phase diagram ($\bullet$, $\circ^{(10)}$) and the linearly temperature dependent specific heat coefficient γ_{exp} ($\circ^{(10)(12)}$) for amorphous [Co-Cr] alloys. See the earlier Figures for symbols.

ed, as far as an alloy is in the stable ferromagnetic regime. Note here that the electron-phonon enhancement effect in the measured γ is generally small relative to the band structure contribution in these transition metal alloys. We proceed our discussion by presuming that the measured value of γ reflects well the density of states at the Fermi level without any correction to the electron-phonon interaction.

The situation becomes extremely complex when the ferromagnetism becomes unstable. The magnetic specific heat C_m is often empirically expressed in the form:

$$C_m = A + \gamma_m T + \alpha_m T^3 + \dots, \quad (4)$$

where A is the temperature independent term often observed in the range 1.5–6 K, γ_m is positive and large and α_m is negative but is com-

Fig. 11

Fig. 12

Fig. 11 Magnetic phase diagram ($\bullet$, $\circ^{(10)}$) for the amorphous [Co-V] alloys. See the earlier Figures for symbols.

Fig. 12 Magnetic phase diagram ($\bullet^{(12)}$) and the linearly temperature dependent specific heat coefficient γ_{exp} ($\circ^{(12)}$) for the amorphous [Ni-Mn] alloys. See the earlier Figures for symbols.

parable in magnitude to the lattice specific heat coefficient $\alpha^{(9)}$. As a result, the separation of the electronic and lattice specific heat contributions from the total is practically infeasible.

The experimentally derived γ_{exp} is plotted at the bottom of each magnetic phase diagram. Obviously, the value of γ_{exp} is highly enhanced in the magnetically unstable region, which covers not only the spin-glass and the temperature-dependent paramagnetic states but also the region where the ferromagnetism is about to collapse. In other words, information about the density of states at the Fermi level can be deduced from the value of γ_{exp} only in either non-magnetic or stable ferromagnetic regimes. The magnetic contribution to γ in the magnetically unstable region is roughly estimated by interpolating the values for the non-magnetic or ferromagnetic alloys and is marked in each Figure by dotted screen. Numerical

Fig. 13 Magnetic phase diagram ($\circ^{(12)}$) and the linearly temperature dependent specific heat coefficient γ_{exp} ($\circ^{(12)}$) for the amorphous [Ni-Cr] alloys. See the earlier Figures for symbols.

data on the low-temperature specific heats are summarized in Table 2, along with the data for the crystallization temperature obtained from the exothermic peak in the DTA measurements.

IV. Discussion

1. Band structure spectrum

A whole spectrum of γ_{exp} for non-magnetic and stable ferromagnetic [a-b] amorphous alloys, which reflects well the density of states at the Fermi level, is shown in Fig. 14(a) against the sequence of the 3d-transition metal elements in the periodic table. In comparison, the spectrum for the 3d-transition metal crystalline alloys⁽¹⁴⁾⁽¹⁵⁾ is shown in Fig. 14(b). The average electron concentration per 3d-transition metal atom e/a is also shown in its abscissa. First of all, it can be seen that the variation of γ_{exp} in the amorphous phase is less prominent than that in the crystalline phase, being indicative of the smearing of the fine structures in the density of states. Nevertheless,

Table 1 Magnetic properties of $(a_{1-x}b_x)_{77}B_{13}Si_{10}$ amorphous alloys.

Sample	$10^{-1} \sigma_s$ (Wb/kg)	μ_s (μ_B)	T_c (K)	T_f (K)	p_{eff} (μ_B)
[Fe-Ti]					
0	2.437	2.128	>300	—	—
0.05	2.027	1.760	>300	—	—
0.10	1.852	1.597	>300	—	—
0.15	1.523	1.305	>300	—	—
0.20	1.216	1.035	>300	—	—
[Fe-V]					
0.05	1.951	1.698	>300	—	—
0.10	1.671	1.449	>300	—	—
0.15	1.297	1.119	>300	—	—
0.20	0.905	0.778	—	—	—
0.40	—	—	—	10	—
[Fe-Cr]					
0.05	1.996	1.738	>300	—	—
0.10	1.611	1.399	>300	—	—
0.15	1.383	1.197	>300	—	—
0.20	1.053	0.908	280	<4.2	—
0.30	—	—	97	6	—
0.40	—	—	—	8	—
0.50	—	—	—	—	3.6
0.60	—	—	—	—	1.7
0.80	—	—	—	—	0.71
[Fe-Mn]					
0.05	1.993	1.740	>300	—	—
0.10	1.839	1.605	>300	—	—
0.15	1.611	1.405	>300	—	—
0.20	1.337	1.164	>300	—	—
0.35	—	—	80	55	—
0.40	—	—	—	33	—
0.60	—	—	—	20	—
0.80	—	—	—	20	—
1.0	—	—	—	9	—
[Fe-Ni]					
0.80	—	—	232	<4.2	—
0.90	—	—	52	26	—
0.95	—	—	—	9	—
[Fe-Cu]					
0.05	2.113	1.858	>300	—	—
0.10	2.049	1.813	>300	—	—
[Co-Ti]					
0	1.319	1.210	>300	—	—
0.05	1.028	0.936	>300	—	—
0.10	0.665	0.599	>300	—	—
[Co-V]					
0.05	0.954	0.870	>300	—	—
0.10	0.686	0.622	>300	—	—
0.15	0.333	0.299	115	—	—
0.20	0.162	0.146	27	<4.2	—
0.25	—	—	15	6	—
0.30	—	—	—	—	2.1
[Co-Cr]					
0.05	0.978	0.893	>300	—	—
0.10	0.731	0.664	>300	—	—
0.15	0.436	0.393	187	—	—

Table 1 continued

Sample	$10^{-1} \sigma_s$ (Wb/kg)	μ_s (μ_B)	T_c (K)	T_f (K)	p_{eff} (μ_B)
0.20	0.255	0.229	74	<4.2	—
0.25	—	—	11	5	—
0.27	—	—	—	—	3.0
0.30	—	—	—	—	2.0
0.40	—	—	—	—	0.87
0.60	—	—	—	—	0.52
0.80	—	—	—	—	0.10
[Co-Mn]					
0.05	1.302	1.191	>300	—	—
0.10	1.322	1.205	>300	—	—
0.15	1.299	1.182	>300	—	—
0.20	1.177	1.067	>300	<4.2	—
0.30	—	—	>300	15	—
0.35	—	—	145	60	—
0.40	—	—	—	53	—
0.50	—	—	—	50	—
0.60	—	—	—	59	—
0.80	—	—	—	48	—
0.90	—	—	—	24	—
[Co-Ni]					
0.70	—	—	125	<4.2	—
0.80	—	—	34	18	—
0.85	—	—	—	6	—
0.90	—	—	—	—	2.2
0.95	—	—	—	—	0.88
[Co-Cu]					
0.05	1.087	1.001	>300	—	—
[Ni-Cr]					
0.20	—	—	—	—	0.56
0.40	—	—	—	—	0.50

σ_s is the saturation magnetization at 4.2 K determined under the magnetic field up to 5 T. The value in unit of Wb/kg can be converted to the conventional unit of emu/g by dividing it over $4\pi \times 10^{-5}$.

μ_s is the saturation moment per 3d-transition metal atom and is calculated from eq. (5).

T_c is the Curie temperature in K.
 T_f is the spin freezing temperature in K.

p_{eff} is the paramagnetic effective moment deduced from eqs. (1) and (2) in the text.

there exist several notable features in its trend: a fairly sharp minimum at about $e/a=5.5$, a shallow minimum at about 8.5 and a rapid decrease above about 10.0.

A rapid fall in the γ_{exp} value above 10.0 arises from the complete filling of the 3d-band, indicating the move of the Fermi level from the 3d-band to sp-band⁽¹¹⁾. The same feature is seen at 10.5 for the fcc alloys. An apparent shift of the e/a axis by 0.5 towards left for the amorphous alloys can be attributed to the 3d-

Table 2 Low-temperature specific heat and crystallization temperature for $(a_{1-x}b_x)_{77}B_{13}Si_{10}$ amorphous alloys.

Sample	γ_{exp} (mJ/molK ²)	α_{exp} (mJ/molK ⁴)	θ_D (K)	A (mJ/molK)	σ_n (mJK/mol)	T_x (K)
[Ti-V]						
0	4.61	0.055	329	—	—	—
0.20	5.05	0.023	438	—	—	—
0.40	5.61	0.047	346	—	—	—
1.00	4.25	0.012	541	—	—	888
[V-Cr]						
0.40	3.14	0.017	481	—	—	—
0.80	4.29	0.015	506	—	—	—
1.00	4.73	0.028	409	—	—	907
[Ni-V]						
0	2.93	0.057	324	—	—	769
0.20	3.31	0.029	404	—	—	—
0.40	3.69	0.015	521	—	—	—
[Ni-Cu]						
0.10	2.17	0.048	344	—	—	—
[Fe-Cr]						
0	6.74	0.033	389	—	—	822
0.20	10.47	0.049	—	0.63	—	849
0.40	24.10	-0.066	—	6.50	—	899
0.60	12.43	-0.044	—	6.00	—	946
0.80	7.87	0.001	—	0.79	—	925
[Fe-Mn]						
0.20	17.78	0.032	—	0.0	—	827
0.40	28.60	-0.049	—	-22.60	—	834
0.60	28.49	-0.022	—	-8.50	—	843
0.80	27.69	-0.007	—	-3.90	—	859
1.00	29.37	0.029	—	-0.80	—	851
[Fe-Co]						
0.20	5.82	0.070	303	—	1.25	823
0.40	5.53	0.044	354	—	1.10	818
0.60	5.34	0.057	324	—	1.18	806
0.80	5.65	0.056	326	—	1.29	800
1.00	6.45	0.035	383	—	1.40	765
[Fe-Ni]						
0.20	5.65	0.060	319	—	—	807
0.40	5.34	0.061	317	—	—	784
0.60	5.39	0.022	447	—	—	772
0.80	8.45	0.053	—	—	—	748
0.90	13.03	0.025	—	—	—	769
0.95	15.70	0.055	—	—	—	771
[Co-Cr]						
0.20	14.89	0.042	—	1.90	—	842
0.40	9.42	0.026	—	0.98	—	911
0.60	6.54	0.027	—	0.40	—	957
0.75	—	—	—	—	—	990
0.80	5.55	0.006	686	—	—	1001
[Co-Mn]						
0.20	12.39	0.021	—	-1.20	—	825
0.40	14.74	0.050	—	-1.30	—	860
0.60	14.96	0.027	—	-1.21	—	890
0.80	18.84	0.024	—	-1.60	—	877
[Co-Ni]						
0.20	6.56	0.115	257	—	1.40	715
0.40	6.66	0.052	333	—	0.52	692

Table 2 continued

Sample	γ_{exp} (mJ/molK ²)	α_{exp} (mJ/molK ⁴)	θ_D (K)	A (mJ/molK)	σ_n (mJK/mol)	T_x (K)
0.60	6.50	0.029	407	—	—	709
0.70	8.63	0.053	—	1.40	—	730
0.80	10.88	0.036	—	4.44	—	728
0.90	6.43	0.025	—	18.00	—	769
0.95	4.41	0.048	—	5.81	—	767
[Ni-Cr]						
0.20	7.07	0.020	—	4.46	—	770
0.40	6.49	0.021	—	3.00	—	859
[Ni-Mn]						
0.20	14.28	0.086	—	-6.70	—	794
0.40	7.34	0.008	—	-0.70	—	831
0.60	6.89	0.024	—	0.19	—	867
0.80	13.30	0.033	—	-0.50	—	905

band filling assisted by electrons of metalloids B and Si. If the same amount of shift occurs regardless of the e/a value, then the minimum

Fig. 14 A spectrum of the experimentally derived electronic specific heat coefficient γ_{exp} for (a) the amorphous [a-b]⁽⁷⁾⁻⁽⁹⁾⁽¹²⁾ and (b) crystalline 3d-transition metal alloys. Symbols are as follows: ∇ : [Ti-V] and hcp and bcc Ti-V⁽¹⁴⁾, $\blacklozenge$: [V-Cr] and bcc V-Cr⁽¹⁴⁾⁽¹⁵⁾, $\blacksquare$: [Co-Cr] $\square$: bcc Fe-Cr⁽¹⁵⁾, $\blacklozenge$: [Fe-Co] and bcc Fe-Co⁽¹⁵⁾, $\circ$: [Co-Ni] and fcc Co-Ni⁽¹⁴⁾, $\square$: fcc Fe-Ni⁽¹⁴⁾, $\triangle$: [Ni-Cu] and fcc Ni-Cu⁽¹⁴⁾ and $\blacktriangle$: amorphous Ni-Cu-P⁽¹¹⁾. The numbers 4-11 in the abscissa in (b) refer to the valence electrons per 3d-transition metal atom.

at 5.5 for the amorphous alloys should correspond to the minimum observed for the bcc Cr. The minimum in the bcc Cr has been interpreted as arising from the fall of the Fermi level in the valley formed between the bonding and antibonding states, which is characteristic of the bcc structure⁽¹⁶⁾. According to the periodic table, an element with e/a below 6 tends to crystallize into the bcc structure. The reason for this is that, as long as the electron concentration is below 6, the Fermi level falls in the bonding states and, as a result, a system tends to crystallize in favor of the bcc structure. Our finding of the presence of a density of states minimum at about 5.5 for the amorphous alloys suggests that even the rapid quenching cannot completely suppress the formation of the electronically favorable arrangement of atoms.

An interpretation for the shallow minimum observed around $e/a=8.5$ for the amorphous [Fe-Co] alloys is less clear. A similar but more prominent density of states minimum is seen at the same e/a value in the crystalline Fe-Co alloys. Hasegawa and Kanamori⁽¹⁷⁾ discussed the minimum by calculating the electronic structure of Fe-based bcc ferromagnetic alloys in the coherent potential approximation. They pointed out that an initial decrease in the band structure γ value upon adding Co to Fe is caused by a rapid decrease of the spin-up subband contribution but, when the Co content exceeds about 30 at.%, an increase in the spin-down

subband contribution supersedes, resulting in the formation of the minimum in the γ value near $x=0.3$. Here it should be emphasized that the minimum in the γ value for the bcc Fe-Co alloys is theoretically interpreted as a result of the delicate interplay of the electron filling in the spin-up and spin-down subbands and that it is not a feature expected for any bcc structure at this particular electron concentration. Indeed, the minimum has been neither observed by the experiment nor theoretically predicted at the same e/a in the bcc Fe-Ni alloys⁽¹⁷⁾. Provided that the presence of metalloids always causes the shift of the e/a axis by 0.5 towards left, the minimum in the amorphous phase would have been placed around $e/a=8.0$. However, no corresponding minimum is found in the γ trend. It seems premature to discuss further if the two minima observed at the same e/a for both bcc Fe-Co and the [Fe-Co] amorphous alloys stems from the same origin.

2. Saturation magnetization spectrum

The saturation magnetization for the ferromagnetic [a-b] amorphous alloys is determined from the magnetic field dependence of the magnetization under the dc field up to 5 T at 4.2 K. The results are shown in Fig. 15(a) against the sequence of the 3d-transition metal elements in the periodic table. The Slater-Pauling curve for the crystalline alloys⁽¹⁸⁾ are shown in Fig. 15(b) as a function of the average electron concentration per transition metal atom. The average magnetic moment μ_s per 3d-transition metal atom is calculated using equation:

$$\mu_s = \sigma_s M / 0.77 N_A \mu_B, \quad (5)$$

where σ_s is the saturation magnetization per gram, M is the average atomic weight, N_A is the Avogadro number, μ_B is the Bohr magneton. The factor $0.77 N_A$ represents the total number of the transition metal atoms per mol.

It can be seen from Fig. 15(a) that the value of μ_s falls almost on a universal straight line for the [a-b] amorphous alloys with elements a and b chosen from any combinations of the late transition metal elements Fe, Co, Ni and

Fig. 15 A spectrum of the saturation magnetization for (a) the amorphous [a-b]⁽⁹⁾⁽¹²⁾ alloys and (b) crystalline 3d-transition metal alloys. Symbols are as follows; +: [Fe-Cu], $\circ$: [Fe-Ni] and bcc and fcc Fe-Ni⁽¹⁸⁾, $\square$: [Fe-Co] and bcc Fe-Co⁽¹⁸⁾, $\blacktriangledown$: [Fe-Mn], $\triangle$: [Fe-Cr] and bcc Fe-Cr⁽¹⁸⁾, $\oplus$: [Fe-V] and bcc Fe-V, $\diamond$: [Fe-Ti], $\times$: [Co-Cu], ∇ : [Co-Ni] and fcc Co-Ni⁽¹⁸⁾, $\blacksquare$: [Co-Mn] and Co-Mn⁽¹⁸⁾, $\triangle$: [Co-Cr] and Co-Cr⁽¹⁸⁾, $\ominus$: [Co-V], $\diamond$: [Co-Ti], $\oplus$: fcc Ni-Cu⁽¹⁸⁾, $\square$: fcc Ni-Mn⁽¹⁸⁾, $\blacktriangle$: fcc Ni-Cr⁽¹⁸⁾ and $\bullet$: fcc Ni-V⁽¹⁸⁾.

Cu. An apparent resemblance to the Slater-Pauling curve has been originally revealed by Mizoguchi *et al.*⁽¹⁾ using $(a_{1-x}b_x)_{80}B_{10}P_{10}$ amorphous alloys. The valence band in the ferromagnets [Fe] and [Co] containing 13 at.%B and 10 at.%Si is believed to be described with the picture that the spin-up subband is fully filled and that only the spin-down subband possesses the 3d-holes. Indeed, the total amount of metalloids $B_{13}Si_{10}$ is sufficiently high to fill the spin-up subband⁽¹⁹⁾. In such "strong ferromagnet" regime, an increase in e/a should directly lead to a reduction in the 3d-holes and, hence, to the reduction in magnetic moment. This can explain why the magnetic moment decreases by $1\mu_B$ when the e/a value increases by 1. It may be worthwhile mentioning that the Invar effect has been discovered

in the Fe-B and Fe-P amorphous alloys and become more prominent with reducing metalloid content below 15 at. %⁽²⁰⁾⁽²¹⁾. The occurrence of the Invar effect has been discussed in relation to the appearance of the weak ferromagnetism, which is characterized as having holes in both spin-up and spin-down subbands⁽¹⁹⁾⁻⁽²²⁾.

The universal line intercepts with the e/a axis at about 10.0, being consistent with the early argument on the paramagnetism of [Ni]. It should be emphasized that the universal line obtained for the amorphous alloys is almost parallel to the right-hand portion of the Slater-Pauling curve and that the former coincides well with the latter by displacing the e/a axis by 0.5. The displacement of 0.5 agrees exactly with that deduced from the γ_{exp} spectrum shown in Fig. 14(a). However, it should be recognized that the metalloid elements like B and Si perturb the valence band structure in a complicated manner⁽²²⁾ and, hence, the experimentally derived universal displacement of the e/a axis in the amorphous phase cannot be simply taken as the evidence for the charge transfer brought about by electrons of metalloids within the framework of the rigid band picture.

The addition of the early transition metal elements Ti, V, Cr and Mn to [Fe] or [Co] reduces the magnetic moment as well as the average electron concentration. In addition, the μ_s value plotted against e/a constitutes no longer a universal line but yields different branches, depending on an individual alloy system. As discussed above, a linear relationship between μ_s and e/a holds, only when the spin-up subband is completely filled and the hole exists only in the spin-down subband. This condition may break, when e/a is decreased below that of [Fe]. If this happens by adding the early transition metal to [Fe], the magnetic moment would be given by the sum of the 3d-holes in both spin-up and spin-down subbands. The observed decrease in magnetic moment by adding various early transition elements to [Fe] may be explained along this line, if an increase in the 3d-holes in the spin-up subband is more significant than that in the spin-down subband.

A different interpretation is needed for the data on the Co-based alloys, where the 3d-holes are present only in the spin-down subband. We believe that the outer electrons of the early transition metal element most likely contribute to fill the 3d-holes in the spin-down band. The magnetic moment behaves as if the late transition metal were added to [Co] and, hence, is decreased in spite of a decrease in e/a . Indeed, similar discussion has been made for the crystalline Co-M and Ni-M ($M = \text{V, Cr}$ etc) alloys⁽²³⁾.

3. Crystallization temperature spectrum

The crystallization temperature T_x for the [a-b] amorphous alloys is plotted in Fig. 16(a) as a function of the average electron concentration per transition metal atom. Included are the data for the $(a_{1-x}b_x)_{80}B_{10}Si_{10}$ amorphous alloys with a and b selected from 3d, 4d and 5d elements⁽²⁴⁾, the noble metal-based amorphous alloys⁽²⁵⁾ and Ca-Al amorphous alloys⁽²⁶⁾. In spite of the scatter of the data points, we can clearly see the formation of a peak centered around $e/a = 6$. The maximum crystallization of 1000 K is achieved near this electron concentration, i.e., the $[\text{Cr}_{0.8}\text{Co}_{0.2}]$ alloy in the 3d-transition metal amorphous alloys.

Figure 16(b) illustrates the distributions of the melting temperature for 3d, 4d and 5d transition metals. It has been argued⁽¹⁶⁾ that whether the Fermi level falls in the bonding or antibonding states is critically important in determining the bonding strength of atoms in typical bcc, fcc and hcp structures. This criterion is particularly important in bcc, since the splitting of bonding and antibonding states is most prominent⁽¹⁶⁾. Indeed, the maximum melting temperature is observed in the bcc elements with $e/a = 6$, i.e. Cr, Mo and W. We consider that this behavior is also reflected in the crystallization temperature, suggesting that the bonding strength in the amorphous alloys reaches a maximum in the neighborhood of $e/a = 6$. As already mentioned in Section IV.1, an alloy tends to crystallize in favor of the bcc structure, when the electron concentration e/a is in the neighborhood of 6. This tendency still holds even under the extremely high quenching conditions and is most likely responsible for

Fig. 16 A spectrum of (a) the crystallization temperature T_x for the amorphous [a-b] alloys and (b) the melting temperature T_m for elements in the 4th ($\circ$), 5th ($\triangle$) and 6th ($\square$) row of the periodic table. Symbols used are as follows; $\bullet$: [Fe-Ni], $\square$: [Fe-Co], $\blacktriangledown$: [Fe-Mn], $\triangle$: [Fe-Cr], $\circ$: [Co-Ni], $\times$: [Co-Mn], $\triangle$: [Co-Cr], $\square$: [Ni-Mn], $\blacksquare$: [Ni-Cr], ∇ : [Ti-V]⁽²⁴⁾, $\triangle$: Ag-Cu-Mg⁽²⁵⁾, $\circ$: Ca-Al⁽²⁶⁾, $\blacksquare$: [Zr-Nb]⁽²⁴⁾, $\blacklozenge$: [Nb-Mo], $\diamond$: [Hf-Ta]⁽²⁴⁾ and $\blacktriangle$: [Ta-W]⁽²⁴⁾.

the highest crystallization temperature attained in this critical concentration range.

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