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The possible influence of crystal-like atom clusters on the magnetic properties of metallic glasses

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Abstract. The magnetic anomaly of weak unidirectional magnetic anisotropy in $(Co_{0.8}Fe_{0.2})_{80}B_{20}$ has been studied. The low-field magnetization loops are strongly perturbed in the presence of this type of magnetic anisotropy. This effect is more pronounced in metallic glasses obtained at high quenching rates. We propose that the magnetic anisotropy is caused by the presence of two magnetic phases with different local anisotropies and weak magnetic couplings. One of these—the amorphous matrix—would have a very small local magnetic anisotropy, while the other—clusters with nearly crystalline order—would have a high local magnetic anisotropy.

1. Introduction

In this work, several magnetic anomalies are detected in $(Co_{0.8}Fe_{0.2})_{80}B_{20}$ and the weak unidirectional magnetic anisotropy is particularly interesting. Magnetic anisotropy seems to be the magnetic parameter that changes most when a metal changes from the glass to the crystal phase. This difference has been attributed to the lack of crystalline anisotropy in glasses. The main source of magnetic anisotropy has a magnetoelastic origin in metallic glasses [1, 2]. However, it would seem somewhat risky to rule out completely the possibility that there is some local magnetic anisotropy of structural origin in metallic glasses since the literature contains references pointing to the notion that in many glasses there are atom clusters with a well defined local order [3–8] and that in some cases these clusters are magnetic [7]. The reason for the appearance of these inhomogeneities must be related to the fact that different, more or less rapid kinetic processes of an approximately thermodynamic equilibrium (crystalline order) nature occur in different local regions of the sample during the quenching process. Therefore we think it reasonable to assume that in some regions an order closer to the crystalline phase with thermodynamic equilibrium can exist. This model does not pretend to revive the microcrystalline model for metallic amorphous structures but rather considers some of the possible defects of the amorphous structure as stable or metastable atom clusters with nearly crystalline order. We assume that these crystal-like clusters are so small and distorted that they do not give sharp peaks in x-ray, neutron or electron diffraction diagrams.

The presence of the suggested clusters must influence the magnetic properties of the material. This has allowed us to find a satisfactory explanation for results otherwise

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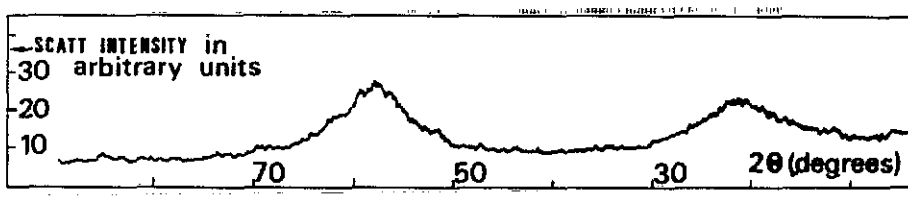

Figure 1. X-ray diffractogram (Fe Kα radiation) for the $(Co_{0.8}Fe_{0.2})_{80}B_{20}$ amorphous alloy studied here.

unexplained, such as the origin of the strong magnetic anisotropy induced by annealing under stress in several metallic glasses in the approximate temperature range 300–400 °C [9, 10]. Recently it has been observed that reversible and irreversible structural changes such as those mentioned above are responsible for the anisotropy induced by annealing under stress. Stress causes the appearance of polarizing effects on the structural orientation of some metastable magnetic clusters during the reversible phase change suggested [7]. The presence of these metastable atom clusters may also account for other anomalous kinds of magnetic behaviour, such as the surprising conduct described in the present paper. This behaviour is studied in a Co–Fe–B metallic glass obtained at an extremely high quenching rate. We have also observed the magnetic anomalies described below, in other metallic glasses, also obtained at high quenching rates.

2. Experiment and results

An amorphous $(Co_{0.8}Fe_{0.2})_{80}B_{20}$ ribbon 0.8 mm wide and 23 μm thick was prepared by the single-roller quenching method. The total lack of crystalline order was observed by x-ray diffraction. Figure 1 shows an x-ray diffractogram, obtained using Fe Kα radiation. The tiny traces of peaks noticeable in the picture are not reproducible and it is therefore concluded that they are due to electronic noise.

The magnetic study was carried out by placing a 10 cm ribbon inside a solenoid producing a $6 \times 10^5/4\pi$ A m^{-1} per A of current magnetic field. The sample was subjected to a positive stress along its axis, and a small secondary coil, containing 50 turns, was placed in the middle of the sample. This coil was used to collect the signal induced during the magnetization process. An auxiliary secondary coil also compensated for the signal due to the applied magnetic field, thus obtaining a signal proportional to the time derivative of the magnetization. This signal could be integrated by observing the M–H hysteresis loop on an oscilloscope. Finally, the magnetic domains in the sample were visualized using Bitter's technique in order to determine the distribution of the magnetization.

Figure 2 shows the M–H loop for the $(Co_{0.8}Fe_{0.2})_{80}B_{20}$ amorphous alloy. The loop shows that technical saturation was achieved for $H \simeq 7/4\pi$ kA m^{-1} and indicates the existence of two different magnetization processes. The central part of the loop is associated with the motion of domain walls in zones with magnetization along the applied field (high-permeability magnetization processes). The rest is probably due to a 90° magnetization rotation in initial perpendicular magnetization zones (low-permeability magnetization processes). This distribution is usually explained by the inhomogeneous distribution of internal stresses in the sample [11]. We studied the possibility that we were dealing with the same effect in our sample by observing the magnetic behaviour of the sample under applied stress.

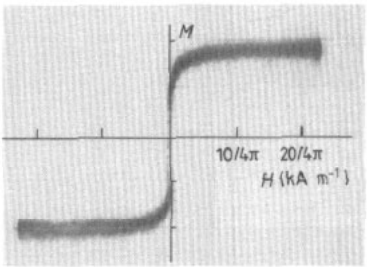

Figure 2. M–H hysteresis loop corresponding to the $(Co_{0.8}Fe_{0.2})_{80}B_{20}$ amorphous alloy. (M is in arbitrary units.)

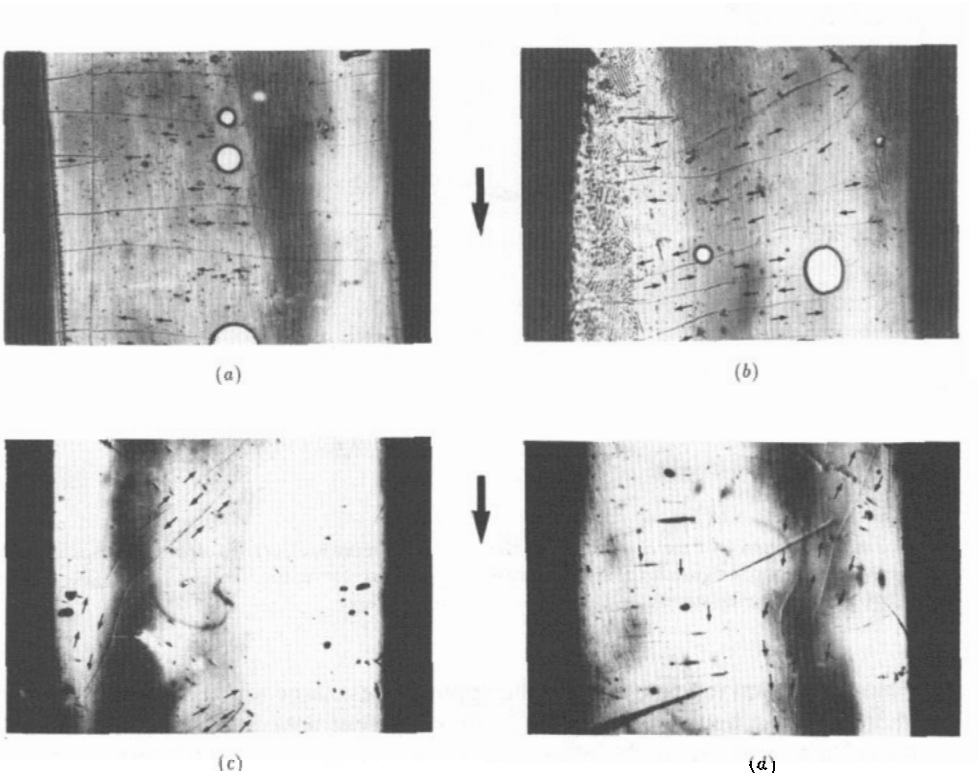

Figure 3. Bitter patterns of the domain structure in the $(Co_{0.8}Fe_{0.2})_{80}B_{20}$ amorphous sample (a), (b) without external tension; (c), (d) on application of a tensile stress of approximately 70 MPa. The arrows in each magnetic domain indicate the direction of magnetization.

Figures 3(a) and 3(b) show the magnetic domains of different regions in the sample, without an applied stress. They reveal a multiple-magnetic-domain structure with in-plane magnetization transversal to the ribbon axis. The figure shows that the dispersion of the magnetization depends on the region under observation. In figure 3(b), some maze domains are viewed near the sample edges. Domain patterns similar to figure 3(a) are more frequent than those similar to figure 3(b). The previous Bitter patterns show that transverse magnetic anisotropy exists for most of the volume of the 'as-obtained sample', while there are also some zones near edges with perpendicular anisotropy (maze domains). After the sample had been stressed (positive σ) in approximately the 70 MPa range, very few walls were seen and the domain patterns show that

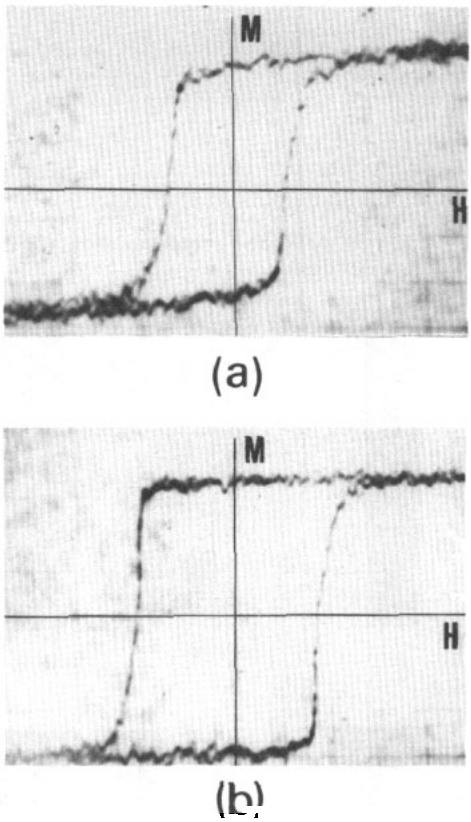

Figure 4. Magnification of the central part of the M–H hysteresis loop in figure 2: (*a*) applied stress $\sigma \simeq 16$ MPa; (*b*) applied stress $\sigma \simeq 114$ MPa.

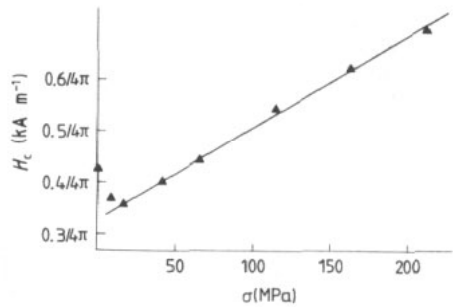

Figure 5. Coercive force (H_c) versus applied stress (σ) curve for the $(Co_{0.8}Fe_{0.2})_{80}B_{20}$ amorphous alloy.

the magnetization tends to align in the applied stress direction, as shown in figures 3(*c*) and 3(*d*). These figures correspond to two different regions in the specimen with an external applied stress. In the latter case, all the maze domains have almost disappeared.

Figure 4 represents an amplification of the central part of the M–H loop for two different values of the applied stress. The increases in the remanent magnetization and the coercive field H_c with stress are quite clear. In figure 5, H_c is shown as a function of σ for small and intermediate values of σ. Excluding very small values of σ, there is a linear relation for H against σ. For high values of σ ($\geqslant 250$ MPa), the H versus σ curve is also non-linear. These results suggest that under stress the central part of the M–H loop corresponds to domain wall motion in regions subjected to the action of the magnetic anisotropy induced by the stress.

Assuming that $H_c \simeq H_k$ (anisotropy field), and applying

$$H_k = 2K_\sigma/\mu_0 M_s = 3\lambda\sigma/\mu_0 M_s \tag{1}$$

we obtain

$$\lambda = (\mu_0 M_s \Delta H)/(3\,\Delta\sigma). \tag{2}$$

For $\Delta\sigma = 50$ MPa, we get (figure 5) $\Delta H_c = 8$ A m^{-1}. Using $\mu_0 M_s \simeq 1.2$ T, we find that $\lambda \simeq 6 \times 10^{-8}$.

The calculation performed is only an approximation but is good enough to show that the value of λ for the sample is not too high. It is surprising that the internal stresses determine the distribution of the magnetization of the sample when such a small value of λ is found (except in the maze domains).

In order to obtain more information, the internal stresses of the sample were removed by annealing in an inert atmosphere of argon (in a rotating magnetic field in order to avoid the possible induced magnetic anisotropies) at 360 °C for 20 min. This temperature was chosen because a maximum in the exothermic structural relaxation process has previously been observed at around 350 °C [7]. Figure 6(*a*) shows the magnetization distribution at room temperature of a region of the annealed sample; in other regions the distribution is that in figure 6(*b*). In figure 6(*a*) the magnetization is longitudinal while in figure 6(*b*) it is transverse. No maze domains are observed after annealing. These results show that the transverse magnetic anisotropy does not disappear after annealing, suggesting a non-magnetoelastic origin. We think that the origin may be the same as for the anisotropy induced by annealing under stress [7]. In this case, transverse polarization of the clusters could be induced in part during the process of rapid cooling owing to thermal gradients. On annealing up to 360 °C, the polarization disappears partially because of the reversible structural transformation in the clusters taking place in the 300–400 °C range [7].

The cluster model can also explain other magnetic phenomena not yet described in metallic glasses but which we shall now discuss. A positive stress is applied to orient the magnetization of the amorphous matrix in the ribbon axis direction (we assume that the local magnetization of the clusters is oriented in an intermediate position between the local strong transverse anisotropy field and the axis direction). In our experiment a tensile stress $\sigma = 60$ MPa is applied, and then a DC pulse on the primary coil (enough to reach technical saturation) is also applied. We then applied an increasing alternating magnetic field (50 Hz). Figures 7(*a*-1)–7(*a*-3) show the evolution of the *M*–*H* loops as the AC magnetic field increases. The maximum AC field applied was below $80/4\pi$ A m^{-1}. Following this experiment, a new DC pulse was applied, but in the opposite direction to the first. On magnetizing the sample by increasing the applied AC magnetic field, we obtain the *M*–*H* loops shown in figures 7(*b*-1)—7(*b*-3). When a new DC pulse is applied in the same direction as the first, the initial loops shown in figures 7(*a*-1)–7(*a*-3) are again obtained.

The results in figure 7 show unambiguously the existence of a weak unidirectional magnetic anisotropy of unknown origin that perturbs the hysteresis loops at a low field. One of the possible explanations may be that proposed above to explain the origin of the transverse magnetic anisotropy. The results in figure 7 may be explained by assuming the existence of nearly crystalline magnetic clusters in the amorphous matrix, which are not uniformly distributed but form a transverse texture along the ribbon. We suppose that the matrix is a phase with weak local magnetic anisotropy and that the clusters are a second phase with strong local magnetic anisotropy—both magnetic phases with weak coupling. When a magnetic field which is sufficiently large to overcome the anisotropy field of the clusters is applied, the magnetization of both phases will be oriented jointly in the applied field direction. However, what will happen when the applied field does not overcome the clusters' anisotropy field? In this case the magnetization of the clusters could slightly reorient by rotating around its local anisotropy axis, whereas the magnetization of the matrix is oriented in the applied field direction; thus exchange interactions appear between both magnetic phases. The exchange interaction can be expressed through a unidirectional anisotropy field; hence it can be switched by applying a high enough reverse magnetic field.

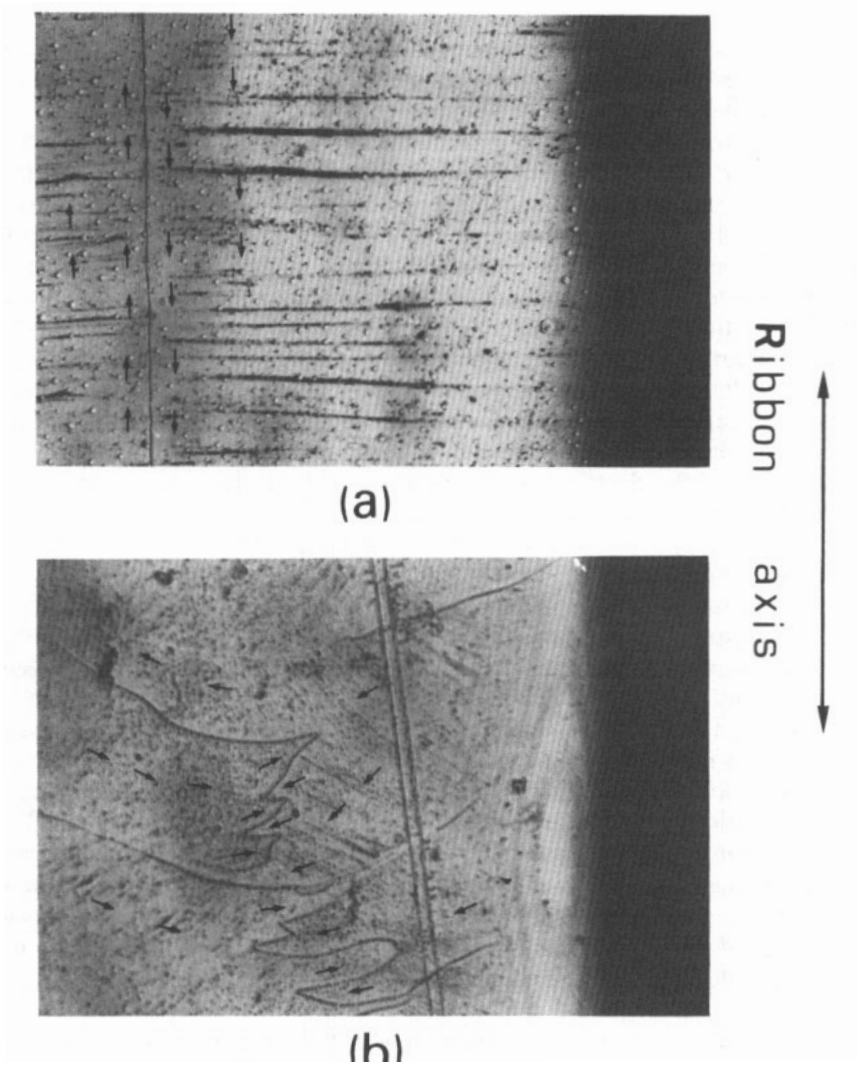

Figure 6. Bitter patterns of the domain structure in the $(Co_{0.8}Fe_{0.2})_{80}B_{20}$ amorphous sample (which had been annealed at 360 °C) obtained by applying a rotatory magnetic field: (*a*) a Bloch wall parallel to the ribbon axis; (*b*) a 'zigzag' wall between domains with nearly transverse magnetization. The arrows in each magnetic domain indicate the approximate direction of the magnetization.

For amorphous ribbons obtained at lower quenched rates, the reported magnetic anomalous behaviour greatly decreases and the material is magnetically softer. This last result can also be explained with our model. A low cooling rate (but high enough to produce an amorphous structure) may induce many metastable atom clusters to evolve into a more stable structure at room temperature. This structure probably is not as anisotropic as the corresponding structure frozen in at high quenching rates and, consequently, its influence will be less in the bulk magnetization processes of the sample.

Unidirectional anisotropies similar to that described in this work have also been observed by us in other metallic glasses, e.g. $Co_{80}Nb_8B_{12}$ metallic glass. All of them had

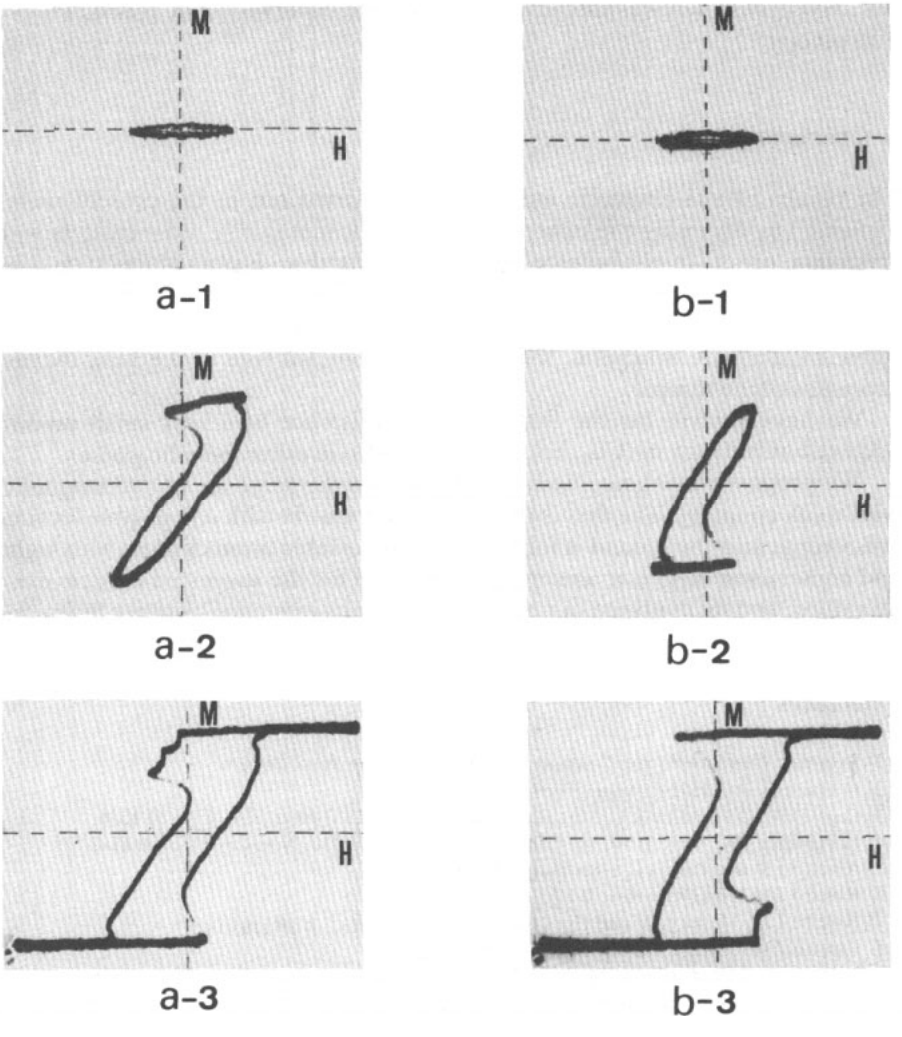

Figure 7. *M–H* hysteresis loop in arbitrary units, corresponding to the $(Co_{0.8}Fe_{0.2})_{80}B_{20}$ amorphous alloy under an applied stress of about 60 MPa: (*a*) after a DC pulse (intense enough to saturate the sample) had been applied; (*b*) after a second DC pulse in the opposite direction to the first had been applied (maximum applied AC field, about $78/4\pi$ A m^{-1}).

a thickness of about 20 μm. The amorphous alloy described here has shown this effect more clearly.

Unfortunately, the proposed clusters could not be observed with direct observation techniques such as electron diffraction or high-resolution electron microscopy. This last technique is very promising but is not straightforward with respect to sample preparation. In this situation other hypotheses may be advanced such as (1) a surface layer with different composition from that of the bulk, (2) the existence of microvoids and (3) the existence of pits, etc. When severe electrolytic polishing was carried out in orthophosphoric acid, producing a reduction in thickness of about 40%, the unidirectional magnetic anisotropy was still observed, and therefore hypotheses (1) and (3) were ruled

out. Hypothesis (2) was discarded after sample observation by transmission electron microscopy.

3. Conclusions

The results of the magnetic measurements carried out in the present work can be explained by assuming the existence of magnetic metastable atom clusters with nearly crystalline order. In our opinion, stable or metastable clusters of this type constitute a defect present in all metallic glasses obtained by conventional rapid quenching methods, the metastable fraction increasing as the quenching rate is increased. When the metastable clusters are magnetic, they play an important role in the bulk magnetization processes of the sample.

We have shown, for the first time, the existence of a very small unidirectional magnetic anisotropy in $(Co_{0.8}Fe_{0.2})_{80}B_{20}$, and also in other metallic glasses.

We propose that these anomalies are due to the presence of two magnetic phases with weak coupling. The first is the amorphous matrix with a negligible local magnetic anisotropy, and the second is formed from metastable atom clusters with higher order and higher local magnetic anisotropy. Evidence for the suggested clusters exists in the literature, and we continue our efforts to clarify its existence by other techniques.

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