Weak itinerant ferromagnetism in amorphous $M_{90}Zr_{10}$ (M = Fe, Co, Ni) alloys

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Results of the magnetization measurements performed in the temperature range 4.2–300 K in fields up to 15 kOe on amorphous $Fe_{90}Zr_{10}$, $Co_{90}Zr_{10}$, and $Ni_{90}Zr_{10}$ alloys, prepared by the single-roller-quenching technique, are presented. While the glassy $Co_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ alloys at low fields show a normal ferromagnetic behavior down to 4.2 K, amorphous $Fe_{90}Zr_{10}$ exhibits a transition from the ferromagnetic state to the mictomagnetic state at a temperature T_f which lies well below the ferromagnetic ordering temperature. T_f decreases linearly with increasing H up to fields $H \sim 250$ Oe and this linear dependence on H gives $T_f(H=0)=40\pm1$ K. The magnetic behavior at high fields and the temperature dependence of spontaneous magnetization can be satisfactorily accounted for in terms of a theory proposed for weak itinerant ferromagnets. The unusually large value of the high-field susceptibility at 4.2 K observed for $Fe_{90}Zr_{10}$, in particular, is found to contain, besides the contribution arising due to the Invar characteristics of this alloy, a contribution typical of that observed in mictomagnetic alloys. Finally, from an appraisal of the present results and those previously reported on glassy $Fe_{90}Zr_{10}$, it is concluded that this alloy contains two types of magnetic electrons: those possessing itinerant character and giving rise to ferromagnetism (single-particle contribution) and Invar anomalies, and those having localized nature and responsible for both the ferromagnetic (spin-wave contribution) and the mictomagnetic behavior.

I. INTRODUCTION

Study of the physical properties of amorphous transitions-metal–metalloid ($\mathcal{T}$-M) alloys constituted a major part of the scientific activity[1,2] in the field of amorphous magnetism during the past two decades. In the recent years, however, the interest has shifted more towards amorphous alloys of the type $\mathcal{T}_{100-x}Zr_x$, $\mathcal{T}$ = Fe, Co, Ni, or their combinations, primarily because such alloy systems provide a unique opportunity to investigate the role that metal–metal bonds play in determining the various physical properties without any complications, arising from the additional metal–metalloid bonds, normally encountered in amorphous $\mathcal{T}$-M alloys. Like the crystalline Fe-Ni Invar alloys, $\mathcal{T}$-Zr amorphous alloys in a certain concentration range are found to exhibit (i) a maximum[3,4] in the composition dependence of both the magnetic moment and the Curie temperature T_C, (ii) a very low thermal-expansion coefficient,[3] (iii) a large positive spontaneous volume magnetostriction[3] at 0 K, (iv) a large but negative shift in T_C with pressure,[5–7] (v) a large high-field susceptibility,[8] and (vi) a rapid decrease[3] of magnetization with increasing temperature. All these properties are taken to characterize the Invar-like behavior of these amorphous ferromagnetic alloys. In addition to the above-mentioned anomalies in the magnetic behavior, rapidly quenched amorphous $Fe_{100-x}Zr_x$ alloys on the Fe-rich side (i.e., $8 \leq x \leq 12$) have been found to exhibit spin-glass (or cluster spin-glass) like behavior[9,10] at low temperatures. Invar properties and the spin-glass behavior of these alloys have been understood from two basically opposite points of view: While the variation of T_C with pressure as well as the large spontaneous volume magnetostriction associated with the Invar-like low thermal expansion are found to be consistent[3,7] with the predictions based on a model for weak itinerant ferromagnets, above observations (i), (v), and the spin-glass-like behavior at low temperatures have found satisfactory explanation in terms of the coexistence of ferromagnetic and antiferromagnetic states[9] within the framework of a localized model. Based just on the experimental data reported so far on these alloy systems, it is difficult to decide which of the above interpretations of these results is correct.

In weak itinerant ferromagnets, the single-particle excitations, which vary with temperature as T^2, are solely responsible for the fast decrease of magnetization with increasing temperature (the contribution to

the temperature dependence of magnetization arising from spin-wave excitations being too small by comparison) and give rise to extremely large values for the high-field susceptibility. Systematic magnetization measurements on $\mathscr{T}$-Zr amorphous alloys with this point in view are highly desirable since their results can either strengthen or weaken the arguments in favor of weak itinerant ferromagnetism in these alloys.

Among the data published so far on amorphous $\mathscr{T}$-Zr alloys, a bulk of the experimental results exist on and around the composition $Fe_{90}Zr_{10}$. By comparison, the analogous alloys with other $3d$ transition metals, e.g., $Co_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$, have received less or even no attention. The main reason for this appears to be the finding that $Fe_{100-x}Zr_x$ $(8 \leq x \leq 12)$ and $(Fe_{1-x}M_x)_{90}Zr_{10}$, with M=Co, Ni, and x in the vicinity of 0.2, amorphous alloys[3] possess Invar characteristics similar to those previously observed in amorphous $Fe_{100-x}B_x$ $(11 \leq x \leq 15)$ alloys,[11–13] whereas from the analogy, expected and to some extent already found,[4] between the magnetic behaviors of amorphous $\mathscr{T}$-M and $\mathscr{T}$-Zr alloys, glassy $Co_{100-x}Zr_x$ and $Ni_{100-x}Zr_x$ alloys are not likely to be interesting candidates so far as the Invar behavior is concerned. However, in view of the recent magnetic measurements[14] on amorphous $Ni_{81.6}B_{18.4}$ alloy that have shown this alloy to possess magnetic characteristics similar to those of the crystalline Fe-Ni Invar alloys, a study of the magnetic properties of amorphous $Ni_{100-x}Zr_x$ alloys especially on the Ni-rich side becomes all the more interesting. But the choice of alloys in this concentration range on which such a study could be carried out is rather limited because the amorphous-phase formation in the $Ni_{100-x}Zr_x$ system on the Ni-rich side is confined to only a very narrow range[4] around $x=10$.

Keeping in mind the foregoing remarks, a detailed magnetization study of amorphous $Fe_{90}Zr_{10}$, $Co_{90}Zr_{10}$, and $Ni_{90}Zr_{10}$ alloys has been undertaken. In this work, the results of such an investigation are presented and discussed. The most important observation among others is that the theory proposed for weak itinerant ferromagnets, though it completely accounts for the magnetic behavior observed for amorphous $Co_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ alloys, enjoys only a partial success in the case of glassy $Fe_{90}Zr_{10}$ in the sense that it proves to be inadequate to explain the unusually large value of the high-field susceptibility at 4.2 K and the mictomagnetic behavior at low temperatures found in glassy $Fe_{90}Zr_{10}$. This observation coupled with other previously reported properties of the amorphous $Fe_{90}Zr_{10}$ leads us to the conclusion that this alloy, in particular, contains two types of magnetic electrons: those possessing itinerant character and giving rise to ferromagnetism (single-particle contribution) and Invar anomalies, and those having localized character and responsible for both the ferromagnetic (spin-wave contribution) and the mictomagnetic behavior.

II. EXPERIMENTAL

Amorphous $\mathscr{T}_{90}Zr_{10}$ ($\mathscr{T}$=Fe, Co, or Ni) alloys were prepared in the form of ribbons $\sim$1-mm wide and (0.02—0.03)-mm thick by a single-roller-quenching technique in helium atmosphere (helium-gas pressure $\sim$200 mbar) from the starting materials Fe, Co, Ni, and Zr of 99.9%, 99.99%, 99.9%, and 99.5% purity, respectively. The amorphous state of the fabricated alloys was at first controlled by the x-ray diffraction method using Mo $K\alpha$ radiation and then verified by the high-resolution electron-microscopic technique. Magnetization measurements on the "as-quenched" alloy ribbons that include the temperature dependence of magnetization σ taken at various constant values of the applied magnetic field H in the interval 25 Oe $\leq H \leq$ 15 kOe over the temperature range from 4.2 to 300 K, and the σ-vs-H isotherms at 4.2 and 300 K in fields up to 15 kOe were carried out using the Faraday method. A typical rate of 0.5 K/min was maintained while either cooling the sample from 300 K or heating it from 4.2 K. The details about the measuring procedure, sensitivity of the equipment, and the temperature measurement are given in our earlier report.[14]

III. RESULTS AND DISCUSSION

Results of the magnetization measurements taken as a function of temperature for various constant applied magnetic field values in the low-field region on amorphous $Fe_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ alloys are summarized in Fig. 1. In this figure, the solid and dashed curves for $Fe_{90}Zr_{10}$ represent the data obtained when magnetization at the indicated field value is measured as a function of temperature while heating the sample from 4.2 K after it had been cooled to 4.2 K in zero field from 300 K, and while cooling the specimen from 300 K, respectively. The most important features of these curves are a sharp increase in σ at $T_C \cong 240$ K signaling the onset of ferromagnetism and a bifurcation of the heating and cooling curves at a temperature T_f which decreases linearly with increasing field strength H up to $H \sim 250$ Oe (see the inset of Fig. 1 wherein similar data taken from Ref. 9 are also included). This linear dependence on H when extrapolated to $H=0$ gives T_f $(H=0)=40\pm1$ K. Moreover, for temperatures below T_f, the thermomagnetic and thermoremanent effects associated with the mictomag-

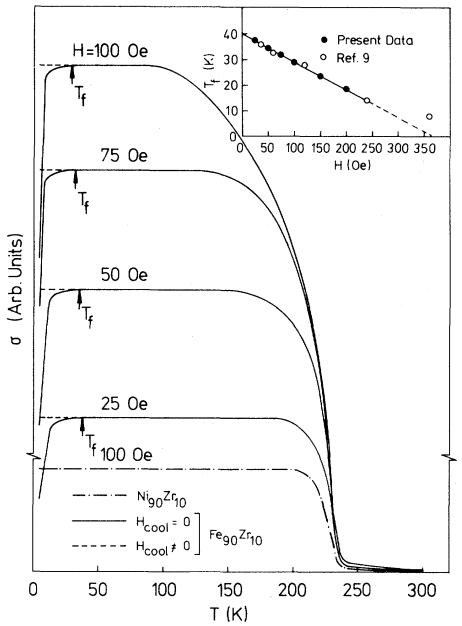

FIG. 1. Temperature dependence of magnetization at various constant applied field values for amorphous $Fe_{90}Zr_{10}$ (solid and dashed curves) and $Ni_{90}Zr_{10}$ (dashed-dotted curve) alloys. Solid and dashed curves for $Fe_{90}Zr_{10}$ are obtained when magnetization at the indicated field value is measured as a function of temperature while heating the alloy from 4.2 K after it had been cooled to 4.2 K in zero field from 300 K and while cooling the sample from 300 K, respectively. Inset shows the field dependence of T_f, the temperature at which a transition from the ferromagnetic to the mictomagnetic state occurs. Results obtained in Ref. 9 are also included in this insert for comparison.

netic state, and a normal ferromagnetic behavior down to 4.2 K for fields ≥ 600 Oe when the bifurcation in the magnetization curves completely disappears, have been observed. All these features of the low-field magnetization data characterize a typical behavior of alloys which exhibit a transition from the ferromagnetic state to the mictomagnetic (cluster spin-glass) state at a temperature T_f which lies well below their ferromagnetic ordering temperature T_C. By contrast, $Co_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ (dashed-dotted curve in Fig. 1) amorphous alloys show a normal ferromagnetic behavior down to 4.2 K. σ-versus-temperature T curves for $Co_{90}Zr_{10}$ (not shown in Fig. 1) taken at different constant H values in the interval $25 \leq H \leq 500$ Oe are found to be completely flat (i.e., practically no variation in σ with T) in the temperature range from 4.2 to 300 K. This finding is consistent with the ferromagnetic behavior expected for an alloy which has T_C well above its crystallization temperature (~ 770 K for the $Co_{90}Zr_{10}$ glassy alloy[3]).

Observations similar to those mentioned above for $Fe_{90}Zr_{10}$ have been recently reported by Hiroyoshi and Fukamichi[9] for amorphous $Fe_{100-x}Zr_x$ alloys with x ranging from 8 to 12. These authors interpret the thermomagnetic history and the asymmetric hysteresis loops associated with the mictomagnetic state in these alloys in terms of the exchange anisotropy which arises from the coexistence of ferromagnetic and antiferromagnetic spin states[9] and contend that the coexistence of these spin states within the framework of a localized model can also provide a satisfactory explanation for the Invar-like characteristics previously observed[3] in amorphous $Fe_{90}Zr_{10}$. Although the Invar anomalies, in general, can be explained in terms of a localized model, a number of properties characterizing the Invar behavior in these alloys are found to closely follow[3,7] the predictions of a theory developed for weak itinerant ferromagnets, as already mentioned in the Introduction. In the present paper we confine ourselves particularly to the discussion of the ferromagnetic aspect of the magnetic behavior found presently for $Fe_{90}Zr_{10}$; the main reason for this choice being to ascertain which of the models (localized or itinerant) correctly describes the observed behavior.

Figure 2 shows the σ-vs-H isotherm taken at 4.2 K in fields up to 15 kOe while Fig. 3 depicts the relative deviation of magnetization from its value at 0 K, i.e.,

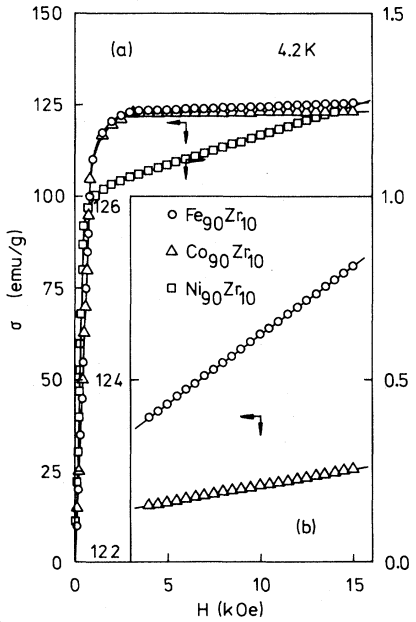

FIG. 2. (a) Magnetization σ as a function of magnetic field H at 4.2 K for the amorphous $Fe_{90}Zr_{10}$, $Co_{90}Zr_{10}$, and $Ni_{90}Zr_{10}$ alloys. (b) Magnified view of the high-field portion of the σ-vs-H curves shown in (a) for $Fe_{90}Zr_{10}$ and $Co_{90}Zr_{10}$.

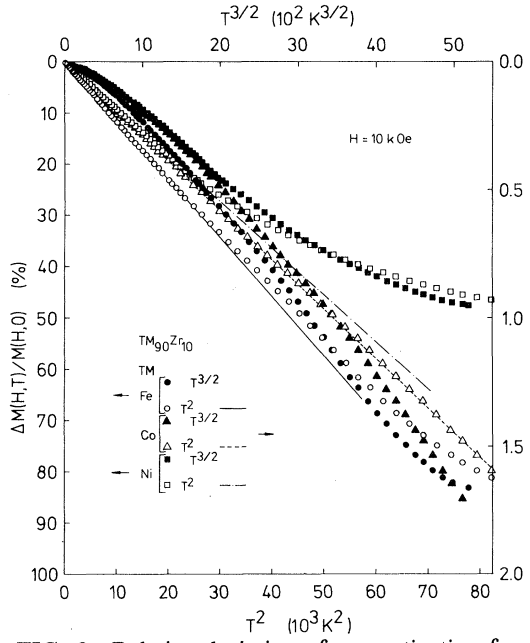

FIG. 3. Relative deviation of magnetization from its value at 0 K, $\Delta M(H,T)/M(H,0)$, measured at $H=10$ kOe plotted against T^2 (open symbols) and $T^{3/2}$ (closed symbols) power laws for the amorphous $\mathscr{T}_{90}Zr_{10}$ ($\mathscr{T}$=Fe, Co, or Ni) alloys. Straight lines drawn through the data points are only a guide to the eye.

$$\Delta M(H,T)/M(H,0)=[\sigma(H,0)-\sigma(H,T)]/\sigma(H,0)\ ,$$

for $H=10$ kOe at different temperatures in the temperature range from 4.2–300 K plotted against T^2 (open symbols) and against $T^{3/2}$ (closed symbols) for amorphous $Fe_{90}Zr_{10}$, $Co_{90}Zr_{10}$, and $Ni_{90}Zr_{10}$ alloys. It is evident from these figures that (i) the magnetization at 4.2 K does not saturate even for fields as high as 15 kOe [values of the high-field differential susceptibility $\chi_{hf}(0)$ are not only larger by at least 1 order of magnitude than the corresponding values[15] observed for crystalline Fe, Co, and Ni but also too large to be explainable in terms of the paramagnetic contribution[15] to magnetization arising from the orbital moment of the partially filled d-band electrons in these pure crystalline elements], and (ii) the T^2 law gives decidedly a better fit to the data over a wide temperature range at low temperatures than the $T^{3/2}$ law does. Furthermore, the plots similar to the ones shown in Fig. 3 taken at different constant-field values reveal that the temperature range over which the T^2 law provides a better fit to the data than the $T^{3/2}$ law *increases* as the field strength *decreases,* a result which has been previously reported[16] for the weak itinerant ferromagnet $ZrZn_2$. These observations coupled with the fact that a finite high-field susceptibility is predicted by the collective (itinerant) electron model even when sufficiently low temperatures and high fields completely suppress the spin-wave contribution whereas σ-vs-H curves should exhibit a complete saturation under the same conditions according to the localized-spin model, led us to seek the interpretation of our magnetization data in terms of a theory based on the itinerant electron model proposed for very weak ferromagnets by Wohlfarth and his coworkers.[17–20] While disregarding the spin-wave contribution to thermal demagnetization and expanding the Stoner's equations[21] in the presence of an applied field in powers of relative magnetization,

$$\zeta(H,T)=\sigma(H,T)/nN_g\mu_B\ ,$$

over the temperature range $T\ll T_F$, this theory, in the limit of very weak itinerant ferromagnetism, gives the functional dependence of magnetization σ on field H and temperature T as

$$[\sigma(H,T)]^2=[\sigma(0,0)]^2\{[1-(T/T_C)^2]+2\chi(0,0)[H/\sigma(H,T)]\}\ , \tag{1}$$

with the zero-field differential susceptibility at 0 K, $\chi(0,0)$ given by

$$\chi(0,0)=N_gN(E_F)\mu_B^2(T_F/T_C)^2=N_gN(E_F)\mu_B^2S\ , \tag{2}$$

where

$$T_F^{-2}=(\pi^2k_B^2/6)\{[N'(E_F)/N(E_F)]^2-[N''(E_F)/N(E_F)]\}=(\pi^2k_B^2/6)\nu \tag{3}$$

and

$$S=[IN(E_F)-1]^{-1} \tag{4}$$

are the effective degeneracy temperature and the Stoner enhancement factor, respectively, $I=2k_B\Theta'/n$ is a measure of the exchange interaction, n is the number of particles per atom, N_g is the number of atoms per gram, $N(E_F)$ is the density of single-particle states at the Fermi level E_F, and $N'(E_F)$ [$N''(E_F)$] is its first (second) energy derivative. Equation (1) implies that the $[\sigma(H,T)]^2$ vs $H/\sigma(H,T)$ isotherms in the temperature range $T\ll T_F$ should be a series of parallel lines (the one at $T=T_C$ passing through the origin) with their slope and intercept on the σ^2 axis given by

$$2\chi(0,0)[\sigma(0,0)]^2 \tag{5}$$

and

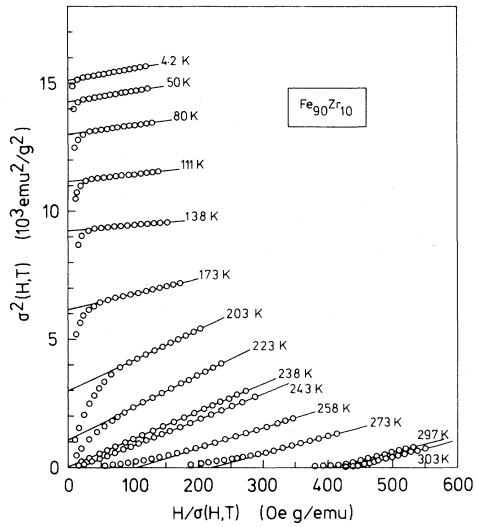

FIG. 4. σ^2-vs-H/σ isotherms for amorphous $Fe_{90}Zr_{10}$.

$$[\sigma(0,T)]^2=[\sigma(0,0)]^2[1-(T/T_C)^2]\ , \tag{6}$$

respectively.

Magnetization data in the form of σ^2-vs-H/σ plots for a few representative temperature values for $Fe_{90}Zr_{10}$, $Co_{90}Zr_{10}$, and $Ni_{90}Zr_{10}$ amorphous alloys are shown in Figs. 4–6. In conformity with the above theoretical prediction, the high-field linear portions of the σ^2-vs-H/σ isotherms are roughly parallel to one another in the temperature ranges 4.2–170, 4.2–302, and 4.2–300 K for $Fe_{90}Zr_{10}$, $Co_{90}Zr_{10}$, and $Ni_{90}Zr_{10}$, respectively. The deviations from linearity observed at low fields can be due to either domain rotation or local inhomogeneities (clusters) or both. To test the validity of Eq. (6), the normalized value of the intercept on the σ^2 axis, $[\sigma(0,T)/\sigma(0,0)]^2$, has been plotted against T^2 in Fig. 7. The data are found to follow the linear variation predicted by Eq. (6) in the entire temperature range from 4.2–300 K for $Co_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$. By contrast, this relation is satisfied over a limited temperature range above 4.2 K, i.e., $4.2<T\lesssim 90$ K, and for $T\gtrsim T_C$ for $Fe_{90}Zr_{10}$. For $Ni_{90}Zr_{10}$, the data points fall on two straight lines (one for $T<T_C$ and the other for $T>T_C$) which have different slopes, presumably due to short-range order[17,18] above T_C,

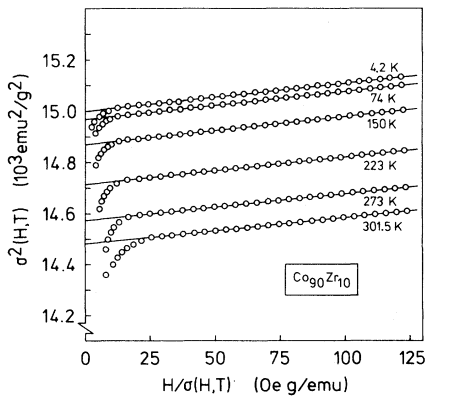

FIG. 5. σ^2-vs-H/σ plots at different temperatures for amorphous $Co_{90}Zr_{10}$.

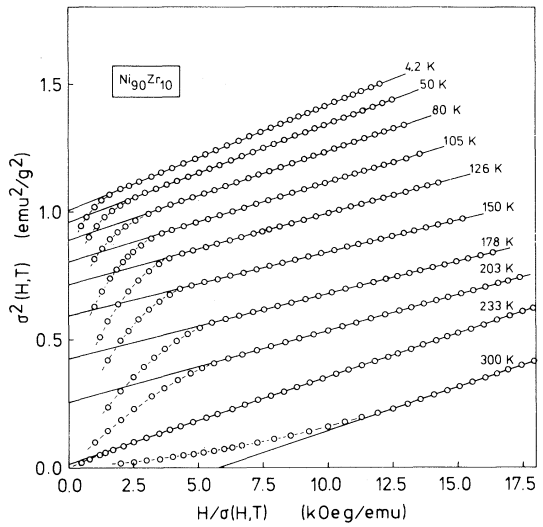

FIG. 6. σ^2 plotted against H/σ for various fixed temperature values for amorphous $Ni_{90}Zr_{10}$.

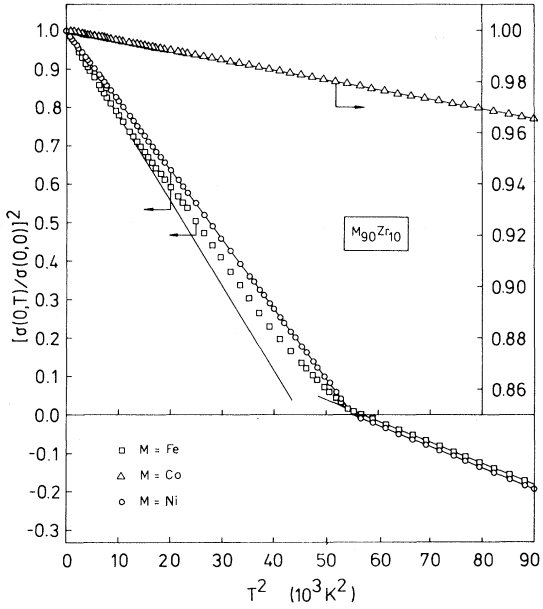

FIG. 7. Normalized values of the intercept on the σ^2 axis $[\sigma(0,T)/\sigma(0,0)]^2$, for different temperature values, obtained by extrapolating the high-field linear portions of the σ^2-vs-H/σ plots shown in Figs. 4–6 to $H/\sigma=0$, as a function of T^2 for amorphous $\mathscr{T}_{90}Zr_{10}$ ($\mathscr{T}$=Fe, Co, or Ni) alloys.

and join each other on the T^2 axis at the Curie-temperature value, $T_C = 235 \pm 1$ K. The observation that the present data below T_C show for $Fe_{90}Zr_{10}$ a trend that is different from that exhibited by the other two alloys suggests that the theory [leading to Eq. (6)], which suffices to account for the behavior observed in $Co_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$, should be extended to include the higher-order terms in the expansion of Stoner equations. In doing so, Eq. (6) gets modified to[22]

$$\begin{aligned}[\sigma(0,T)/\sigma(0,0)]^2 &= 1-(\alpha^{-1}A_1+B_1)T^2 \\ &\quad -(\alpha^{-1}A_2-\alpha^{-1}A_1B_1+B_2-B_1^2)T^4-\cdots \\ &= 1-(T_C^{-2}+B_1)T^2 \\ &\quad -(T_C^{-2}T_F^2A_2-T_C^{-2}B_1+B_2-B_1^2)T^4-\cdots\end{aligned} \tag{7}$$

where $\alpha^{-1}=S$, $A_1=T_F^{-2}$, and the coefficients A_i, B_i involve derivatives of the density of states (DOS) at the Fermi level up to the order $2i$ and their explicit form is given in Ref. 23. We arrive at the above remark that the correction terms (especially the T^4 term) in the extended theory [Eq. (7)] become important for $Fe_{90}Zr_{10}$ above $T \cong 90$ K on the ground that a much better fit to the observed temperature dependence of spontaneous magnetization of $Fe_{90}Zr_{10}$ over an extended temperature range $0 < T < 0.7T_C$ is obtained by using the relation

$$\begin{aligned}\Delta M(0,T)/M(0,0) &= 1-\sigma(0,T)/\sigma(0,0) \\ &= AT^2 ,\end{aligned} \tag{8}$$

which in an alternative form can be written as

$$[\sigma(0,T)/\sigma(0,0)]^2 = 1-2AT^2+A^2T^4 . \tag{9}$$

Equation (9) obviously reduces to Eq. (6), with the coefficient A defined as[24]

$$A = (\tfrac{1}{2})T_C^{-2} \tag{10}$$

when the T^4 term in Eq. (9) is negligibly small in comparison with the T^2 term. Such a situation can arise in either of the two cases: (a) at low temperatures even if the coefficient of T^4 term is large (e.g., in $Fe_{90}Zr_{10}$), and (b) even for temperatures as high as 300 K if this coefficient is too small (e.g., in $Co_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$). At this stage, it should be emphasized that in view of Eq. (7) neither the coefficients of the T^2 and T^4 terms nor the coefficient of the T^2 term, A, and T_C are as simply related to each other as Eqs. (9) and (10) would normally suggest. A glance at the Eqs. (7) and (9) reveals that the relation between T_C and the observed value of A involves different derivatives of DOS at the Fermi level. Therefore, a quantitative estimate of T_C from such a relation is possible only when the DOS function is known. Moreover, the value of the coefficient of T^4 term is decided by the extent to which the different terms in this coefficient [see Eq. (7)] cancel one another and this canceling effect, in turn, depends upon the form of the DOS function.

From the foregoing text it may appear that the temperature dependence of spontaneous magnetization, $\sigma(0,T)$, for temperatures $T \lesssim 0.7T_C$ for $Fe_{90}Zr_{10}$, $T \lesssim 300$ K for $Co_{90}Zr_{10}$, and $T \lesssim T_C$ for $Ni_{90}Zr_{10}$, can be completely accounted for in terms of the sole contribution to thermal demagnetization arising from single-particle excitations; but in view of the two following observations the above statement should, in the correct form, read: the single-particle excitations give a dominant contribution to thermal demagnetization of these alloys in the above temperature ranges. (i) From a good T^2 fit to the experimental results one is not justified to conclude that the spin waves are absent and vice versa. (ii) We found it difficult to decide between the equally good fits to the $\sigma(0,T)$ data based on Eq. (8) and on the $T^{3/2}$ law alone in the temperature range $0.5 \lesssim T \lesssim 0.7T_C$ for $Fe_{90}Zr_{10}$ while the former fit is undoubtedly better than the latter one in the temperature range $0 < T \lesssim 0.5T_C$. From $0.7T_C$ to $\sim T_C$, $\sigma(0,T)$ data for $Fe_{90}Zr_{10}$ could be satisfactorily fitted to a combination of $T^{3/2}$ and $T^{5/2}$ power laws. Thus, spin-wave excitations also give an important contribution to the thermal demagnetization for these alloys but it is only in the case of $Fe_{90}Zr_{10}$ that their actual presence is felt. However, we could not succeed in separating *unambiguously* the single-particle and spin-wave contributions to the temperature dependence of magnetization even for $Fe_{90}Zr_{10}$ in which such a separation should, in principle, have been possible. A separation of this type has also been found to be extremely difficult for crystalline[16,25,26] and amorphous[14] weak itinerant ferromagnets. Other important observations made on $Fe_{90}Zr_{10}$ for temperatures in the vicinity of and above T_C are (a) the increase in the slope of σ^2-vs-H/σ isotherms (see Fig. 4) and the increasing deviation of $\sigma(0,T)$ data points (see Fig. 7) from the T^2 power law, predicted theoretically for weak itinerant ferromagnets, as the temperature approaches T_C, mark the characteristic behavior found in crystalline Fe-Ni Invar alloys,[27] and (b) a linear relation between the intercept on the σ^2 axis and T^2 found to hold above T_C when extrapolated to $T < T_C$ smoothly joins three data points below T_C and cuts the T^2 axis at the Curie-temperature value, $T_C = 240 \pm 1$ K.

Figure 8 depicts the temperature dependence of

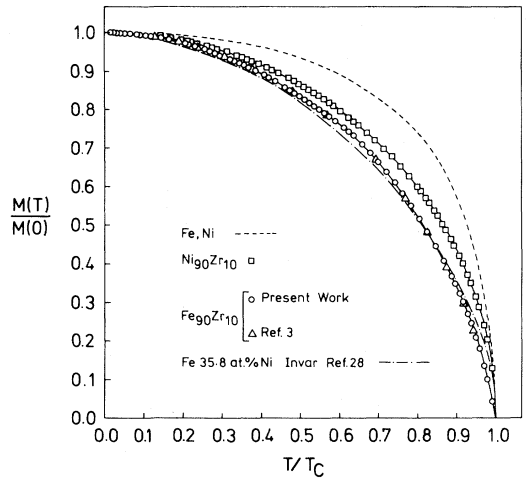

FIG. 8. Reduced magnetization $M(T)/M(0) = \sigma(0,T)/\sigma(0,0)$ vs reduced temperature T/T_C curve for amorphous $Fe_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ alloys. Also included in this figure are the $M(T)/M(0)$ vs T/T_C data for glassy $Fe_{90}Zr_{10}$ from Ref. 3 (triangles), those for crystalline Fe—35.8-at.% Ni Invar alloy from Ref. 28 (dashed-dotted curve), and those for crystalline ferromagnets Fe and Ni (dashed curve).

reduced magnetization,

$$M(T)/M(0) = \sigma(0,T)/\sigma(0,0) ,$$

for the amorphous $Fe_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ alloys. Similar data on the glassy $Fe_{90}Zr_{10}$ previously reported[3] are also included in this figure for comparison. These data are found to be in striking agreement with the present results. Spontaneous magnetization of these alloys is noticed to decrease with increasing temperature at a rate which is much faster than that in crystalline Fe or Ni. The decreasing trend in the $M(T)/M(0)$ vs T/T_C curve for $Fe_{90}Zr_{10}$, though quite similar to that shown by the crystalline Fe—35.8-at.% Ni, Invar[28] alloy, is not so rapid as that found[3] in the amorphous $Fe_{88}B_{12}$ alloy which, like the glassy $Fe_{90}Zr_{10}$, exhibits Invar properties.[11–13] By comparison, the reduced magnetization curve for $Ni_{90}Zr_{10}$ represents a behavior characteristic[29] of a number of amorphous ferromagnetic alloys.

Referring back to Figs. 4—6, the values of $\sigma(0,0)$ deduced using the observed values of the intercept on the σ^2 axis at 4.2 K in Eq. (6) have been employed to obtain the corresponding values for the zero-field differential susceptibility at 0 K, $\chi(0,0)$ from Eq. (5). The values so obtained together with those found for the high-field susceptibility at 0 K, $\chi_{hf}(0)$ (Fig. 2) and T_C (Fig. 7), listed in Table I agree reasonably (see the footnotes relevant to Table I) well with their corresponding literature[4,7–9,30–32] values also included in this table. Note that no distinction between the parameter values at 0 and 4.2 K has been made in the present work primarily because they are expected to be nearly the same due to the high T_C values for the alloys in question. Table I demonstrates that for the $Co_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ alloys, $\chi_{hf}(0)$ and $\chi(0,0)$ possess values that are comparable in magnitude with those reported[14] for crystalline weak itinerant ferromagnets; but these parameters have anomalously large values for $Fe_{90}Zr_{10}$. Though Invar alloys are known[14] to have an enhanced value for $\chi_{hf}(0)$ compared with those for other weak itinerant ferromagnets in the crystalline state, the values for $\chi_{hf}(0)$ reported for crystalline $Fe_{65}Ni_{35}$ [$\chi_{hf}(0) = 5 \pm 1 \times 10^{-5}$ emu/g Oe] (Ref. 33) and amorphous $Fe_{88}B_{12}$ [$\chi_{hf}(0) = 5.8 \times 10^{-5}$ emu/g Oe for the co-sputtered film[13] and 3.5×10^{-5} emu/g Oe for the splat-quenched ribbon[11]] are still much smaller than the present value of 15×10^{-5} emu/g Oe for $Fe_{90}Zr_{10}$, suggesting thereby that the Invar behavior alone cannot account for the unusually large value of $\chi_{hf}(0)$ for this alloy. Recalling that a large high-field susceptibility[34,35] represents one of the most characteristic properties of spin-glasses and mictomagnets and keeping in view the present finding that the $Fe_{90}Zr_{10}$ shows a mictomagnetic behavior at low temperatures, we conclude that $\chi_{hf}(0)$ and consequently $\chi(0,0)$ for this amorphous alloy contains a large contribution typical of that observed in mictomagnetic (and spin-glass) alloys. Such a contribution to $\chi_{hf}(0)$ basically arises from those spins or spin-clusters that are antiferromagnetically coupled. Further evidence supporting the above conclusion is provided by the recent low-temperature specific-heat (C_p) measurements[10] on amorphous $Fe_{90}Zr_{10}$ which give too big a value for γ, the coefficient of the electronic contribution to C_p (~ 2.5 times larger than the γ values reported for crystalline Fe-Ni and amorphous Fe-B Invar alloys) that, besides the Invar contribution, contains a large magnetic contribution arising by virtue of the mictomagnetic character of this alloy at low temperatures. Contrary to the claim that in a localized model coexistence of the ferromagnetic and antiferromagnetic spin states can explain the spin-glass as well as the Invar properties of glassy $Fe_{90}Zr_{10}$ made by Hiroyoshi and Fukamichi,[9] the above conclusion in conjunction with our foregoing observations and those made in the literature[3,7,8] concerning the magnetic and Invar behavior of this alloy points to the fact that in this alloy we have to do with two types of magnetic electrons: those possessing itinerant character and giving rise to ferromagnetism (single-particle contribution)[36] and Invar behavior, and those having localized character and responsible for both the ferromagnetic (spin-wave contribution) and the spin-glass behavior.

TABLE I. Parameters characterizing the weak itinerant ferromagnetic behavior of amorphous $\mathscr{T}_{90}Zr_{10}$ ($\mathscr{T}$=Fe, Co, Ni) alloys. Abbreviations: $\chi_{hf}(0)$—high-field susceptibility at 4.2 K, $\mathscr{T}$—3*d* transition-metal atom, *R*—ribbon, *F*—film, SRT—single-roller technique, MS—melt spinning, CS—co-sputtering, and atm.—atmosphere.

Alloy	μ ($\mu_B/\mathscr{T}$)	$\chi_{hf}(0)$ (10^{-5} emu/g Oe)	$\chi(0,0)$ (10^{-5} emu/g Oe)	T_C (K)	$N(E_F)$ (states/eV at.)	T_F (K)	ν (eV^{-2})	S	$IN(E_F)$	I (eV)	A[a] (10^{-6} K^{-2})	Remarks
$Fe_{90}Zr_{10}$	1.45(1)[b]	15.0(5)	15.4(6)	240(1)	9.89(21)[c]	1285(45)	50(4)	28.6(18)	1.035(2)	0.11	11.44(16)	R,SRT,He atm.
				209(1)[d]	2.98[e]	2340(50)	15(1)	95(4)	1.0105(4)	0.34		R,SRT,He atm.
	1.47[f]			242[f]								R,MS,Ar atm.
	1.28[g]											R,MS,Ar atm.
	1.29[h]		15.2[i]	243[h]								R,SRT
	1.27[j]	16.5[j,k]										F,CS
				240[l]								R,SRT,Ar atm.
$Co_{90}Zr_{10}$	1.52(1)	3.5(10)	3.65(100)	1615(5)[d]	2.25(6)[c]	9020(1395)	1.00(25)	31.2(96)	1.032(8)	0.46(2)	0.192(2)	R,SRT,He atm.
	1.54[h]											R,SRT
	1.37[m]											R,MS,Ar atm.
$Ni_{90}Zr_{10}$	0.012(2)	1.65(15)	2.1(2)	235(1)	2.94[e]	870(45)	108(10)	13.7(13)	1.073(6)	0.37(1)	9.05(15)	R,SRT,He atm.
				235(2)[d]								
	0.04[h]											R,SRT
	0.16[m,n]											R,MS,Ar atm.
$Ni_{81.6}B^{o}_{18.4}$	0.007	1.10(15)	1.25(20)	450(10)[d]	1.9	1434(110)	40(6)	10.2(16)	1.099(14)	0.58(1)	2.4(2)	R,SRT,Ar atm.

[a]Fractional thermal demagnetization closely follows Eq. (8) of the text over a wide temperature range for $Fe_{90}Zr_{10}$ and $Co_{90}Zr_{10}$ with the values of the coefficient A of the T^2 term given in this table, whereas a better fit to the data on $Ni_{90}Zr_{10}$ is obtained when the T^4 term in Eq. (8) is dropped, i.e., when the relation $[\sigma(0,T)/\sigma(0,0)]^2=1-2A\,T^2$ is used instead of Eq. (8) with the given A value.

[b]Numbers in the parentheses denote estimated uncertainty in the least significant figure.

[c]Values calculated from the measured (Ref. 10) values of the coefficient $\gamma=(\pi^2k_B^2/3)N(E_F)$ of the electronic specific heat without making any corrections for the electron-electron and electron-phonon enhancement.

[d]Values computed using the determined A values in Eq. (10) of the text.

[e]$N(E_F)$ values estimated from the local density of states: 43, 42.5, and 18 (in units of Ry^{-1} per atom) for Fe, Ni, and Zr, respectively, given in Ref. 39.

[f]Data given for $Fe_{91}Zr_9$ in Ref. 30. However, in a later paper (Ref. 31), Buschow gives the value $1.29\mu_B$/Fe for the magnetic moment of the alloy with the same composition. This observation implies that in this composition range, the magnetic moment value is quite sensitive to not only the preparation method but also to the preparation conditions.

[g]Reference 31.

[h]Reference 4.

TABLE I. (*Continued.*)

[i]Value of $\chi(0,0)$ calculated using the values of α, KC, and T_C given in Ref. 7 in the relation $\chi(0,0)=(\alpha/2KC)T_C^{-2}$. For the meaning of these symbols see Ref. 7.
[j]Reference 8.
[k]This χ_{hf} value has been measured with the external magnetic field applied perpendicular to the film plane and is expected to be larger than that measured with field applied parallel to the film plane due to the lack of saturation in the perpendicular case caused by the anisotropy effects.
[l]Reference 9.
[m]Reference 32.
[n]We believe that an order-of-magnitude difference in the values of μ for $Ni_{90}Zr_{10}$ does not arise from the different preparation techniques or conditions used for the fabrication of this alloy but from the impurity contribution to the magnetic moment which at low temperatures can be several times the actual value of μ. To elucidate this point further, we obtain for our $Ni_{90}Zr_{10}$ alloy (which was prepared from 99.9%-pure Ni and 99.5%-pure Zr) a magnetic moment value of $0.07\mu_B$/Ni without making any corrections for the impurity contribution. This contribution manifests itself in an additional Curie-Weiss term in the temperature dependence of magnetization measured at various fixed values of the applied magnetic field. The present value for μ is obtained after subtracting the impurity contribution to the magnetic moment.
[o]Data taken from Ref. 14.

In order to find out how the values of exchange and band parameters for the present alloys compare with the corresponding values found[14] for other crystalline and amorphous weak itinerant ferromagnets, a calculation of these parameters has been undertaken. But from Eqs. (2)—(4) one immediately notices that such a calculation requires a prior knowledge of T_C and $N(E_F)$ values for these alloys. While the T_C values given in Table I for $Fe_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ could be determined experimentally in this work, the value of Curie temperature for $Co_{90}Zr_{10}$ (expected to be much higher than the crystallization temperature,[3] $\cong$770 K) in Table I has been estimated using the observed value of the coefficient A of the T^2 term in Eq. (10).[37] Two different approaches have been followed to evaluate the values of $N(E_F)$. In the first approach, $N(E_F)$ for $Fe_{90}Zr_{10}$ and $Co_{90}Zr_{10}$ amorphous alloys has been calculated from the recently measured[10] values of the coefficient $\gamma=(\pi^2k_B^2/3)\,N(E_F)$ of the electronic specific heat without making any corrections for the paramagnon, electron-electron, and electron-phonon enhancement; the value of γ for $Ni_{90}Zr_{10}$ has not been reported so far. The second approach, based on the recent observation[38—40] that the overall shape of the DOS curves revealed for the glassy $\mathscr{T}$-Zr alloys by the photoemission spectroscopy experiments closely resembles that of the total DOS constructed for hypothetical closed-packed ordered compounds of approximately the same stoichiometry from the local DOS of the alloy constituents calculated using self-consistent augmented-spherical-wave band-structure—calculation method, makes use of the local DOS at the Fermi level (43, 42.5, and 18 Ry^{-1} per atom for Fe, Ni, and Zr, respectively[39]), weighted by the relative concentrations of the constituents, to arrive at $N(E_F)$ values given for $Fe_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ in Table I; no reliable estimate of the local $N(E_F)$ value for Co is available. The values of T_C and $N(E_F)$ so computed are then used in Eqs. (2)—(4) to obtain the values for T_F, ν, S, $IN(E_F)$, and I tabulated in Table I (the corresponding parameter values for amorphous $Ni_{81.6}B_{18.4}$ are also included for comparison). Though the present values show an overall agreement with the recently summarized[14] values for crystalline weak itinerant ferromagnets, they are closer to those found for crystalline Fe-Ni Invar alloys. Also, a reasonably good agreement between the parameter values deduced for amorphous $Ni_{90}Zr_{10}$ and $Ni_{81.6}B_{18.4}$ alloys is found. In view of the observation[38—40] that the 3d bands become narrower and nearly Gaussian-type in shape as the 3d transition-metal ($\mathscr{T}$) concentration in amorphous $\mathscr{T}$-Zr alloys increases, the values of ν in Table I suggest that the Fermi level (E_F) for all the three alloys lies fairly close to the top, $(3d)_{top}$, of the

narrow $3d$ band; E_F lying just below $(3d)_{\text{top}}$ for glassy $Fe_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ alloys and just above $(3d)_{\text{top}}$ for glassy $Co_{90}Zr_{10}$. Thus ferromagnetism is favored in these alloys, a result which is further supported by the finding that the Stoner's criterion $IN(E_F)>1$ for the occurrence of ferromagnetism is satisfied. Finally, a direct correlation (see Table I) has been found between the corresponding values of ν and A, the coefficient of the T^2 term, as expected from the relation $A=(\pi^2 k_B^2/6)S\nu$ derived from Eqs. (1)—(3) or from Eq. (7) when the small correction term B_1 in the coefficient of T^2 is ignored.

IV. SUMMARY AND CONCLUSIONS

Magnetization measurements have been performed in the temperature range 4.2—300 K in fields up to 15 kOe on the amorphous $Fe_{90}Zr_{10}$, $Co_{90}Zr_{10}$, and $Ni_{90}Zr_{10}$ alloys prepared by the single-roller-quenching technique in a helium atmosphere. The results obtained and the conclusions drawn from them are summarized as follows.

(i) Low-field magnetization data reveal that the glassy alloys $Co_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ show a normal ferromagnetic behavior down to 4.2 K, whereas $Fe_{90}Zr_{10}$ shows a behavior typical of alloys which exhibit a transition from the ferromagnetic state to the mictomagnetic state at a temperature T_f which lies well below their ferromagnetic ordering temperature T_C. T_f decreases linearly with increasing field strength H up to $H\sim 250$ Oe. This linear dependence on H when extrapolated to $H=0$ gives $T_f\,(H=0)=40\pm 1$ K.

(ii) Magnetization at 4.2 K does not saturate even for fields as high as 15 kOe; values of the high-field differential susceptibility $\chi_{\text{hf}}(0)$ are larger by at least 1 order of magnitude than the corresponding values observed for crystalline Fe, Co, and Ni.

(iii) The decrease of spontaneous magnetization with increasing temperature for temperatures up to $0.7T_C$ for $Fe_{90}Zr_{10}$, 300 K for $Co_{90}Zr_{10}$, and T_C for $Ni_{90}Zr_{10}$ is found to mainly result from the single-particle contribution.

(iv) The above features (ii) and (iii) of the magnetization data find a straightforward explanation in terms of a theory developed by Wohlfarth and his co-workers for weak itinerant ferromagnets.

(v) The values for exchange and band parameters for the alloys in question computed using the theoretical calculations of Wohlfarth *et al.*, though in overall agreement with the corresponding values deduced for crystalline weak itinerant ferromagnets, are closer to those found for crystalline Fe-Ni Invar alloys. Moreover, the values of the band parameter ν suggest that the Fermi level E_F lies fairly close to the top, $(3d)_{\text{top}}$, of the narrow $3d$ band; E_F lies just below $(3d)_{\text{top}}$ for glassy $Fe_{90}Zr_{10}$ and $Ni_{90}Zr_{10}$ alloys, and just above $(3d)_{\text{top}}$ for $Co_{90}Zr_{10}$. Thus, ferromagnetism is favored in these alloys. This result is further supported by the finding that the Stoner's criterion $IN(E_F)>1$ for the occurrence of ferromagnetism is satisfied.

(vi) A direct correlation between ν and A, the coefficient of the T^2 term, as expected from the theory of Wohlfarth *et al.* has been found to hold for the present alloys.

(vii) From a comparison between the high-field-susceptibility (χ_{hf}) values observed for the present amorphous alloys and those found for crystalline weak itinerant ferromagnets, including the Invar alloys, it is concluded that χ_{hf} for the glassy alloy $Fe_{90}Zr_{10}$, in particular, contains besides the Invar contribution, a contribution typical of that observed in mictomagnetic alloys.

(viii) The present results when combined with those previously reported on the amorphous $Fe_{90}Zr_{10}$ lead us to the conclusion that in this alloy we have to do with two types of magnetic electrons: those possessing itinerant character and giving rise to ferromagnetism (single-particle contribution) and Invar behavior, and those having localized nature and responsible for both the ferromagnetic (spin-wave contribution) and the mictomagnetic behavior.

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