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Comments on the analysis of hyperfine-field distributions in amorphous magnetic solids using a spectrum-subtraction method

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We show in this Comment that the applicability of the spectrum-subtraction method to analyze the hyperfine-field distribution $\{P(H)\}$ is limited to a small class of amorphous ferromagnetic alloys. If a small magnetic field does not completely align the magnetic moments in the sample, some of the novel features of the $P(H)$ may be artificially subtracted out before the analysis of $P(H)$ can be made. The differences in the $P(H)$ of METGLAS ® 2826-A ($Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$) will also be examined.

Schaafsma reports in the preceding paper[1] (hereafter referred to as Ref. 1) that by using a spectrum-subtraction procedure,[2] a hyperfine-field distribution $\{P(H)\}$ of a metallic glass sample METGLAS ® 2826-A (nominal composition $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$) has been obtained. In this subtraction procedure, one (in Ref. 1) or in general both[2] spectra are taken under a small external magnetic field. It is asserted that the $P(H)$ so obtained for METGLAS ® for 2826-A is different in the low-field portion from that obtained by Chien,[3] who used a Fourier analysis[4] on a single Mössbauer spectrum without an external field.

It is crucial to the spectrum-subtraction method that *all* the magnetic moments must be aligned in the sample. Since an external field has at least a directly subtractive (at $T \simeq 0$ K) and much larger (at higher T) effect on the values of the hyperfine field, its magnitude is limited to only a few KOe.[5] With a small field of a few hundred Oe, one can align only the moments in a very soft ferromagnet (with small coercivity but sizable $4\pi M$) and only in the sample plane. By taking spectra with two known orientations,[6] one in principle knows the values of $b = 4\sin^2\theta/(1+\cos^2\theta)$, where θ is the angle between the γ ray and the magnetic moments.[5] As described in Ref. 1 and elsewhere,[2] by the use of an *adjustable* factor, one subtracts the two spectra until lines 1, 3, 4, and 6 are removed *before* proceeding with the $P(H)$ analysis of lines 2 and 5.

However, some of the magnetic moments may *not* be completely aligned by a small magnetic field as assumed. If one then proceeds with the subtraction, their contributions to the spectrum will *partially or completely be subtracted out before* the $P(H)$ is analyzed. There are at least four cases which are found in amorphous magnetic systems that fall into this category[7]: (a) Some moments (especially in a multimetal amorphous solid) have higher single-ion anisotropy than others; (b) weakly coupled moments; (c) atoms with negligible moments which are therefore quasi-non-magnetic; and (d) moments that form a spin-glass-like ordering. In (b) and (c), the corresponding hyperfine fields are likely to be also small. In the case of a spin-glass-like ordering, a field of a hundred Oe will not change the orientations of the moments at all.[8,9] After subtraction, one would have *no* spectrum left to do the $P(H)$ analysis.

It is clear then the spectrum-subtraction method is applicable only in simple ferromagnets, and furthermore, only in those in which a small external magnetic field can, *with certainty,* align *all* the moments. The characterization of an alloy as a simple ferromagnet must come from other measurements, e.g., magnetization, hysteresis, susceptibility, etc. There are a number of amorphous magnetic systems, such as Fe metalloid (high Fe content), (Fe-Co) metalloid, where these conditions are met. In these systems, the coercivity is only a few Oe, therefore a field of a few hundred Oe can align the moments in the sample plane. However, there are a far greater number of amorphous systems which *do not* fall into this category. To name a few, these include most of the rare-earth–transition-metal systems, the (Fe-X)-metalloid systems with appreciable content of $X =$ Cr, Mn, Pd, Mo, Ni, etc.[7-11] These may be ferromagnetic but with high coercivity, or have a noncollinear spin structure unalignable by a small field or may not be ferromagnets at all.

The difference in the $P(H)$ of amorphous METGLAS ® 2826-A ($Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$) will now be discussed. The $P(H)$ obtained by the spectrum-subtraction method is shown in Fig. 1. Although Schaafsma insists that there is only a monotonically decreasing tail in the $P(H)$, the histogram does seem to indicate a second maximum at the low-field side. Furthermore, the capability of a histogram with so few bins to resolve a small maximum is limited. In fact, 16 sets of hyperfine patterns are clearly too few since the actual spectrum does not show the resultant "glitches" (Fig. 1 of Ref. 1).

It should be noted that the spectrum shown in Fig.

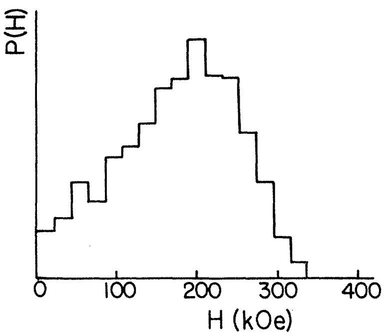

FIG. 1. Hyperfine field distribution of METGLAS® 2826-A ($Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$) at 5 K as obtained by the spectrum-subtraction method (Ref. 1).

1(a) of Ref. 1 was taken when adhesive tapes that stuck to the samples were used to apply stress to the sample upon cooling. Whether this practice is reliable, reproducible, and capable of aligning *all* the Fe moments *perpendicular* to the sample plane is unclear. It is further assumed in Ref. 1 that METGLAS® 2826-A is a soft ferromagnet and, therefore, the moments can be aligned by a field of only 200 Oe. Magnetic data on METGLAS® 2826-A showed that it is far from being a soft ferromagnet.[12] There is a high-field susceptibility which persists at temperatures far below T_c (about 250 K). At $T < T_c$, the magnetic isotherms indicate that the magnetic moments are *not* completely aligned in the sample plane by applied fields of up to 10 000 Oe. We know of no magnetic data which shows the alignment of the moments at 5 K under a field of only 200 Oe. The appearance of the Mössbauer spectrum is hardly adequate especially since the differences of $P(H)$ in question are slight. Furthermore, the value of $b = 3.7 \pm 0.1$ instead of 4 is indicative of misalignment. One wonders, therefore, how much, if any, of the $P(H)$ in METGLAS® 2826-A has been subtracted out in the process due to incomplete alignment.

If a complete alignment of the magnetic moments is not achieved, but one knows *a priori* that the misalignment is the *same* for all the Fe moments, one effectively has only one b value. However, this assumption which Schaafsma made, would require the same anisotropy energy and the same response under stress for all Fe moments, an improbable situation.

More recently, we have studied a series of amorphous (Fe-Cr)-metalloid samples with a wide range of Cr content under a high magnetic field (up to 70 kOe).[13] In samples with increasing Cr content, while the Fe with larger hyperfine fields are more readily aligned by the external field, those with small hyperfine fields are *not*. For samples with higher Cr content ($\gtrsim 20$ at.%), the Fe moments appear to form a spin-glass-like ordering. Similar results in (Fe-Mn)-metalloid systems have recently been observed.[14] These results show that samples which contain substantial amounts of Cr are not simple soft ferromagnets. Equally important, these measurements demonstrate that the assumption of an average b value for all hyperfine fields is not valid.

Schaafsma claims that the bimodal $P(H)$ that we have previously determined in Ref. 3 is due to an excessive value chosen for b. In reality the b value is not chosen by preference, but allowed to vary in the computation to give a best fit to the data. What we have assumed in Ref. 3, however, is a single b value for the bulk sample, an assumption Schaafsma continues to use, but it is inaccurate as indicated by the high-field measurements. For this reason, we have prepared a powder sample by grinding bulk METGLAS® 2826-A samples with quartz powder. The advantage is a single value of $b = 2$ can now be ascertained. The spectrum and the $P(H)$ of the powder sample at 4.2 K are shown in Fig. 2. It is evident that the $P(H)$ is *bimodal*. The lower maximum in $P(H)$ of the bulk sample in Ref. 3 is increased in magnitude due to the approximation of a single b value. Thus the Fourier method does not tend to

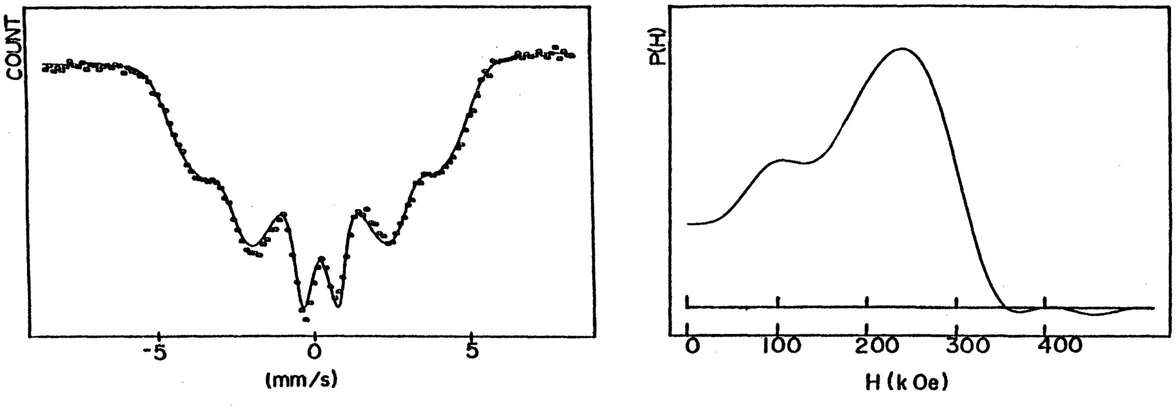

FIG. 2. Spectrum and $P(H)$ of METGLAS® 2826-A in powder form at 4.2 K.

create or destroy the sizable peak in $P(H)$ as previously shown by numerical tests.[15]

Numerous amorphous (e.g., Y-Fe, Fe-Si, Fe-Mn, Fr-Cr, Fe-Ge, Fe-Mo, etc.[7-11]) and crystalline systems have exhibited $P(H)$ with more than one maxima. Although Schaafsma inclines to discount any $P(H)$ with more than one maxima as spurious, no reference has been given for this assertion. It should also be mentioned that in a homogeneous multielement amorphous system, the microscopic environment must vary from site to site, leading therefore to microscopic chemical disorder. This fact, which is not surprising at all, is based simply on probability and occurs in all such systems regardless of the $P(H)$ they exhibit. It is increasingly clear that the shape of $P(H)$ depends on the elements involved and their concentrations. There are situations where a broad, bimodal or more complicated $P(H)$ are realized. For example, in some systems, the forming of a sizable hyperfine field requires a critical number of specific neighbors thus resulting in a bimodal-type $P(H)$.[7,9,11]

Finally, a single isomer shift and no effective quadrupole interaction are often assumed in most $P(H)$ analyses, including both the method in Ref. 1 and the Fourier method. These assumptions are vulnerable for the low-field side of the $P(H)$. Thus the discrepancy in METGLAS ® 2826-A tends to be partly academic. However, we do wish to point out that the spectrum-subtraction method relies critically on the complete alignment of all the moments under a very small field. This method is therefore applicable only in a small class of soft amorphous ferromagnetic solids, which does not include METGLAS ® 2826-A.

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[3] C. L. Chien, Phys. Rev. B 19, 81 (1979).

[4] B. Window, J. Phys. E 4, 401 (1971).

[5] See, e.g., *Chemical Applications of Mössbauer Spectroscopy*, edited by V. I. Goldanskii and R. H. Herber (Academic, New York, 1968).

[6] The spectral linewidths are noticeably different in the two orientations due to different absorber thickness but not taken into account in the subtraction of spectra.

[7] See, e.g., J. M. D. Coey, J. Appl. Phys. 49, 1646 (1978).

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