PHYSICAL REVIEW B, VOLUME 65, 104423

Magnetic properties of amorphous, crystalline, and liquid Ni-B alloys

I. Bakonyi*
Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary

E. Babić and M. Miljak
Institute of Physics, University of Zagreb, P.O. Box 304, CR-41001 Zagreb, Croatia

R. Lück and J. Bahle
Max-Planck-Institut für Metallforschung, Seestraße 92, D-70174 Stuttgart, Germany

R. Hasegawa
Honeywell International Inc., 440 Allied Drive, Conway, South Carolina 29526

J. Kollár
Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary

(Received 2 July 2001; revised manuscript received 22 October 2001; published 20 February 2002)

From a comprehensive study of the magnetic properties of amorphous and liquid $Ni_{100-x}B_x$ alloys with $18.5 \leqslant x \leqslant 40$, the individual contributions to the magnetization are identified and determined separately. The matrix of the amorphous Ni-B alloys is found to exhibit Pauli paramagnetism even for $x = 18.5$, where the observed magnetization was dominated by superparamagnetic particles. The Pauli susceptibility decreases monotonically with increasing B-content and, for a given composition, it agrees well with extrapolated room-temperature liquid state data and with the value of the corresponding crystalline stoichiometric compound. The critical concentration for the onset of spontaneous magnetic order is established to be more than 81.5-at. % Ni. On the basis of the electronic density of states (DOS) deduced from previous low-temperature specific-heat measurements for various Ni-metalloid alloys, the Stoner-enhanced Pauli susceptibility is calculated for the Ni-B system and a good agreement with the experimental conduction electron susceptibility is obtained. The temperature dependence of the Pauli susceptibility is also discussed for amorphous Ni-B alloys and for liquid Ni-metalloid alloys, the features being explained in terms of the DOS data.

DOI: 10.1103/PhysRevB.65.104423 PACS number(s): 71.22.+i, 71.23.Cq, 75.50.Kj

I. INTRODUCTION

Pure Ni metal is known to be a strong itinerant ferromagnet in which the uncompensated electron spins of spin-down *d* subbands give rise to the observed ferromagnetism. Alloying Ni with *sp* elements (e.g., metalloids such as B or P) reduces the strength of the exchange interaction between electrons in the *d* band of Ni, leading to a decrease of the saturation magnetic moment and Curie temperature.[1,2] At sufficiently high metalloid contents, ferromagnetism completely disappears and Pauli paramagnetism can be observed.[3]

The nature of this ferromagnetic-paramagnetic FM-PM transition was recently studied in detail for the amorphous Ni-P alloy system in the composition range from 10- to 25-at. % P.[4] The critical concentration for the onset of FM order could be identified as 85.7-at. % Ni (14.3-at. % P), beyond which very weak itinerant ferromagnetism (VWIF) could be observed. It should be mentioned, however, that the magnetization of Ni-P alloys for intermediate compositions (14–17-at. % P) was dominated by superparamagnetic (SPM) particles which were strongly Ni-enriched segregations embedded in a homogeneous amorphous matrix. The existence of such SPM particles could be demonstrated in the VWIF phase as well. Magnetic inhomogeneities could also be revealed in the paramagnetic phase ($P > 17$ at. %) in the form of ferromagnetic precipitates (crystalline Ni or Ni-rich regions) and giant-moment paramagnetic clusters [amorphous Ni-rich segregations carrying a magnetic moment of typically $(5-10)\mu_B$]. The behavior of the latter can be described by a Curie-Weiss-type susceptibility, and their contribution could be properly separated from the matrix magnetization.

In the Ni-B alloy system, several studies of the magnetic properties were already reported on chemically reduced[5,6] and melt-quenched[7–16] amorphous alloys. By considering previous works on the preparation of melt-quenched amorphous Ni-B alloys,[17–21] it can be established that two glass-forming ranges were usually found, although the limiting concentrations varied to some extent from work to work. The very narrow first range is around the eutectics at 17-at. % B and the second range spans between about 30- and 40-at. % B. Exceptionally, the formation of an amorphous state of a melt-quenched $Ni_{75}B_{25}$ alloy was reported.[21]

In the concentration range from 30- to 40-at. % B, amorphous alloys can been obtained without the presence of a significant amount of crystalline precipitates. On the other hand, for Ni-B alloys at about 18.5-at. % B, the formation of not entirely amorphous regions (e.g., crystalline Ni and Ni_3B particles of about 10–30-μm diameter[7,18]) cannot usually be avoided, and they can constitute as much as 2–3 % of the total sample volume. As discussed below, Ni-B alloys at this particular B-content are already close to the PM-FM transition. In Ni-based alloys, either crystalline[22] or amorphous[4,23] Ni atoms have a very strong tendency toward segregation in the neighborhood of the critical concentration for the appearance of ferromagnetism. Besides the required very high cooling rate necessary to avoid the formation of Ni precipitates completely, this phenomenon may also play a significant role in the difficulties to obtain fully amorphous $Ni_{81.5}B_{18.5}$ samples by melt-quenching.

Similarly to the case of the glass-forming ability, amorphous Ni-B alloys can be divided into two groups, also from the viewpoint of their observed magnetic behavior. For compositions around 18.5-at. % B, ferromagneticlike magnetization characteristics were observed in all reported studies.[5–11,13–16] The interpretation of the observed magnetization characteristics of amorphous Ni-B alloys around 18.5-at. % B has remained controversial up to now: either Pauli paramagnetism[8,9,11,13–15] or the VWIF[10] was concluded. In support of the latter view, ferromagnetic resonance (FMR) measurements[24] were also performed, whereas evidence of Pauli paramagnetism was obtained from measurements of the susceptibility of the liquid state[8,9,13,14] and from a combined high-field magnetization and ^{11}B NMR Knight shift study.[11]

On the other hand, for all the amorphous Ni-B alloys with $\geqslant$25-at. % B, a Pauli paramagnetic behavior was found.[9,10,12,13] It is generally accepted that the majority of the atoms in the amorphous matrix are nonmagnetic, and that their main susceptibility contribution is of Pauli paramagnetic type. However, the reported results concerning the temperature dependence of the Pauli susceptibility are still contradictory.[10,13]

One of the purposes of the present paper is to clear up the still existing controversies in the reported magnetic behavior of amorphous Ni-B alloys. Here we will give a more detailed account of our previous magnetization studies[11,12,14] on melt-quenched amorphous Ni-B alloy ribbons, and present results for the liquid state as well. Special emphasis will be devoted to evaluating available magnetization data of amorphous, crystalline, and liquid Ni-B alloys in order to show the following: (i) The ferromagneticlike behavior observed for amorphous $Ni_{81.5}B_{18.5}$ alloys can be attributed to SPM particles, whereas the alloy matrix is paramagnetic with a large, Stoner-enhanced Pauli susceptibility. (ii) For amorphous Ni-B alloys with 25-at. % $\leqslant$ B $\leqslant$ 40 at. %, the matrix Pauli susceptibility is practically temperature independent, and decreases linearly with increasing B content. Results on the liquid state susceptibility of Ni-B alloys allowed us to trace out a weak temperature dependence of the Pauli susceptibility of the structurally disordered phase at such high temperatures. We shall also discuss the variation of the temperature coefficient of the conduction electron susceptibility with alloy composition in liquid Ni-metalloid systems, and will explain it in terms of their electronic band structure.

The paper is organized as follows. Section II describes the details of sample preparation and magnetic measurements. In Sec. III results are presented for amorphous, liquid, and crystalline Ni-B alloys, with special emphasis on the magnetic behavior of the amorphous alloys around 18.5-at. % B. In Sec. IV, first the composition dependence of the Pauli susceptibility of Ni-B alloys is discussed on the basis of previously reported low-temperature electronic specific-heat data. Then the temperature dependence of the Pauli susceptibility of amorphous Ni-B alloys with $\geqslant$25-at. % B and the temperature coefficient of the conduction-electron susceptibility in liquid Ni-metalloid alloys are discussed. All these features will be explained in terms of the electronic band structure of Ni-B alloys. In Sec. V, the conclusions of the present study are summarized.

II. EXPERIMENT

A. Samples

Here we shall be concerned mainly with the same amorphous $Ni_{100-x}B_x$ alloy ribbons prepared by melt spinning with $x = 18.5$, 25, 31, 33, 35, and 40, on which we have already reported some magnetization and ^{11}B NMR studies.[11,12,15,21] Results for another melt-quenched amorphous $Ni_{81.5}B_{18.5}$ alloy, which was part of a Ni-P-B alloy series,[14] will also be included. More details of the sample preparation and sample characterization were described previously.[11,14,21]

B. Magnetic measurements

The magnetic properties of amorphous ribbons were measured by Faraday-type magnetic balances in magnetic fields up to 50 kOe (18.5-at. % B) and up to 9.4 kOe ($\geqslant$25-at. % B). For each alloy, both the field and temperature dependences of the magnetization were determined from the liquid-helium range to room temperature.

In a high-temperature magnetic Faraday balance, the temperature dependence of the magnetization was determined from 300 K into the molten state (up to about 1500 K) in a magnetic field of 17 kOe at a heating rate of 5 K/min.

III. RESULTS AND DATA ANALYSIS

A. Magnetic properties of amorphous Ni-B alloys

1. Magnetization isotherms of amorphous Ni-B alloys with 25-at. % $\leqslant$ B $\leqslant$ 40 at. %

The magnetization isotherms of amorphous $Ni_{100-x}B_x$ alloys in the composition range 25–to 40-at. % B were found to be qualitatively very similar to those reported recently for PM amorphous Ni-P, Ni-P-B, and Ni-B-Si alloys.[4,14,25] Here we shall follow the scheme of Ref. 4 in analyzing the data. At a given temperature, the magnetization (σ) of the Ni-B amorphous alloys can be separated into (i) a small ferromagnetic contribution $\sigma_s(T)$, being saturated for magnetic fields $H \geqslant H_s$ (according to our experience, H_s varied typically from 2 to 4 kOe); and (ii) a linear term characterized by the temperature dependent initial susceptibility $\chi_o(T)$. In this manner, for magnetic fields $H > H_s$, the magnetization could be described as

$$\sigma(H,T) = \sigma_s(T) + \chi_0(T)H. \tag{1}$$

The susceptibility $\chi_0(T)$ could be written for the whole temperature range as

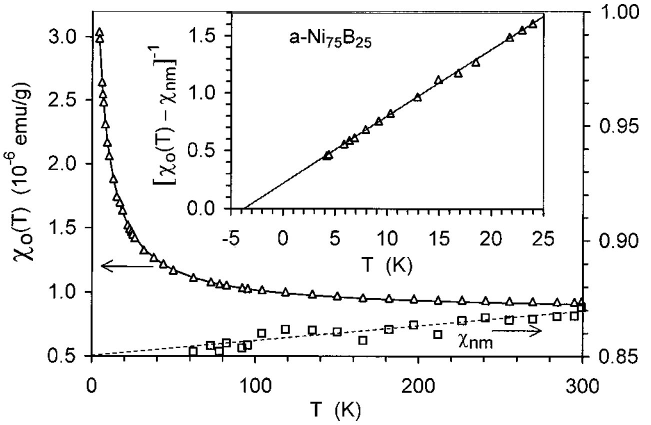

FIG. 1. Temperature dependence of the initial susceptibility $\chi_0(T)$ for the a-Ni$_{75}$B$_{25}$ alloy. The inset shows that at the lowest temperatures, Eq. (2) is valid with a temperature-independent value $\chi_{\mathrm{nm}}=0.85\times10^{-6}$ emu/g, and this plot also yields the value of C_{CW} and θ (see Table I). The quantity $\chi_0(T)-\chi_{\mathrm{CW}}$ ($\equiv\chi_{\mathrm{nm}}$) is also plotted at the bottom of the figure on an enlarged scale, demonstrating the possible very weak, linear temperature dependence of χ_{nm}.

$$\chi_0(T)=\chi_{\mathrm{nm}}+C_{\mathrm{CW}}/(T+\theta), \tag{2}$$

where χ_{nm} is a temperature-independent susceptibility, and the second term is a Curie-Weiss (CW)-type susceptibility with the constant C_{CW} and a characteristic temperature θ.

Figure 1 demonstrates that Eq. (2) indeed describes very well the temperature dependence of the initial susceptibility for a-Ni$_{75}$B$_{25}$. Also plotted in the bottom of the figure are the data obtained after removing the fitted Curie-Weiss term from the measured susceptibility in a range from 60 to 300 K. An extremely weak temperature dependence ($d\chi_{\mathrm{nm}}/dT=0.003\times10^{-6}$ emu/mol K) could only be revealed. However, the evolution of χ_{nm} with temperature was found to be very sensitive to the fitting parameters within a range where the quality of the fit remained practically unchanged. It should also be noted that due to a possible decomposition of larger Curie-Weiss-type clusters into smaller ones with increasing temperature, as discussed previously[22] for Ni-based alloys, may also lead to an apparent temperature dependence of χ_{nm}. Therefore, due to the presence of the Curie-Weiss term, a reliable temperature dependence of χ_{nm} cannot be deduced for the amorphous Ni-B alloys, especially for higher B contents.

According to the work of Amamou and Durand,[23] the FM magnetization component can be attributed to crystalline Ni or Ni(B) precipitates, and the CW term can be ascribed to the presence of giant-moment paramagnetic clusters consisting of Ni-rich amorphous regions embedded in the amorphous matrix. The temperature independent susceptibility χ_{nm} can be associated with the contribution of non-magnetic atoms of the amorphous phase, and it is composed of a conduction electron susceptibility (χ_{cond}) and an ion-core diamagnetic susceptibility ($\chi_{\mathrm{dia,core}}$). The conduction-electron susceptibility χ_{cond} is thus obtained as

$$\chi_{\mathrm{cond}}=\chi_{\mathrm{nm}}-\chi_{\mathrm{dia,core}}. \tag{3}$$

For the diamagnetic correction $\chi_{\mathrm{dia,core}}$, we take the values as given by Selwood[26]: -12×10^{-6} emu/mol for Ni^{2+} and -0.2×10^{-6} emu/mol for B^{3+}. In the case of nickel-metalloid alloys, χ_{cond} can be identified with a Pauli susceptibility that depends on the electronic density of states (DOS) at the Fermi level, $N(E_F)$, as discussed in Sec. IV A. The values of the magnetic parameters $\sigma_s(300\ \mathrm{K})$, C_{CW}, θ, χ_{nm}, and χ_{cond} determined in the above manner for the amorphous Ni-B alloys with ⩾25-at. % B are given in Table I, together with relevant data from the literature.[10,13]

The saturating ferromagnetic component $\sigma_s(T)$ due to ferromagnetic precipitates (crystalline Ni) was only slightly decreasing with increasing temperature up to 300 K. The value of $\sigma_s(300\ \mathrm{K})$ which depends on the specific details of the melt-quenching process is very small in all the alloys studied here. The observed magnitudes of $\sigma_s(T)$ correspond to a magnetization of about 10–50-wt ppm pure crystalline Ni in our samples. The value of C_{CW} decreases continuously with increasing B content, becoming very small for

TABLE I. Magnetic parameters of amorphous Ni-B alloys with ⩾25-at. % B. In the present work, χ_{nm} was a temperature-independent parameter in fitting the susceptibility data measured in the range 4.2⩽K T ⩽300 K. The χ_{nm} data from Refs. 10 and 13 are the reported χ_{nm}(0 K) and χ_0(100 K) values, respectively.

B content (at. %)	σ_s(300 K) (10^{-3} emu/g)	C_{CW} (10^{-6} K emu/g)	θ (K)	χ_{nm} (10^{-6} emu/g)	χ_{cond} (10^{-6} emu/mol)	Ref.
25	1.0	17	3.7	0.85±0.02	49±1	
31	2.9	11	3.7	0.87±0.09	47±4	
33	3.9	6	3.5	0.75±0.08	40±3	this work
35	3.1	3	2	0.68±0.14	36±6	
40	0.5	<1		0.42±0.07	24±3	
30.8		162.7	18.5	0.85±0.01	46±1	
34		124.2	33.1	0.74±0.01	39±1	10
37		12.8	5.9	0.64±0.01	34±1	
33.3				0.60±0.05	34±3	13
37				0.50±0.05	28±3	

a-Ni$_{60}$B$_{40}$. Since $C_{\mathrm{CW}}=n\mu^2/3k_B$, where μ is the average magnetic moment of the giant-moment clusters, n is their concentration in the sample, and k_B is Boltzmann's constant, it follows that either the size or the concentration of the clusters (or both) become smaller when the alloy is enriched in B. This finding is expected since the more B atoms are in the alloy, the lower is the probability for the formation of Ni-rich segregations. The very small θ values for the present Ni-B alloys indicate that the giant-moment clusters remain paramagnetic in the whole temperature range investigated. It is noted that the $\theta>0$ values in Table I can occur eventually, also due to the approximate description of the real temperature dependence by Eq. (2).

According to the parameters characterizing the magnetic inhomogeneities in the amorphous matrix as listed in Table I, their contribution to the total observed magnetization is fairly small in our samples (see Table I), especially in comparison with previous studies. Therefore, the conduction electron susceptibility could be reliably extracted from the experimental data. The composition dependence of χ_{cond} will be discussed in more detail in Sec. IV A.

2. Magnetism of amorphous Ni-B alloys with B≈18.5 at. %

As discussed in Sec. I, during the preparation of amorphous Ni-B alloys with ⩾25-at. % B, amorphous and crystalline inhomogeneities may occur in the form of giant-moment paramagnetic clusters and ferromagnetic precipitates, respectively. The formation (i.e., the number and size) of these magnetic inhomogeneities is influenced by the composition of the matrix and by the preparation technique (in the case of melt quenching, by the cooling rate and the glass-forming ability). It was pointed out in Sec. III A 1 that for a given starting material (i.e., a given impurity content) and cooling conditions, either the size or the concentration of the giant-moment paramagnetic clusters, or both, increases when increasing the Ni content. For this reason, at ≈18.5-at. % B one may expect the formation of larger giant-moment clusters than for 25-at. %⩽B⩽40-at. %. Furthermore, the rather low glass-forming ability at 18.5-at. % B may also influence the size and concentration of the ferromagnetic precipitates. Any of these two facts may lead to the situation that, at ≈18.5-at. % B, besides the normal ferromagnetic crystalline precipitates and giant-moment paramagnetic clusters which are characteristic for the higher B content (⩾25-at. % B) alloys, magnetic inhomogeneities in size between those of the other two types are also formed during the melt-quenching process. If the size of the magnetic inhomogeneities becomes significantly higher than the usual giant-moment cluster size $[(5-10)\mu_B$ (Ref. 23)] but still remains below a critical value for a given temperature, then we have to deal with SPM particles.[27,28] The magnetic behavior of the latter is intermediate between the giant-moment clusters and bulk ferromagnetics.

It has indeed been demonstrated for amorphous Ni-P alloys[4] that when the Ni content approaches the critical concentration for the PM-FM transition, the magnetization of these alloys is dominated by the contribution of SPM particles. In this section, it will be shown that the observed magnetization characteristics of amorphous Ni$_{81.5}$B$_{18.5}$ can be interpreted in the same framework.

In a recent paper,[29] we compared the previously reported magnetization isotherms[7,10,11,14] of melt-quenched amorphous Ni$_{81.5}$B$_{18.5}$ alloys. A rapid increase up to a few kOe was found in each case and then, in fields of 10–20 kOe, the magnetization reached an apparent saturation value of about 1 emu/g. This saturation value varied only little with temperature between 4.2 and 300 K. From the magnetization isotherms reported in Ref. 11, the Arrott plots $[\sigma^2(H,T)$ vs $H/\sigma(H,T)]$ were constructed.[29] Their analysis yielded a Curie point of 510 K that is very close to the result (450 K) of Kaul and Rosenberg[10] from a similar analysis for a melt-quenched amorphous Ni$_{81.6}$B$_{18.4}$ alloy. For the a-Ni$_{81.5}$B$_{18.5}$ alloy reported in Ref. 14, an Arrott plot evaluation of the magnetization isotherms between 5.1 and 300 K also indicated a Curie point well above room temperature.

On the other hand, a comparison of the magnetization data of the a-Ni$_{81.5}$B$_{18.5}$ alloy with results on a-Ni$_{81.5-x}$Fe$_x$B$_{18.5}$ alloys[29] revealed that the partial replacement of Ni by Fe in the a-Ni$_{81.5}$B$_{18.5}$ alloy drastically reduced the magnetization values and the magnetic transition temperatures (a Curie point as low as about 50 K was observed even for $x=3$). This finding was attributed[29] to the fact that the introduction of Fe into the binary Ni$_{81.5}$B$_{18.5}$ alloy significantly improved the glass-forming ability, and helped avoid the formation of strongly magnetic inhomogeneities during the melt-quenching process. In the binary alloy, these inhomogeneities (Ni-rich segregations) will be identified below as particles with a SPM behavior.[27,28]

We will proceed similarly as was done in the case of amorphous Ni-P alloys around the critical concentration for the onset of magnetism.[4] Therefore, the magnetization of the a-Ni$_{81.5}$B$_{18.5}$ alloys will be analyzed by the Langevin function[27,28]

$$\sigma(H,T)=n\mu[\coth(\mu H/k_BT)-k_BT/\mu H]. \tag{4}$$

Here μ and n are the average magnetic moment and concentration of the SPM particles, respectively. According to Eq. (4), the magnetization of an assembly of SPM particles is a function of H/T only.

Figure 2 shows the $\sigma(H,T)$ vs H/T plot for the a-Ni$_{81.5}$B$_{18.5}$ alloy reported in Ref. 14 and, in the inset, for the data from Ref. 11. It can be established that, above about 90 K, the magnetization data at various temperatures follow a common trend for both alloys. The solid lines represent Langevin functions fitted as close as possible to the experimental data. These lines correspond to the magnetization contribution of SPM particles having an average moment of several thousand Bohr magnetons and a particle density of the order of 10^{16}/g. By taking $0.6\mu_B$/Ni atom, a typical SPM particle in these a-Ni$_{81.5}$B$_{18.5}$ alloys consists of about 10^4 Ni atoms. Such a particle corresponds to a cube having about 22 atoms along each edge. By taking 0.5 nm for the diameter of a Ni atom, one ends up with a particle size of about 10 nm, which is quite reasonable.

These SPM particles are apparently much larger that those deduced from a similar analysis of electrodeposited amorphous Ni-P alloys[4] around the PM-FM transition (15–17-

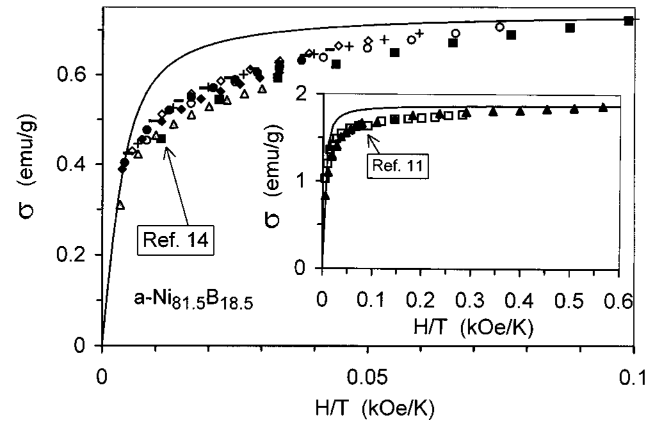

FIG. 2. Magnetization (σ) vs. H/T plot for a-$Ni_{81.5}B_{18.5}$ by using data from Ref. 14. The different symbols refer to different temperatures in the range 90–300 K. The solid line represents a Langevin function describing the magnetic behavior of SPM particles according to Eq. (4) with the parameters $\mu = 7500\ \mu_B$ and $n = 1.1\times10^{16}$ particles/g. The inset shows the same plot for the a-$Ni_{81.5}B_{18.5}$ alloy by using data from Ref. 11 for $T = 90$ and 180 K, and the solid line is the Langevin function with $\mu = 6000\ \mu_B$ and $n = 3.4\times10^{16}$ particles/g.

at. % P) where the particles consisted of typically 200 Ni atoms. On the other hand, the particle density was about an order of magnitude higher for the Ni-P alloys.[4] It is obviously hard to estimate to what extent the differences in particle size and density arise due to the different preparation techniques and due to the different influence of P and B on the glass-forming ability even if we know that the glass-forming ability is definitely much lower for the Ni-B system around 18.5-at. % metalloid content. Nevertheless, some of the very large particles in the a-$Ni_{81.5}B_{18.5}$ alloy may already behave as FM precipitates. This fact may partly explain the deviation of the experimental data (Fig. 2) from the ideal SPM behavior according to Eq. (4). Another reason for the discrepancy can be a distribution of SPM particle size (and, correspondingly, the magnetic moment) that was shown[30] to lead to a deviation of the experimental data from the Langevin function, just as observed in Fig. 2.

On the basis of the analysis in this section, it can be established that the magnetization of amorphous alloys around the composition $Ni_{81.5}B_{18.5}$ is dominated by SPM particles which are embedded in a Pauli paramagnetic amorphous matrix, in agreement with the conclusion of several previous studies.[11,29]

B. Magnetic susceptibility of liquid Ni-B alloys

The magnetic susceptibility was studied for liquid Ni-B alloys in the composition range 18.5–40-at. % B. The behavior of the susceptibility with temperature around the melting and solidification points was found to be similar for all the alloys studied here as already reported for a $Ni_{81.5}B_{18.5}$ alloy[14] and for Ni-P[4] and Ni-P-B alloys.[14] At the high temperatures of the molten state ($T > 1300$ K), neither FM phases nor magnetic inhomogeneities with localized magnetic moment are present since the Curie point of Ni is 631 K. Therefore, the measured susceptibility is characteristic for the molten state of the alloy only. Usually, the magnetic susceptibility χ_{nm} of liquid Ni-metalloid alloys exhibits a weak, linear temperature dependence,[14] and such a behavior was observed also in the present work and previously.[13,14,31] The liquid state susceptibility data of Ni-B alloys are collected in Table II, together with corresponding data from the literature.

C. Magnetic susceptibility of crystalline Ni-B compounds

In the composition range of the amorphous phase formation of Ni-B alloys, there are several stoichiometric interme-

TABLE II. Magnetic susceptibility data of liquid Ni-B and two ternary Ni-metalloid alloys.

B content (at. %)	$d\chi_1/dT$ (10^{-6} emu/mol K)	χ_1(1400 K) (10^{-6} emu/mol)	$\chi_{1,\mathrm{cond}}$(1400 K) (10^{-6} emu/mol)	Ref.
18.5		168	178	this work
25	+0.031	66	75	
31	+0.034	62	70	
33	+0.020	57	65	
35	+0.032	57	65	
40	+0.019	39	46	
15		150	160	13
18.5		210	220	
22		94	103	
25		63	72	
33.3		45	53	
37		38	45	
18.5	−0.009	156	166	14
19.3	−0.005	140	150	31
$Ni_{78}B_{14}Si_8$	+0.018	116	126	this work
$Ni_{80}P_{14}B_6$	+0.027	123	133	

TABLE III. Room-temperature magnetic susceptibility of crystalline Ni-B compounds. The conduction electron susceptibility is given for reliable matrix susceptibility values only.

Compound	χ_{nm} (10^{-6} emu/g)	χ_{cond} (10^{-6} emu/mol)	Ref.
	1.41		32
Ni_3B	0.95	54 ± 1	33
	0.96 ± 0.02	54 ± 1	12
	0.87		34
Ni_2B	0.73		32
	0.72 ± 0.03		35
	0.70 ± 0.03	36 ± 1	12
Ni_4B_3	0.47 ± 0.02	25 ± 1	12
	$0.20-0.17$		36
	0.14 ± 0.03		35
NiB	0.04 ± 0.02		37
	-0.04	4 ± 1	34
	-0.08	4 ± 1	32

tallic compounds: Ni_3B, Ni_2B, Ni_4B_3, and NiB. The available room-temperature magnetic susceptibility data of Ni-B compounds are collected in Table III. The apparently too large values reported in some cases will be omitted from the further evaluation (see the third column of Table III), since these data indicate the presence of a large amount of Ni-rich segregations as we have discussed in detail for the case of the NiB compound.[38]

IV. DISCUSSION

A. Composition dependence of the conduction-electron susceptibility of Ni-B alloys

As mentioned in Sec. III A 1, the conduction-electron susceptibility can be obtained from the measured matrix susceptibility by correcting for ion-core diamagnetism according to Eq. (3). Based on the χ_{cond} data summarized in Tables I–III, the composition dependence of the conduction electron susceptibility of Ni-B alloys is shown in Fig. 3. The susceptibility χ_{cond} decreases nearly linearly with a B content of $\geqslant$25 at. %, and its value is practically the same for the amorphous and crystalline modifications. The liquid state data at 1400 K are somewhat higher; however, when extrapolated according to the observed temperature dependence down to 300 K, they fall fairly close to the data of the amorphous and crystalline states.

For Ni-metalloid alloys, the main contribution to χ_{cond} is the Pauli susceptibility χ_P (Refs. 4 and 10) since, due to the nearly filled d band, the Van Vleck orbital susceptibility can be neglected. The Pauli susceptibility can be written as

$$\chi_P = \mu_B^2 N(E_F). \tag{5}$$

Due to an intraatomic electron-electron exchange interaction, the Pauli susceptibility is enhanced by the Stoner factor S and the enhanced Pauli susceptibility can be expressed as

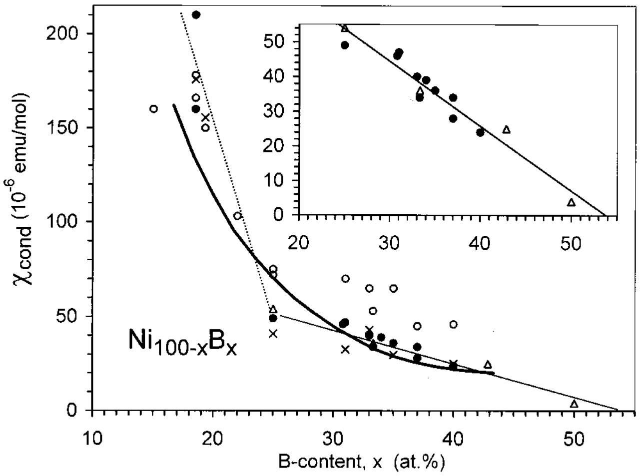

FIG. 3. Composition dependence of the conduction-electron susceptibility χ_{cond} of amorphous (●), crystalline (△), and liquid (○) Ni-B alloys by using the data in Tables I, II, and III. For amorphous and crystalline states the data refer to low temperatures (0–300 K), and for the liquid state to 1400 K. The thin solid line represents a linear fit to the amorphous and crystalline Ni-B alloy data for the composition range 25–50-at. % B (also shown on an enlarged scale in the inset) and the dotted line represents merely a trend for lower B contents. The data points denoted by "×" refer to the liquid state susceptibility when extrapolated to 300 K. The thick solid curve corresponds to the Stoner-enhanced Pauli susceptibility χ_{PS} according to Eq. (6).

$$\chi_{\mathrm{PS}} = S\chi_P = \mu_B^2 N(E_F)/[1 - IN(E_F)], \tag{6}$$

where I is the exchange integral characterizing the strength of the electron-electron interaction. In the case of alloys, as a first approach, we may take a simple compositionally weighted value of I or a more sophisticated weighting as suggested in Ref. 39. Since $I=0$ can be assumed for all metalloid atoms, both kinds of averaging lead practically to the same I value for a given alloy composition.

By taking $I(\mathrm{Ni}) = 0.498$ eV (Ref. 40), we can now calculate the Stoner-enhanced Pauli susceptibility χ_{PS} of Ni-B alloys as a function of composition. This calculation can be performed by using the electronic DOS data derived from reported low-temperature specific-heat measurements on Ni-metalloid alloys. In order to compare the $N(E_F)$ data obtained from the electronic specific-heat coefficient for Ni-based alloys with different metalloids, the authors of Ref. 41 used the quantity xZ^M for characterizing the average electronic concentration for an alloy $Ni_{1-x}M_x$ where Z^M is the chemical valence of the metalloid M ($Z^{\mathrm{B}}=3$, $Z^{\mathrm{Si}}=4$, and $Z^{\mathrm{P}}=5$).[42–47] The parameter xZ^M corresponds to the average magnetic valence Z_m introduced in Ref. 48 (in this scheme, $Z^{\mathrm{Ni}}=0$ and $Z^{\mathrm{Cu}}=1$). In Fig. 4, the $N(E_F)$ values derived from available specific-heat data for Ni-metalloid alloys are plotted against Z_m over wide composition ranges and for different metalloids. The variation of $N(E_F)$ with Z_m can be considered as representing the DOS curve $N(E)$ as a function of the electron energy E.

By using the approximate average of the $N(E_F)$ data indicated by the thick line in Fig. 4, the Stoner-enhanced Pauli susceptibility χ_{PS} was calculated for Ni-B alloys. These data are displayed in Fig. 3 by the thick line, showing a fairly good agreement with the experimental χ_{cond} data.

It is particularly interesting to consider the a-$\mathrm{Ni}_{81.5}\mathrm{B}_{18.5}$ alloy for which the Stoner enhancement factor is obtained as $S(\mathrm{Ni}_{81.5}\mathrm{B}_{18.5})=2.6$. On the other hand, the theoretically calculated value for Pd metal is $S(\mathrm{Pd})=4.46$ (Ref. 40). Accordingly, for the paramagnetic Pd metal the Stoner enhancement factor is about twice as high as that of a-$\mathrm{Ni}_{81.5}\mathrm{B}_{18.5}$. Therefore, the latter alloy is also expected to exhibit a Pauli paramagnetic matrix and not ferromagnetism. This conclusion is also in line with a recent theoretical band-structure calculation[49] according to which a-$\mathrm{Ni}_{80}\mathrm{B}_{20}$ is a paramagnetic metal.

B. On the temperature-dependence of the conduction-electron susceptibility of amorphous Ni-B alloys with ⩾25-at. % B

As described in Sec. III A 1, the contribution of nonmagnetic matrix atoms in amorphous Ni-B alloys in the range 4.2–300 K can be characterized by a nearly temperature independent susceptibility χ_{nm} for ⩾25-at. % B. On the other hand, other investigators have reported on either a decreasing[10] or increasing[13] matrix susceptibility with increasing temperature for the same composition range of melt-quenched amorphous Ni-B alloys. Therefore, it is necessary to consider first the possible origin of a temperature dependence of χ_{cond}.

For Ni-metalloid alloys, the dominant contribution to χ_{cond} is the Pauli susceptibility. Therefore, if χ_{cond} is temperature dependent, it should be primarily through the temperature dependence of χ_P, which is given by[10]

$$\chi_P(T)=\chi_P(0)[1+(\pi^2k_B^2/6)\nu T^2] \tag{7}$$

for alloys in which the Stoner enhancement is not too high. Here $\chi_P(0)=\mu_B^2N(E_F)$ is the Pauli susceptibility at the absolute zero. The quantity ν in Eq. (7) is defined as

$$\nu=N''(E_F)/N(E_F)-[N'(E_F)/N(E_F)]^2 \tag{8}$$

where the $N'(E_F)$ and $N''(E_F)$ denote the first and second derivatives of the electronic DOS at the Fermi level E_F, respectively. It can be seen from the above formulas that χ_P should have a quadratic dependence on temperature, and that the sign of the curvature is determined, through ν, by the shape of the DOS curve at E_F. When the Fermi level is at a valley of the DOS, the value of ν [see Eq. (8)], is positive and when it is at a peak of the DOS it is negative.

Kaul and Rosenberg,[10] as well as the authors of Ref. 13, fitted their experimental data to Eq. (7) and obtained $\nu<0$ and $\nu>0$, respectively, for amorphous Ni-B alloys with ⩾30-at. % B. However, the interpretation of susceptibility data in terms of Eqs. (7) and (8) leads to contradictory conclusions concerning the shape of the DOS in amorphous Ni-B alloys. By considering Fig. 4 as representing the shape of the DOS curve in Ni-metalloid alloys, we can fairly safely state that there is no peak in the DOS curve for Ni-B amorphous alloys in the composition range investigated in Ref. 10, i.e., ν cannot be negative. A minimum in the DOS curve also does not seem to appear in Fig. 4, at most a flattening occurs at high B contents that might be consistent with a small positive ν value only. Therefore, a large positive value of ν also does not seem to be real, in contradiction to the interpretation in Ref. 13 for the increase of χ_{nm} with increasing T.

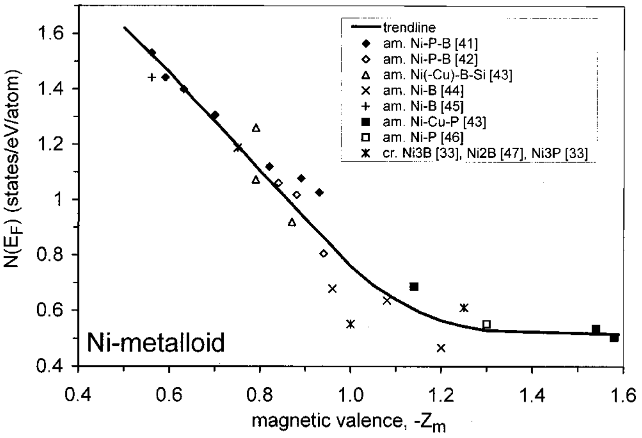

FIG. 4. Electronic density of states at the Fermi level, $N(E_F)$, derived from low-temperature electronic specific-heat data for various Ni-metalloid alloys indicated in the legend. The $N(E_F)$ values are displayed as a function of the magnetic valence introduced in Ref. 48 (for more details, see the text). The thick solid line represents an approximate average through the data points.

It is concluded on the basis of the arguments given above that a quadratic temperature dependence of χ_P according to Eq. (7) can be excluded for amorphous $\mathrm{Ni}_{100-x}\mathrm{B}_x$ alloys with $25\leqslant x\leqslant 40$ in contrast to the suggestion of Refs. 10 and 13. Magnetic inhomogeneities in the form of FM precipitates and/or giant-moment paramagnetic clusters are always present to some extent in the matrix of these amorphous alloys. According to Table I, the amount of such magnetic inhomogeneities was especially large for the samples studied in Ref. 10. This may well have caused the apparent decrease of χ_{nm} with temperature after removing the contribution of the magnetic inhomogeneities from the measured magnetization. The temperature dependence of the matrix susceptibility, if any, cannot be deduced, therefore, in most cases reliably for such amorphous alloys. According to the available experimental evidence presented for amorphous Ni-B alloys here (Fig. 1) and in Ref. 13, as well as for a-$\mathrm{Ni}_{80}\mathrm{P}_{14}\mathrm{B}_6$ in Refs. 25 and 50, there may be at most a vary weak, approximately linear temperature dependence of χ_{cond} with a positive slope in the temperature range 100–500 K.

At the high temperatures of the molten state; however, no magnetic inhomogeneities can be present in Ni-metalloid alloys. Thus, the temperature dependence of the liquid state susceptibility can be more accurately determined and these data will now be discussed.

C. Temperature coefficient of the magnetic susceptibility in liquid Ni-metalloid alloys

We have previously reported[14] that for liquid $\mathrm{Ni}_{81.5}\mathrm{B}_x\mathrm{P}_{18.5-x}$ alloys there is a correlation between the mag-

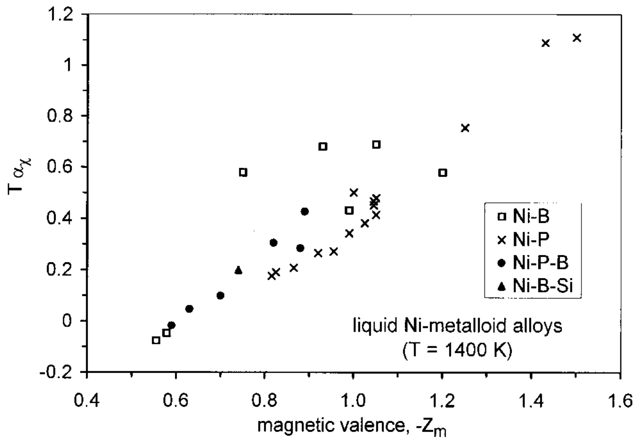

FIG. 5. Variation of the quantity $T\alpha_\chi$, where α_χ is the temperature coefficient of the conduction-electron susceptibility with magnetic valence Z_m for Ni-metalloid alloys. The data are from Table II (Ni-B, Ni-P-B, and Ni-B-Si) and from Refs. 14 (Ni-P, Ni-P-B), 51 (Ni-P), and 52 (Ni-P).

nitude of the conduction electron magnetic susceptibility and the slope of its linear temperature-dependent variation ($d\chi_{l,\mathrm{cond}}/dT$). It is found that $d\chi_{l,\mathrm{cond}}/dT$ decreases with increasing $\chi_{l,\mathrm{cond}}$ and it becomes even negative for the highest $\chi_{l,\mathrm{cond}}$ values. The correlation could be explained[53] based on the electronic DOS of Ni-metalloid alloys as derived from low-temperature specific-heat measurements (see Fig. 4).

According to Ref. 53, the temperature derivative of χ_P is determined by taking into account (i) the explicit T dependence of the Fermi function and (ii) the volume (V) dependence of $N(E_F)$ and its variation through thermal expansion. For the latter contribution, it can be assumed that $N(E_F)$ is proportional to V^n [for free electrons $n=\frac{2}{3}$ (Ref. 54), for transition-metal d bands $n\approx\frac{5}{3}$ (Ref. 55)]. In this manner, we can write

$$d\ln\chi_P/d\ln T = n\alpha_V T + \partial\ln\chi_P/\partial\ln T, \tag{9}$$

where α_V stands for the thermal volume expansion coefficient. It can be easily shown[53] that the temperature coefficient of the Pauli susceptibility is enhanced by the Stoner factor.

In Ref. 53, the analysis of the correlation between $d\chi_{l,\mathrm{cond}}/dT$ and $\chi_{l,\mathrm{cond}}$ was based on a model DOS curve representing the variation of E_F and $N(E_F)$ with alloying. According to Fig. 4, the change of the magnetic valence can be considered as corresponding to the shift of the Fermi energy when the alloy composition is changed (a low value of $-Z_m$ corresponds to low E_F, and vice versa). Since $d\ln\chi/d\ln T=(T/\chi)d\chi/dT=T\alpha_\chi$ where $\alpha_\chi=(1/\chi)d\chi/dT$ is the temperature coefficient of the magnetic susceptibility, it might be more useful for a more direct comparison of Eq. (9) with experiments if we plot the quantity $T\alpha_\chi$ as a function of the magnetic valence. By using data for all Ni-metalloid alloys from the present work (Table II) and from all previous studies, Fig. 5 shows that $T\alpha_\chi$ increases nearly linearly with the variation of the magnetic valence (or the Fermi energy). The change of $T\alpha_\chi$ in Fig. 5 closely resembles the results of calculations based on Eq. (9) (see Fig. 2 in Ref. 53).

In order to estimate the importance of the volume expansion term ($n\alpha_V T$) in Eq. (9), we can make the following considerations. For pure fcc-Ni, the thermal-expansion coefficient is $\alpha_V=40\times10^{-6}$/K (Ref. 56), and very similar values were reported for various Ni-metalloid glasses and crystalline compounds: $\alpha_V(c\text{-Ni}_3\text{B})=41\times10^{-6}$/K (Ref. 57), $\alpha_V(a\text{-Ni}_{75}\text{P}_{25})=42\times10^{-6}$/K (the latter value remained practically unchanged upon crystallization),[58] and $\alpha_V(a\text{-Ni-B-Si})=(34\text{–}39\times10^{-6}/\text{K})$ (Ref. 59). As a typical value for Ni-metalloid alloys, we may take $\alpha_V=40\times10^{-6}$/K. The value of n can vary between $\frac{2}{3}$ and $\frac{5}{3}$, and since the data in Fig. 5 refer to $T=1400$ K, we obtain $n\alpha_V T=0.037$ and 0.093, respectively, for the two limiting values of n.

According to Fig. 5, the experimental values of $T\alpha_\chi$ span from about -0.1 to $+1.1$ for the various Ni-metalloid alloys. As estimated above, the thermal expansion contribution ($n\alpha_V T$) is fairly small in comparison with the experimental values of $T\alpha_\chi$ (and remains nearly the same for all alloys). Therefore, the dominant contribution to the temperature coefficient of the conduction electron susceptibility in liquid Ni-metalloid alloys arises from the variation of $N(E_F)$ with temperature via the explicit temperature dependence of the Fermi function.

V. CONCLUSIONS

The compositional evolution of the magnetic properties was established in the Ni-B system for different structural states. After removing the magnetization contribution of Ni-rich chemical inhomogeneities, the matrix of all amorphous alloys investigated (18.5-at.%$\leqslant$B$\leqslant$40-at.%) was found to exhibit Pauli paramagnetism. The liquid state susceptibility data when extrapolated to room temperature and the susceptibility of the crystalline Ni-B stoichiometric compounds were in good agreement with the corresponding amorphous alloy data.

By using $N(E_F)$ data deduced from previous low-temperature specific-heat experiments, the Stoner-enhanced Pauli susceptibility of Ni-B alloys was calculated, which showed a reasonable agreement with the experimental conduction electron susceptibility. This means that the Pauli susceptibility of Ni-B alloys could be successfully accounted for in terms of the known electronic DOS data of this system.

Concerning previous controversial results on the temperature dependence of the matrix susceptibility of the amorphous Ni-B alloys, it was established that fitting the reported temperature dependence of χ_P to a T^2 function cannot be valid since this procedure leads to conclusions in contradiction with the known electronic DOS curve for these alloys. The temperature dependence, if any, is very weak, at most a small linear increase can be traced out as demonstrated for an $a\text{-Ni}_{75}\text{B}_{25}$ alloy here. In most cases, a temperature dependence, if any, is masked by the contribution of magnetic inhomogeneities.

On the other hand, in the liquid state a very clear linear temperature dependence of the conduction electron susceptibility can be observed for Ni-metalloid alloy systems, including Ni-B. A monotonic, nearly linear increase of the temperature coefficient of the conduction electron susceptibility with the magnetic valence was established in these liquid alloys. By taking into account the variation of $N(E_F)$ as a function of the magnetic valence for the same Ni-metalloid alloys, the observed change of the temperature coefficient of the susceptibility could be explained as arising mainly from the explicit temperature dependence of the Fermi function.

The critical concentration for the PM-FM transition in the Ni-B system could be estimated to be beyond 81.5-at. % Ni from the present study. Relying on the experimental $N(E_F)$ data, this finding is also supported by estimates of the Stoner enhancement factor. Namely, for the a-$Ni_{81.5}B_{18.5}$ alloy S could be estimated to be only half of the value for paramagnetic Pd metal.

---

*Corresponding author. Email address: bakonyi@szfki.hu

[1] J. Crangle and M. J. C. Martin, Philos. Mag. **4**, 1006 (1959).

[2] P. A. Albert, Z. Kovac, H. R. Lilienthal, T. R. McGuire, and Y. Nakamura, J. Appl. Phys. **38**, 1258 (1967).

[3] R. J. Gambino, T. R. McGuire, and Y. Nakamura, J. Appl. Phys. **38**, 1253 (1967).

[4] I. Bakonyi, A. Burgstaller, W. Socher, J. Voitländer, E. Tóth-Kádár, A. Lovas, H. Ebert, E. Wachtel, N. Willmann, and H. H. Liebermann, Phys. Rev. B **47**, 14 961 (1993).

[5] T. Watanabe, Y. Tanabe, and N. Imamura, Mem. Fac. Technology, Tokyo Metropolitan Univ. **29**, 2859 (1979).

[6] T. Watanabe and Y. Tanabe, in *Proceedings of the Fourth International Conference on Rapidly Quenched Metals, Sendai, 1981*, edited by K. Suzuki and T. Masumoto (Japanese Institute of Metals, Sendai, 1982), Vol. I, p. 51.

[7] M. Takahashi, C. O. Kim, M. Koshimura, and T. Suzuki, Jpn. J. Appl. Phys. **17**, 741 (1978).

[8] M. Takahashi and F. Sato, J. Magn. Magn. Mater. **15–18**, 1407 (1980).

[9] M. Takahashi, S. Ishio, and F. Sato, Sci. Rep. Res. Inst. Tohoku Univ., Suppl., A **28**, 287 (1980).

[10] S. N. Kaul and M. Rosenberg, Phys. Rev. B **25**, 5863 (1982).

[11] I. Bakonyi, P. Panissod, and R. Hasegawa, J. Appl. Phys. **53**, 7771 (1982).

[12] I. Bakonyi, P. Panissod, J. Durand, and R. Hasegawa, J. Non-Cryst. Solids **61–62**, 1189 (1984).

[13] M. Takahashi, F. Sato, and S. Ishio, J. Magn. Magn. Mater. **49**, 145 (1985).

[14] I. Bakonyi, H. Ebert, W. Socher, J. Voitlander, E. Wachtel, N. Willmann, and B. Predel, J. Magn. Magn. Mater. **68**, 47 (1987).

[15] I. Bakonyi, in *Proceedings of the International Conference on Physics of Transition Metals, Kiev, 1988*, edited by V. G. Baryakhtar (Naukova Dumka, Kiev, 1989), Pt. 2, p. 333.

[16] J. M. Rojo, A. Hernando, M. El Ghannami, A. Garcia-Escorial, M. A. González, R. Garcia-Martinez, and L. Ricciarelli, Phys. Rev. Lett. **76**, 4833 (1996).

[17] A. Inoue, A. Kitamura, and T. Masumoto, Trans. Jpn. Inst. Met. **20**, 404 (1979).

[18] M. Takahashi, Y. Tateno, and M. Koshimura, Jpn. J. Appl. Phys. **19**, 2335 (1980).

[19] I. W. Donald and H. A. Davies, J. Mater. Sci. **15**, 2754 (1980).

[20] H. H. Liebermann and J. Wong, J. Non-Cryst. Solids **45**, 195 (1981).

[21] P. Panissod, I. Bakonyi, and R. Hasegawa, Phys. Rev. B **28**, 2374 (1983).

[22] A. Amamou, F. Gautier, and B. Loegel, J. Phys. F **5**, 1342 (1975).

[23] A. Amamou and J. Durand, Commun. Phys. (London) **1**, 191 (1976).

[24] S. N. Kaul and V. Siruguri, J. Phys. F **17**, L255 (1987).

[25] I. Bakonyi, P. Panissod, M. Miljak, and E. Babic, J. Magn. Magn. Mater. **58**, 97 (1986).

[26] P. W. Selwood, *Magnetochemistry* (Interscience, New York, 1956).

[27] I. S. Jacobs and C. P. Bean, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. III, Chap. 6.

[28] B. D. Cullity, *Introduction to Magnetic Materials* (Addison-Wesley, New York, 1972).

[29] L. F. Kiss, I. Bakonyi, A. Lovas, M. Baran, and J. Kadlecová, Phys. Rev. B **64**, 064417 (2001).

[30] E. Kneller, *Handbuch der Physik*, edited by H. P. J. Wijn (Springer Verlag, Berlin, 1966), Vol. XVIII/2, p. 438; T. Furubayashi and I. Nakatani, Solid State Commun. **74**, 821 (1990).

[31] A. Gladys, M. Brohl, F. Schlawne, and H. Alexander, Z. Metallkd. **76**, 254 (1985).

[32] I. I. Kostetskiy and S. N. L'vov, Fiz. Met. Metalloved. **33**, 773 (1972), [Phys. Met. Metallogr. **33**, 95 (1972)].

[33] A. Amamou, D. Aliaga Guerra, P. Panissod, G. Krill, and R. Kuentzler, J. Phys. (Paris), Colloq. **41**, C8 (1980).

[34] M. C. Cadeville, Ph.D. thesis, University L. Pasteur, Strasbourg, 1965.

[35] R. H. Mutlu and A. Aydinuraz, J. Magn. Magn. Mater. **68**, 328 (1987).

[36] V. D. Budozhapov, L. P. Zelenin, L. S. Chemerinskaya, F. A. Sidorenko, and P. V. Gel'd, Izv. Akad. Nauk SSSR, Neorg. Mater. **9**, 1447 (1973) [Inorg. Mater. **9**, 1290 (1973)].

[37] N. Lundquist, H. P. Myers, and R. Westin, Philos. Mag. **7**, 1187 (1962).

[38] I. Bakonyi, J. Magn. Magn. Mater. **73**, 171 (1988).

[39] S. K. Bose, J. Kudrnovsky, F. S. Razavi, and O. K. Andersen, Phys. Rev. B **43**, 110 (1991).

[40] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978); J. F. Janak, Phys. Rev. B **16**, 255 (1977).

[41] R. Kuentzler, I. Bakonyi, and A. Lovas, Solid State Commun. **55**, 567 (1985).

[42] D. G. Onn, T. H. Antoniuk, T. A. Donnelly, W. D. Johnson, T. Egami, J. T. Prater, and J. Durand, J. Appl. Phys. **49**, 1730 (1978); T. A. Donnelly, T. Egami, and D. G. Onn, Phys. Rev. B **20**, 1211 (1979).

[43] U. Mizutani and I. Bakonyi, J. Phys. F **16**, 1583 (1986); U. Mizutani and M. Takeuchi, *ibid.* **16**, 79 (1986).

[44] R. Motsay, I. Q. Wang, D. G. Onn, I. W. Donald, and H. A. Davies, J. Appl. Phys. **53**, 7774 (1982).

[45] R. Kuentzler (unpublished).

[46] P. J. Cote, G. P. Capsimalis, and G. L. Salinger, in *Amorphous Magnetism II*, edited by R. A. Levy and R. Hasegawa (Plenum, New York, 1977), p. 499.

[47] R. Kuentzler, J. Appl. Phys. **41**, 908 (1970).

[48] A. P. Malozemoff, A. R. Williams, and V. L. Moruzzi, Phys. Rev. B **29**, 1620 (1984).

[49] M. Liebs and M. Fähnle, J. Phys.: Condens. Matter **8**, 3207 (1996).

[50] E. Babic, A. Hamzic, and M. Miljak, in *Proceedings of the 17th International Conference on Low-Temperature Physics (LT-17)*, edited by U. Eckern, A. Schmid, W. Weber, and H. Wühl (Elsevier, Amsterdam, 1984), p. 367.

[51] E. Wachtel, J. Bahle, N. Willmann, I. Bakonyi, A. Lovas, and H. H. Liebermann, J. Phys. (Paris) Colloq. **49**, C8-1277 (1988).

[52] N. Willmann, Ph.D. thesis, Universität Stuttgart, 1987.

[53] I. Bakonyi and J. Kollár, Physica B **161**, 36 (1989).

[54] Ch. Kittel, *Introduction to Solid State Physics*, 6th ed. (Wiley, New York, 1986), pp. 132–133.

[55] V. Heine, in *The Physics of Metals*, edited by J. M. Ziman (Cambridge University Press, London, 1968), Vol. 1, p. 1; O. K. Andersen, W. Klose, and H. Nohl, Phys. Rev. B **17**, 1209 (1978).

[56] *Product Information Catalogue 2000/2001* (Goodfellow Cambridge Limited, Huntingdon, England). Also available at www.goodfellow.com

[57] E. Lugscheider and H. Reimann, Z. Metallkd. **71**, 239 (1980).

[58] P. J. Cote, G. P. Capsimalis, and L. V. Meisel, Phys. Rev. B **16**, 4651 (1977).

[59] T. Komatsu, K. Matusita, and R. Yokota, J. Non-Cryst. Solids **72**, 279 (1985).