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1996 J. Phys.: Condens. Matter 8 3207

(http://iopscience.iop.org/0953-8984/8/18/012)

J. Phys.: Condens. Matter **8** (1996) 3207–3213. Printed in the UK

Are amorphous FeNiB systems non-collinear magnets?

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Received 30 November 1995, in final form 18 January 1996

Abstract. The magnetic configuration of amorphous $(Fe_xNi_{1-x})_{80}B_{20}$ alloys with $x = 0$, 0.5 and 1 is studied by *ab initio* band-structure calculations which are performed in a fully self-consistent manner with respect to both magnitude and orientation of the local magnetic moments. $Ni_{80}B_{20}$ appears to be paramagnetic. For $Fe_{80}B_{20}$ asperomagnetic configurations with increasing mean canting angle become stable with increasing mass density. The energetically low-lying configurations of $Fe_{40}Ni_{40}B_{20}$ are ferromagnetic or asperomagnetic with small canting angles and large (small) magnetic moments on the Fe (Ni) sites, in contrast to a recent suggestion of Cowley *et al* for the interpretation of their spin-polarized neutron scattering experiments.

1. Introduction

It is well known (see for instance [1]) that amorphous alloys with composition around $(Fe_xNi_{1-x})_{80}M_{20}$, M=B, Si, P etc, exhibit a spontaneous magnetization for not too small values of x. For a long time it was generally believed [2] that these systems were collinear ferromagnets with large magnetic moments on the Fe sites and at most very small magnetic moments at the Ni sites. Deviations from the perfect spin alignment were expected to occur on a wavelength much larger than the mean nearest-neighbour distance and to arise from magnetoelastic interactions with internal stresses, giving rise to small deviations from the ferromagnetic saturation at finite external fields [3, 4]. This general belief was fundamentally questioned by polarized neutron scattering experiments [5]. The results for the Ni-rich alloys, $x = 0.5$ and 0.25, could be interpreted by assuming 'that the Ni atoms do have a moment which is nearly comparable to that on the Fe atoms, but that this is randomly oriented and does not contribute to the ordered moment when a magnetic field is applied'. For Fe-based alloys ($x = 1$) the results suggested an appreciable random spin canting with a typical mean canting angle between 0 and 30° from the applied field direction for different samples at 2 T. The notion of spin cantings was supported by a number of indirect experiments. From the observed difference in the spin-wave stiffness coefficient D determined from the temperature dependence of the magnetization on the one hand and from the inelastic neutron scattering experiments on the other hand it was concluded [1] that there are spin cantings for $x > 0.75$ but ferromagnetic alignment for $x < 0.75$ (in contrast to the conclusions of [5]). Mössbauer measurements [6] on amorphous $Fe_{83}B_{17}$ also pointed at a non-collinearity in the spin arrangement which appeared to be a little smaller than that suggested by the spin-polarized neutron scattering experiments [5]. Finally, there are hints at non-collinear spin configurations from anisotropy and magnetostriction experiments [7, 8], which, however, do not give any indication of the length scale of the canting.

0953-8984/96/183207+07$19.50

In the present paper we report on a study of the spin configurations in amorphous $(Fe_xNi_{1-x})_{80}M_{20}$ with the *ab initio* electron theory. Former theoretical work on this system did not allow for non-collinear spin configurations. We just mention two calculations which treat the electronic structure problem self-consistently for each atom under the restriction of a collinear spin arrangement: Krompiewski *et al* [9] obtained by calculations based on the tight-binding Hubbard Hamiltonian (using an empirical Slater–Koster parametrization and a fitted value for the Hubbard parameter) for $Fe_{80}B_{20}$ at a density of 7.54 g cm^{-3} a ferromagnetic configuration with a distribution of moments with a mean value of $2.1\mu_B$ and half-width of $0.8\mu_B$ for the Fe atoms. Hafner *et al* [10] performed linear-muffin-tin-orbital calculations (LMTO) in the atomic-sphere approximation (ASA). For $Fe_{80}B_{20}$ they obtained a ferromagnetic arrangement at a density of 7.39 g cm^{-3} and an increasing fraction of antiparallel orientations with increasing density (a few antiparallel orientations were obtained already for 7.54 g cm^{-3}), accompanied by a decrease of the mean magnetic moment (from $1.86 \pm 0.3\mu_B$ at 7.39 g cm^{-3} to $1.39 \pm 0.5\mu_B$ at 7.74 g cm^{-3}). We do not know of any calculations for FeNiB systems.

2. Calculational method

In our calculations, based on the LMTO method in the ASA [11, 12], we take into account non-collinear spin configurations in a fully self-consistent manner concerning the values and the directions of the local magnetic moments, implementing the method of Kübler and co-workers [13, 14] in the LMTO–ASA scheme. The amorphous structure was approximated by supercells containing 20 or 35 atoms and the atomic positions generated by static relaxation of a random structure based on pair potentials as given by Brandt and Kronmüller [15]. Thereby, the same pair potential was used for Fe and Ni, and for the LMTO–ASA calculation the Fe and Ni atoms are distributed randomly on the generated transition-metal sites. For the supercell containing 35 (20) atoms the total and the partial pair correlation functions were up to the third (second) 'shell' of atoms in good agreement with those obtained for a big cluster of 2000 atoms generated in the same way. Thus for our purposes the models provide a realistic representation of a real amorphous alloy. Comparing the final results for the two supercell sizes we can study the influence of the periodic boundary conditions. As starting configurations for the self-consistency cycle we used random distributions of the polar angles θ (for the orientations of the local magnetic moments with respect to an external z-axis) from intervals $[0^\circ, 0^\circ]$, $[0^\circ, 45^\circ]$, $[0^\circ, 60^\circ]$, $[0^\circ, 90^\circ]$ and $[0^\circ, 180^\circ]$, and random distributions of the corresponding azimuthal angles ϕ. From the investigation of the convergence behaviour with respect to the number of k points used for the Brillouin zone sampling we find that energy differences between various final spin configurations are numerically relevant only if they exceed 2 meV (1 meV) per transition metal atom for the supercell containing 20 (35) atoms. It should be noted that the calculations do not take into account spin–orbit coupling effects and hence the influence of random atomic-scale magnetic anisotropies which in principle could also give rise to spin canting effects. For amorphous alloys based on transition-metal atoms the related anisotropy energy per atom amounts to at most a few tenths of a meV [16, 17] and is thus one order of magnitude smaller than the significance threshold of our calculations discussed above. We therefore think that random anisotropies do not generate spin cantings on an atomic scale in these systems.

3. Results and discussion

Because our results for the two supercell sizes agree qualitatively very well, we may assume that the periodic boundary conditions imposed in our calculations do not affect our general statements concerning the size and the orientation of the local magnetic moments.

Table 1. Lists of the obtained spin configurations for the $Fe_{16}B_4$ and $Fe_{28}B_7$ supercells at a density of 7.08 g cm^{-3}. ΔE_{tot} (in meV per transition-metal-atom) is the energy difference to the energetically lowest of the obtained configurations, μ_{tot} is the total magnetic moment for the supercell (in μ_B), $\bar{\mu}_{loc}$ and $\Delta\mu_{loc}$ describe the mean value and the variance of the local moments (in μ_B), $\bar{\theta}_{out}$ is the mean canting angle and θ_{in} describes the range of values from which the canting angles for the starting configurations of the self-consistency cycle are taken randomly. Note that energy differences between various configurations are numerically only relevant if they exceed 2 meV (for $Fe_{16}B_4$) or 1 meV (for $Fe_{28}B_7$) (see the text).

Spin configuration	ΔE_{tot}	μ_{tot}	$\bar{\mu}_{loc} \pm \Delta\mu_{loc}$	$\bar{\theta}_{out}(^\circ)$	$\theta_{in}(^\circ)$
$Fe_{16}B_4$					
1	0	30.93	1.97 ± 0.36	0	0
2	1	16.08	1.68 ± 0.52	50 ± 36	[0, 60]
3	4	26.95	1.85 ± 0.42	21 ± 14	[0, 45]
4	8	14.69	1.62 ± 0.55	51 ± 35	[0, 180]
5	10	15.97	1.62 ± 0.57	50 ± 24	[0, 90]
$Fe_{28}B_7$					
1	0	56.88	2.07 ± 0.31	0	0
2	4	44.91	1.95 ± 0.35	28 ± 25	[0, 60]
3	6	51.12	2.02 ± 0.34	20 ± 13	[0, 45]
4	14	8.55	1.69 ± 0.50	78 ± 35	[0, 180]
5	16	33.18	1.82 ± 0.41	41 ± 28	[0, 90]
6	38	5.87	1.50 ± 0.63	83 ± 36	[0, 180]

For $Ni_{80}B_{20}$ at a density of 8.12 g cm^{-3} (obtained by extrapolating the densities [1] for low Fe concentrations to pure $Ni_{80}B_{20}$) the calculations converged to a non-magnetic solution, independent of the starting configuration. In contrast, pure amorphous Ni without B turned out [18] to be a collinear ferromagnet.

Table 2. A list of the obtained spin configurations for the $Fe_{28}B_7$ supercell at a density of 7.44 g cm^{-3}. For the meanings of the symbols see the caption of table 1.

Spin configuration	ΔE_{tot}	μ_{tot}	$\bar{\mu}_{loc} \pm \Delta\mu_{loc}$	$\bar{\theta}_{out}(^\circ)$	$\theta_{in}(^\circ)$
1	0	18.41	1.35 ± 0.56	58 ± 45	[0, 45]
2	3	21.77	1.35 ± 0.52	56 ± 42	[0, 60]
3	4	4.66	1.19 ± 0.62	85 ± 30	[0, 180]
4	6	19.34	1.30 ± 0.54	50 ± 40	[0, 90]
5	14	37.50	1.43 ± 0.51	collinear	0
6	16	5.11	1.12 ± 0.61	82 ± 42	[0, 180]

For $Fe_{80}B_{20}$ calculations at densities of 7.08 and 7.44 g cm^{-3} were performed according to the densities of the samples investigated by Kaul and Babu [1] and Hasegawa and Ray [19], respectively. At a density of 7.08 g cm^{-3} the ferromagnetic configuration with large average magnetic moment of the Fe atoms (about $2\mu_B$) and a moderate spread in the magnitudes of the local magnetic moments (about $0.3\mu_B$) appeared to be the most stable one among all the configurations found for the two supercell sizes (table 1).

However, we found also asperomagnetic configurations which were energetically very close to the ferromagnetic configuration, and therefore we cannot strictly exclude the possibility that there are other asperomagnetic configurations which are lower in energy than the ferromagnetic configuration but which we did not find in our calculations. For the supercell containing 35 atoms the energetically lowest asperomagnetic configuration had a mean canting angle of 20–30° with a distribution of the magnitudes of the local magnetic moments similar to the ferromagnetic case. At a density of 7.44 g cm^{-3} the obtained low-energy configurations were asperomagnetic (table 2) with a mean canting angle between 50 and 60°, a small average magnetic moment ($1.35\mu_B$) and a large spread in the magnitudes of the local magnetic moments (about $0.55\mu_B$). The ferromagnetic configuration was not stable: when starting from a ferromagnetic alignment we arrived at the collinear configuration 5 from table 2 where one magnetic moment was oriented antiferromagnetically. Altogether, we found for $Fe_{80}B_{20}$ asperomagnetic configurations with the tendency of low canting angles (or even zero canting angle) and large magnetic moments at low densities and large canting angles and smaller magnetic moments for larger densities.

Table 3. Lists of the obtained spin configurations for the $Fe_8Ni_8B_4$ and $Fe_{14}Ni_{14}B_7$ supercells at a density of 7.49 g cm^{-3}. For the meanings of the symbols see the caption of table 1.

Spin configuration	ΔE_{tot}	μ_{tot}	$\bar{\mu}_{loc} \pm \Delta\mu_{loc}$ Fe	Ni	$\bar{\theta}_{out}(^\circ)$	$\theta_{in}(^\circ)$
$Fe_8Ni_8B_4$						
1	0	18.99	2.02 ± 0.52	0.41 ± 0.10	0	0
2	4	17.15	1.98 ± 0.52	0.40 ± 0.11	15 ± 15	[0, 180]
3	6	16.19	1.98 ± 0.52	0.38 ± 0.11	21 ± 14	[0, 180]
4	17	9.86	1.90 ± 0.55	0.30 ± 0.12	36 ± 29	[0, 180]
5	17	7.86	1.88 ± 0.58	0.26 ± 0.13	44 ± 27	[0, 180]
6	22	6.45	1.80 ± 0.64	0.21 ± 0.12	44 ± 41	[0, 180]
$Fe_{14}Ni_{14}B_7$						
1	0	35.55	2.18 ± 0.32	0.42 ± 0.12	0	0
2	2	34.02	2.18 ± 0.35	0.41 ± 0.12	10 ± 9	[0, 90]
3	14	25.19	2.12 ± 0.35	0.33 ± 0.11	28 ± 19	[0, 60]
4	23	20.04	2.07 ± 0.40	0.27 ± 0.11	40 ± 25	[0, 180]

Our theoretical data for $Fe_{80}B_{20}$ agree quite well with the experimental results. At the density of 7.08 g cm^{-3} Kaul and Babu [1] found a magnetization of 185.09 emu g^{-1} and a g factor of 2.1 corresponding to a magnetic spin moment of about $52.4\mu_B$ for seven formula units of Fe_4B, i.e. $Fe_{28}B_7$, which is slightly smaller than our value of $56.88\mu_B$ for the ferromagnetic configuration and slightly larger than the value for our asperomagnetic configuration 3 of table 1. This may be explained by the existence of small spin cantings in the sample of Kaul and Babu, which is supported by their investigations of the spin wave stiffness coefficient D discussed above and which cannot be excluded by our calculations where the ferromagnetic configuration and several asperomagnetic configurations are nearly degenerate. The spin-polarized neutron scattering experiments of Cowley *et al* [5] revealed a mean canting angle between 0 and 30° for various Fe-based alloys with slightly differing metalloid content, again consistent with our results. The agreement of our results with the above-discussed theoretical papers which did not allow for spin cantings is less good: Krompiewski *et al* [9] obtained for a density of 7.54 g cm^{-3} a ferromagnetic configuration with a large average magnetic moment of about $2.1\mu_B$ whereas our calculations suggest an asperomagnetic ground state configuration with a smaller average magnetic moment of

about $1.35\mu_B$. The data from the above-discussed LMTO–ASA calculations of Hafner *et al* [10] are qualitatively consistent with our results when we shift their data by about 0.3 g cm^{-3} to lower densities. One reason for the discrepancies might be a different degree of structural randomness resulting from the different procedures for the generation of the amorphous model structures.

Table 4. A list of the obtained spin configurations for the $Fe_{14}Ni_{14}B_7$ supercell at a density of 7.92 g cm^{-3}. For the meanings of the symbols see the caption of table 1.

Spin configuration	ΔE_{tot}	μ_{tot}	$\bar{\mu}_{loc} \pm \Delta\mu_{loc}$ Fe	Ni	$\bar{\theta}_{out}(^\circ)$	$\theta_{in}(^\circ)$
1	0	32.54	1.98 ± 0.35	0.40 ± 0.12	0	0
2	3	27.55	1.89 ± 0.43	0.35 ± 0.13	21 ± 9	[0, 90]

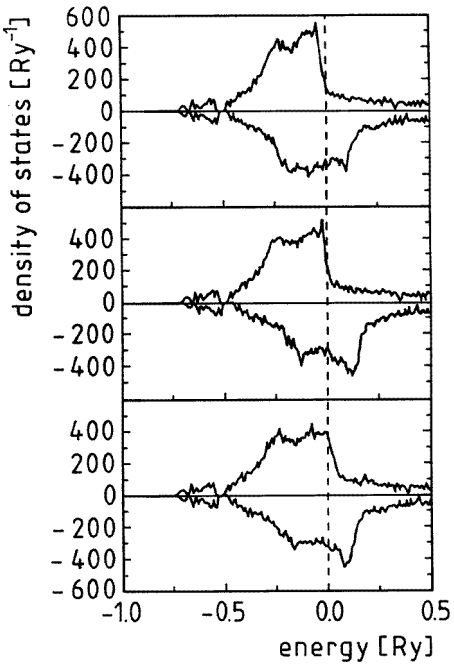

Figure 1. The density of spin-up states (upper parts of the figures) and spin-down states (lower parts) for the collinear configurations in $Fe_{40}Ni_{40}B_{20}$ at a density of 7.49 g cm^{-3} (top), in $Fe_{80}B_{20}$ at 7.08 g cm^{-3} (middle) and in $Fe_{80}B_{20}$ at 7.44 g cm^{-3} (bottom).

For $Fe_{40}Ni_{40}B_{20}$ we performed calculations at a density of 7.49 g cm^{-3} as obtained by Kaul and Babu [1] and at a density of 7.92 g cm^{-3}. The ratio of these two densities is the same as the ratio of the densities for $Fe_{80}B_{20}$ as obtained by Hasegawa and Ray [19] and by Kaul and Babu [1]. At 7.49 g cm^{-3} the ferromagnetic configuration with large average magnetic moments of about $2.2\mu_B$ on the Fe sites appeared to be the most stable. For the asperomagnetic configurations (table 3) the energy increases monotonically with increasing mean canting angle, accompanied by a slight decrease of the average Fe moment and a strong decrease of the average Ni moment. At a density of 7.92 g cm^{-3} we considered only

two configurations, the ferromagnetic one and an asperomagnetic one obtained when using the same starting configuration as for configuration 3 of table 3. Again, the ferromagnetic configuration was the more stable one. Altogether, the energetically low-lying configurations of $Fe_{40}Ni_{40}B_{20}$ which we obtained were all ferromagnetic or asperomagnetic with small magnetic moments on Ni sites, in agreement with the general belief [2]. No configurations with large and strongly canted magnetic moments on the Ni sites were obtained, in contrast to the interpretation given by Cowley *et al* [5] for the spin- polarized neutron scattering experiment.

Concerning the electronic states in alloys of transition metal atoms and metalloid atoms the band-gap theory of Malozemoff *et al* [20] predicted a band gap in the density of states of the spin-majority band due to the hybridization between the metalloid sp states and the transition-metal d states, such that the system behaves like a strong ferromagnet with only minority states present at the Fermi energy E_F. Figure 1 represents the density of states for the collinear configurations in $Fe_{40}Ni_{40}B_{20}$ at a density of 7.49 g cm^{-3}, in $Fe_{80}B_{20}$ at 7.08 g cm^{-3} and in $Fe_{80}B_{20}$ at 7.44 g cm^{-3}. Both for the majority and for the minority states there are two peaks in the density of states arising from the Fe atoms and an additional structure at the lower band edge arising from the B states, in qualitative agreement with results obtained by previous electronic structure calculations for ferromagnetic $Fe_{80}B_{20}$ (see, for instance, [21] and [22]). In none of these systems does the predicted gap appear, i.e. the band-gap theory does not hold in the present case. The collinear $Fe_{80}B_{20}$ magnet represents a weak ferromagnet with both spin-majority and spin-minority states at the Fermi energy. Because non-collinear spin structures involve hybridization effects between majority and minority states, energetically low-lying non-collinear configurations only appear [18] in systems for which the collinear configurations represent weakly magnetic states in the above-discussed sense. In $Fe_{80}B_{20}$ there is only a small density of spin-up states at E_F for $\rho = 7.08$ g cm^{-3}, whereas for 7.44 g cm^{-3} the density of states is comparable for the two spin directions. Consequently, the tendency for spin canting is stronger at the higher density (compare table 1). In $Fe_{40}Ni_{40}B_{20}$ the density of spin-majority states at E_F is very small and therefore there is only a small tendency for spin canting in this system and it should behave more or less like a strong ferromagnet. This is in contrast to the statement of Kaul and Babu [1] based on thermal demagnetization experiments that all the compositions in the amorphous $(Fe_xNi_{1-x})_{80}(B, Si)_{20}$ alloy series behave as weak itinerant ferromagnets.

Acknowledgments

Some of the calculations were performed at the HLRZ c/o KFA Jülich. The authors are indebted to R Cowley for helpful discussions.

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