Comment on "Weak-localization and Coulomb-interaction effects in hydrogen-doped Zr-Ni and Zr-Cu metallic glasses"

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Kokanović, Leontić, and Lukatella [Phys. Rev. B **41**, 958 (1990)] have recently reported on the temperature dependence of electrical-transport properties and magnetic susceptibility of amorphous Zr-Ni and Zr-Cu alloys and their hydrides and interpreted the experimental results in terms of weak-localization and Coulomb-interaction effects. It is pointed out in this Comment that the observed low-temperature upturn of the magnetic susceptibility and the increase of this upturn upon hydriding can be well accounted for also in terms of localized moments of magnetic impurities and the increased segregation tendency of late transition elements due to the presence of H in this type of metallic glasses.

Recently, Kokanović, Leontić and Lukatella.[1] have reported on an experimental study of the temperature dependence of the electrical transport properties and magnetic susceptibility of $Zr_{67}Ni_{33}$ and $Zr_{60}Cu_{40}$ metallic glasses and on the influence of hydrogen doping on the temperature dependence of these properties. As far as the magnetic susceptibility is concerned, these authors observed that in the undoped samples the measured susceptibility (χ_{expt}) decreased slightly from room temperature down to about 30 K below which it increased again with decreasing temperature, reaching about the room temperature value around 4.2 K. After charging the samples with H electrolytically, the χ_{expt} values decreased substantially and the low-temperature upturn became more pronounced, by shifting the apparent minimum to higher temperatures. The peculiar temperature dependence of χ_{expt} and the effect of H on this temperature dependence, together with the results on the electrical transport properties, were interpreted by these authors in terms of theoretical models involving weak localization and electron-electron effects which may be very pronounced in disordered systems.

Whereas it is not debated that such an explanation may be an adequate one in connection with the electrical transport properties, we would like to point out in this Comment that the observed temperature dependence of χ_{expt} in these Zr-based alloys and its variation with H doping may occur for other reasons as well. In particular, the variation of the susceptibility with temperature above the minimum strongly resembles that of pure Zr whereas the low-temperature upturn can arise also due to the presence of localized moments with Curie-Weiss (CW) type behavior. Furthermore, since it has been shown recently[2] that in Zr-based metallic glasses hydrogen can induce substantial atomic rearrangements (leading, e.g., to the appearance of superaramagnetic Ni clusters in Zr-Ni glasses), the stronger upturn of the susceptibility at low temperature upon hydriding might be well ascribed to this H-induced segregation also. Regarding this last item, it is mentioned that since the occurrence of H-induced localized moments was demonstrated also for alloys containing no magnetic components,[3] this also offers an alternative explanation for the behavior of χ_{expt} in H-doped Zr-based glasses, observed by Kokanović, Leontić, and Lukatella[1].

Previously, we have analyzed the individual contributions to the magnetic susceptibility of Zr metal.[4] Below, the experimental results available in the literature will be briefly summarized for the low-temperature hcp modification of Zr (α phase). A common feature of most of the experimental results[5-7] is that from about 150 K up to well above room temperature χ_{expt} increases approximately linearly with temperature whereas below about 100 K, it is practically constant down to the liquid helium range.

In a few studies on Zr metal, a low-temperature upturn of χ_{expt} was observed below about 50 K. This upturn usually resembles the Curie-Weiss-type behavior of localized magnetic moments [$\chi_{CW} \propto 1/(T+\Theta)$ where the characteristic temperature is of the order of ± 5 K] and can be ascribed to the presence of a small amount of atomically dissolved magnetic impurities such as Mn, Fe, Co, or Ni [note that the usual Honda-Owen plot evaluation or an observed field independence of the susceptibility assures only that magnetic impurities with ferromagnetic (i.e., saturating) behavior do not contribute to χ_{expt}]. Attributing the susceptibility upturn in Zr to localized moments of paramagnetic impurities is further justified if we compare the results of Volkenshteyn and Galoshina[8] on Ti (100 ppm Fe impurity), Zr (400 ppm Fe) and Hf (100 ppm Fe): the Fe impurity content is unambiguously manifested in the strength of the low-temperature upturn, namely, it was found to be equally small for the Ti and Hf samples and much stronger for the Zr sample. The lack of this upturn in the sufficiently pure Zr samples studied by others[5-7] also supports this conclusion.

The magnetic susceptibility of amorphous alloys of Zr with late transition (LT) metals (e.g., Ni, Cu, Pd, Rh) has been extensively studied in the past and, in some cases, a detailed temperature dependence for $T \leq 300$ K has also been reported.[9-12] The amorphous $Zr_{0.43}Cu_{0.57}$ and

$(Zr_{0.43}Cu_{0.57})_{0.979}Fe_{0.021}$ alloys[9] were found to exhibit a temperature-independent susceptibility of $\chi_{expt}=83\times10^{-6}$ emu/mol and 96×10^{-6} emu/mol, respectively, from 4.2 to 300 K. Similarly, it was established from measurements between 1.4 and 300 K on amorphous $Zr_{0.40}Cu_{0.60}$ and $Zr_{0.40}Cu_{0.59}Fe_{0.01}$ alloys[10] that these metallic glasses exhibit a temperature-independent susceptibility ($\chi_{expt}=60\times10^{-6}$ emu/mol and 92×10^{-6} emu/mol, respectively) at higher temperatures whereas a small upturn was observed in this study below about 50 K and the upturn was much stronger in the Fe-doped sample. These results are in good agreement with the temperature-independent susceptibility observed by Kokanović, Leontić, and Lukatella[1] for the amorphous $Zr_{0.60}Cu_{0.40}$ alloy between 2 and 300 K.

The fact that the $Zr_{0.40}Cu_{0.60}$ alloy doped with 1 at. % Fe has a significant low-temperature susceptibility upturn whereas the $Zr_{0.43}Cu_{0.57}$ alloy doped with 2 at. % Fe does not can be explained by assuming significant differences in the cooling rates during the preparation of the amorphous alloys by the melt-quenching technique. At a high cooling rate, a larger fraction of the doped Fe atoms can remain dissolved homogeneously in the amorphous matrix, not giving rise to a low-temperature upturn of χ_{expt}. It may be interesting to note in this respect the results of Mizutani, Akutsu, and Mizoguchi[13] on a $Ti_{0.40}Cu_{0.60}$ alloy in the amorphous state and after crystallization. The magnetic susceptibility of the amorphous alloy was found to be temperature independent (as measured from 100 to 300 K) whereas for the crystallized alloy χ_{expt} could be decomposed into a temperature-independent contribution and a CW susceptibility. These results can be explained by assuming that due to the sufficiently high cooling rate during melt quenching, all or most of the magnetic impurity atoms present in the alloy could be atomically dissolved in the amorphous matrix, having no localized magnetic moments [as was in the case of the $(Zr_{0.43}Cu_{0.57})_{0.979}Fe_{0.021}$ amorphous alloy] whereas after crystallization the constituting crystalline Zr-Cu phases were not able to dissolve such an amount of (magnetic) impurities which, therefore, segregated and built up small clusters with localized moments giving rise to a CW susceptibility.

In a previous study of amorphous $(Zr_{0.50}Ni_{0.50})_{1-x}P_x$ alloys with $0\le x\le0.07$ (Ref. 12) we have found that the temperature dependence of χ_{expt} for 5 K $\le T\le$ 300 K could be described by assuming a term linearly increasing with temperature and a CW-type susceptibility. The interplay between the Curie-Weiss and the linear term leads to an apparent minimum of the susceptibility the position of which depends on the relative strength of these terms. Attempts have also been made[12] to fit χ_{expt} by the sum of a CW susceptibility and a quadratically temperature-dependent term but systematic deviation was observed in this way between the data points and the fitting curve which was not the case with the assumption of a linear term. Therefore, it could be concluded that the temperature dependence of the matrix susceptibility χ_{expt}-χ_{CW} does not follow the usual T^2 dependence of the Pauli susceptibility. A similar observation has been made also for amorphous $Zr_{0.67}Pd_{0.33}$ and $Zr_{0.75}Rh_{0.25}$ alloys.[11]

As to the interpretation of the two susceptibility contributions in Zr-Ni type glasses, the Curie-Weiss term can be ascribed to the presence of localized magnetic moments due to the formation of Ni-rich clusters during the melt-quenching process whereas the linearly temperature-dependent term strongly resembles the behavior of Zr above about 150 K. This latter feature is sustantiated also by the facts that the magnitude of both χ_{expt}-χ_{CW} and the temperature coefficient of the linear term are fairly close to each other for Zr metal and for the Zr-Ni glasses.[12]

It is suggested, therefore, that the temperature dependence of χ_{expt} reported by Kokanović, Leontić and Lukatella[1] for the $Zr_{0.67}Ni_{0.33}$ metallic glass can also be described by the above analysis although their way of presenting the data did not allow us to perform a direct fitting.

We shall now discuss the influence of H on the magnetic susceptibility of Zr-Cu and Zr-Ni amorphous alloys. Kokanović, Leontić, and Lukatella[1] reported that the magnitude of the room-temperature susceptibility decreased upon H doping in both alloys which is in good agreement with the results of other studies on Zr-based metallic glasses as well[2,11] and this effect is mainly the result of a diminution of the electronic density of states at the Fermi level, $n(E_F)$, upon hydriding, leading to a decrease of the Pauli susceptibility. On the other hand, the variation of the magnetic susceptibility due to hydriding below about 100 K (appearance or increase of the low-temperature upturn) can be the result, in contrast to the interpretation of Kokanović, Leontić, and Lukatella,[1] of a H-induced formation of localized moments with CW behavior as will be discussed below.

It should be mentioned first that according to diffusion constant measurements in amorphous alloys of Zr with LT metals,[14] the LT elements were found to have a much higher mobility in these systems than Zr (for temperatures below, say, 200 °C Zr may even be considered as an immobile species in comparison with Ni or Cu). On the other hand, it is well known that H can induce, probably due to its rather different chemical affinity to the different metals, substantial atomic rearrangements in alloys, leading even to an amorphization in some cases.[15] These two features are the basic underlying mechanisms for the appearance of strong H-induced segregation that could recently be demonstrated in nearly equiatomic Zr-Ni metallic glasses by both transmission electron microscopy studies and magnetization measurements.[2] Due to the presence of H, a small portion of the more mobile Ni atoms segregates out of the amorphous Zr-Ni matrix and these Ni atoms form small clusters with localized magnetic moments. During prolonged exposure to a high-pressure hydrogen atmosphere, the size of these Ni or Ni-rich clusters may increase to such an extent that they even exhibit superparamagnetic or ferromagnetic behavior.[2] It should be mentioned that this phase separation process has been observed not only for the gas-phase charging process[2] but also for samples charged with H electrolytically as was demonstrated for Ti-Cu metallic glasses.[16]

Therefore, the strong low-temperature upturn of χ_{expt} in the H-doped Zr-Ni amorphous alloy as observed by

Kokanović, Leontić, and Lukatella[1] can be reasonably well accounted for also in terms of a H-induced Ni-clustering process. The decrease of the high-temperature susceptibility term and the increase of the CW term in the hydrided alloys is just expected to result in a shift of the "apparent" susceptibility minimum to higher temperature as observed by Kokanović, Leontić, and Lukatella.[1] Furthermore, it has been recently also observed[17] that also in $Zr_{0.50}Ni_{0.50-x}Cu_x$ metallic glasses up to $x=0.25$ the changes in the magnetic state of the samples can be comparable upon hydriding to those in the binary Zr-Ni system. This might justify the same explanation for the fact that the hydrided $Zr_{0.60}Cu_{0.40}$ alloy studied by Kokanović, Leontić, and Lukatella[1] also exhibits a substantial low-temperature upturn although for the unhydrided alloy χ_{expt} was fairly independent of temperature. If the as-quenched Zr-Cu amorphous alloy contained some amount of magnetic impurities atomically dissolved, these magnetic atoms, due to the presence of H, may have segregated to form magnetic clusters (a comparison with the data of Szofran *et al.*[10] on the $Zr_{0.40}Cu_{0.59}Fe_{0.01}$ alloy suggests that an amount of about 0.1 at. % Fe might give rise to the low-temperature upturn observed by Kokanović, Leontić, and Lukatella[1]). The results of Mizutani, Akutsu, and Mizoguchi[13] discussed above may also be considered as supporting the assumption about possible strong changes in the degree of dissolution of magnetic impurity atoms during a phase transformation.

Finally, it is mentioned that the formation of local magnetic moments has been observed also in alloys with no magnetic components. It was reported[3] that in $Pd_{0.99}Ru_{0.01}$ and $Pd_{0.98}Ru_{0.02}$ alloys at hydrogen contents around $H/M=0.6$ the contribution of localized magnetic moments dominates the measured susceptibility and their effect is shown up also in the low-temperature specific heat. Since the starting Pd metal and Pd-Ru alloys did not show this behavior before hydriding, it was attributed to H-induced magnetic moments localized on the Ru atoms. Very recently, Papaconstantopoulos, Skroch, and Drew[18] have theoretically calculated the product $In(E_F)$ for the monohydrides of the 5*d* metals where I is the exchange correlation integral. Although the Stoner criterion $In(E_F)\geq 1$ for the appearance of ferromagnetism was not fulfilled in any of these hydrides, $In(E_F)$ values as high as almost 0.5 were also obtained. This indicates that a substantial Stoner enhancement $S=1/[1-In(E_F)]$ may sometimes occur in transition metal hydrides which can eventually lead to the appearance of localized magnetic moments as was observed for the Pd-Ru alloys.[3] Since the Stoner enhancement factor S may strongly vary with alloying, it cannot be completely excluded that localized moments can be induced in hydrides of Zr-based alloys as well, especially if we draw attention to the fact that the crystalline $ZrZn_2$ alloy is a well-known example of (very weak itinerant) ferromagnetism without any magnetic component.[19]

In summary, we have pointed out that the low-temperature upturn of the magnetic susceptibility in amorphous Zr-based alloys and, especially, the increase of this upturn upon hydriding can be accounted for fairly well by the presence of magnetic impurity atoms and by their increased tendency for segregation in hydrided alloys. This casts doubt on the interpretation of Kokanović, Leontić, and Lukatella[1] of their magnetic susceptibility data on Zr-Cu-H and Zr-Ni-H amorphous alloys in terms of weak localization and Coulomb interaction effects only and this might relate eventually also to the interpretation of their electrical transport property data on the same alloys.

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