Extreme instability of magnetic Fe-moment in amorphous alloys under pressure

J Kamarád, M Míšek and Z Arnold
Institute of Physics, AS CR, v.v.i., Na Slovance 2, Prague 8, Czech Republic
E-mail: kamarad@fzu.cz

Abstract. The effect of high hydrostatic pressure on magnetization of the selected Fe-, FeNi-, FeCr- and FeW-based amorphous alloys has been studied in pressure range up to 1.2 GPa. The very strong non-linear decrease of magnetization under pressure was observed in all the studied alloys, with the extreme value of $d \ln M / d P = -780 \times 10^{-3}$ GPa$^{-1}$ in the case of the amorphous Fe$_{93}$Zr$_7$ alloy. Moreover, the spin glass behaviour of the alloy at temperatures below 50 K has been strongly changed by pressure. The received results support the theoretical concepts based on a dominant role of the pressure-induced widening of the 3d-band of transition metals under high pressure.

1. Introduction
The volume instability of magnetic moment of the 3d-elements is a source of all the huge (and useful) magneto-volume anomalies observed in transition metals and alloys, particularly in the Invar alloys. The strong magneto-volume instabilities were verified by the enormous decrease of both, the magnetization and the Curie temperature of Invar-like materials with increasing pressure. The changes of magnetic Fe-moment induced by external pressure has been studied theoretically and experimentally in the Fe-based alloys, intermetallics and amorphous materials for a long time and few models have been proposed in the past to understand it [1-5]. Despite of this, an origin of the anomalies is discussed up to now [3,4].

Recently we have presented the direct measurement of magnetization of the crystalline Fe$_{64}$Ni$_{36}$ alloy under high pressure in a diamond anvil cell [6]. A non-linear steep decrease of saturated magnetization of the alloy has been observed at the pressure range from 3 GPa to 4 GPa, where a step-like decrease of Fe-moment was also determined by the selective “local” probes (XES, XMCD, Mössbauer spectra) [7]. As a consequence of both, the structural disorder and the presence of metalloids, magnetism of amorphous transition metal (TM) alloys is more complex than ferromagnetism of crystalline alloys, including the spin glass (SG) state observed at ambient pressure at low temperatures [1,2]. To test effects of the local and the long range atomic order on the Fe-moment instability, we have measured magnetization of selected amorphous Fe-based alloys under hydrostatic pressure up to 1.2 GPa.

2. Experimental
The amorphous Fe-based alloys (Table I) were received in form of ribbons that were prepared by a melt spinning method. Composition of the alloys was determined using EDAX. Magnetization $M$ (per 3d-TM-atom), of the selected alloys was measured under hydrostatic pressure up to 1.2 GPa at magnetic field up to 6 T using the miniature CuBe pressure cell [8] and a SQUID magnetometer. The ribbons were fixed in the pressure cell in direction parallel with magnetic field in SQUID.
3. Results and Discussion

The strongly non-linear pressure dependence of magnetization with a sharp decrease of magnetization at low pressure range has been observed in the most of the studied amorphous alloy, see Fig.1 and Fig.2. The only Fe$_{47}$B$_{16}$ alloy with the linear pressure dependence of $M$ represents an exception among the studied alloys (see Table I). The extreme pressure induced decrease of magnetization, $M$(5K,0T), has been observed in the amorphous Fe$_{93}$Zr$_{7}$ alloy (see Fig.1), on the other hand, the amorphous alloy Fe$_{47}$Ni$_{25}$Si$_{18}$B$_{10}$ exhibit a very slight sensitivity of magnetization to pressure not only at low temperatures, but, even at temperature 200 K, see Fig.2. All results are summarized in Table I, where for comparison, the pressure data of the crystalline pure Fe and the Invar alloy are presented too.

![Fig.1: Pressure dependence of magnetization isotherms of the Fe$_{93}$Zr$_{7}$ alloy at 5 K.](image1)

![Fig.2: Magnetization isotherms of Fe$_{47}$Ni$_{25}$Si$_{18}$B$_{10}$ alloy under different pressures.](image2)

In the case of crystalline TM-based alloys, the high values of $\frac{dlnM}{dP}$ were observed in the FeNi Invar-like alloys with face centered cubic (fcc) crystal structure in contrast to very low value of $\frac{dlnM}{dP}$ in the pure crystalline Fe with body centered cubic (bcc) structure, see Table I. Significantly different densities of states of the bcc-Fe and the fcc-Fe at vicinity of the Fermi energy $N(E_F)$ are considered in theoretical works as an origin of these pressure effects [1,3,5]. The different sensitivity of magnetization to external pressure in the amorphous alloys points to a possible difference in short range order (SRO) of their atoms, i.e., fcc-like and bcc-like SRO, in the Fe$_{93}$Zr$_{7}$ and Fe$_{47}$B$_{16}$ alloys, respectively. The Mössbauer spectra and the X-ray absorption K-edge spectra of the Fe in the amorphous Fe$_{100-x}$B$_{x}$ alloys exhibited clearly similar features as the spectra of crystalline bcc-Fe alloys [9]. Using the Maxwell thermodynamic relation, $dM/dP = -dV/dH$, the pronounced decrease of $M$ under pressure can be compared with forced volume magnetostriction $d\omega/dH$, where $\omega = dV/V$, and with high-field susceptibility $\chi_{hf}$ related to $d\omega/dH \approx 2\kappa C\chi_{hf}M$, where $\kappa$ is compressibility and $C$ is magneto-volume coupling constant [10]. The experimental data received for the amorphous Fe$_{93}$Zr$_{7}$ and Fe$_{47}$B$_{16}$ alloys, $d\omega/dH = 385*10^{-10}$ Oe$^{-1}$ and $50*10^{-10}$ Oe$^{-1}$, respectively [11,12], and data of $\chi_{hf}$ presented in Table I, perfectly reflect the observed giant difference in pressure behaviour of magnetization of the amorphous (and crystalline) 3-d transition metals alloys with different SRO and consequently with different electronic structure.

Due to a similarity of SRO in amorphous and crystalline alloys, itinerant electron model of magnetism is used to the description of magnetism of the amorphous 3d-TM alloys. Hence, the known Stoner criterion for the itinerant ferromagnets, $N(E_F)J_{f} > 1$, can be used to assess the pressure effects in the amorphous alloys. Dominant increase of effective interaction $J_f$ with decreasing interatomic distances should lead to increase of $T_C$ under pressure. On the other hand, a broadening of 3d-band (a decrease of $N(E_F)$ under pressure) leads to a pressure-induced decrease of both, $T_C$ and magnetization, that can be described by Wohlfarth’s relations: $dT_C/dP \sim -A/T_C$ and $dlnM/dP \sim dlnT_C/dP + \kappa B$, where
κ is compressibility and A, B are positive constants [10]. The recent systematic theoretical study of pressure effects on electronic structure and magnetism of 3d-transition metals showed that the dominant

\[ \begin{align*}
\frac{dM}{dT} & \text{ and } \frac{d\ln M}{dP} \text{ on } T_C \text{ reflect the above mentioned relations} \\
\text{Fig.3: Dependences of } & \frac{dM}{dT} \text{ and } \frac{d\ln M}{dP} \text{ on } T_C \text{ reflect the above mentioned relations} \\
\text{Fig.4: Spin glass behaviour of the Fe_93Zr_7 alloy} & \text{ is strongly changed by high pressure} \\
\end{align*} \]

Table I: Magnetization $M$ and the Curie temperature $T_C$ of the studied alloys and their pressure derivatives within the low and the high pressure range and the high field susceptibility $\chi_{hf}$. 

| Composition | $M(5K,0T)$ $\mu_B$/at.TM | $\frac{d\ln M(5K)}{dP}$ $10^3$ GPa$^{-1}$ | $T_C$ K | $\frac{d\ln T_C}{dP}$ $10^3$ GPa$^{-1}$ | $\chi_{hf}(5K)$ $10^5$ |
|-------------|----------------------|-----------------------------|--------|-----------------------------|---------------------|
| Fe – bcc [7] | 2.18 | $-4.5 \pm 0.2$ | 1043 | - | 4.3 |
| Fe$_{67}$Ni$_{33}$ – fcc [7] | 1.66 | $-110 \pm 5$ | 520 | - $85\pm4$ | 120 |
| Fe$_{93}$Zr$_7$ – a | 1.42 | $-780$ | 175 | $-560\pm50$ | 205 |
| Fe$_{86}$B$_{14}$ – a | 2.04 | $-54 \pm 2$ | 595 | $-45\pm5$ | 7.2 |
| Fe$_{77}$W$_8$B$_{15}$ – a | 1.49 | $-150$ | 339 | $-90\pm8$ | 30 |
| Fe$_{70}$Cr$_{10}$B$_{15}$ – a | 1.09 | $-163$ | 287 | $-135\pm10$ | 32 |
| Fe$_{47}$Ni$_{32}$Si$_{15}$B$_{10}$ – a | 1.51 | $-74$ | 595 | $-9\pm1$ | $\sim 1$ |

pressure–induced broadening of the 3d-band leads to the suppression of their magnetism, namely in the case of Fe [5]. The results presented in Fig.3 well agree with theoretical concepts. Values of $T_C$ on the $x$-axis of Fig.3 represent different compositions of the alloys.

The more pronounced decrease of magnetization at low pressure range can be connected with low density (higher compressibility) of amorphous alloys at ambient pressure. Pycnometric measurements
showed lower density (of about -6% to -14%) than one determined by Vegard’s law. However at low pressure range, detailed data of compressibility of the amorphous alloys are missing.

![Fig.5: Effect of pressure and magnetic field on SG-ferromagnet transition in Fe$_{93}$Zr$_7$ alloy](image)

The pronounced difference between ZFC and FC curves of temperature dependence of magnetization of the Fe$_{93}$Zr$_7$ alloy is presented in Fig.4. The earlier experimental and theoretical studies [2] showed that the amorphous Fe-rich alloys form spin glasses (SG) at lowered temperatures and the SG was described as randomly oriented ferromagnetic clusters. The transition of the alloys from SG to ferromagnetic state with increasing temperature was explained by an enhancement of the short-range ferromagnetic interactions with respect to the long-range antiferromagnetic interactions [2]. The observed effect of pressure and magnetic field on SG in the Fe$_{93}$Zr$_7$ alloy is compatible with the above mentioned concept as can be seen in Fig.5. In contrast to temperature, pressure stabilizes the random orientation of ferromagnetic clusters and the critical field of the transition from SG to long-range ferromagnetism increases with increasing pressure. The SG-ferromagnetic transition at temperature 5 K is induced by field of 400 Oe at ambient pressure or by field 2500 Oe under pressure 0.9 GPa. However, magnetization of the clusters is strongly suppressed by pressure.

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