



## LOCAL ORDER IN AMORPHOUS PURE IRON

D.H. Ryan, L.X. Liao and Z. Altounian

McGill University, Physics Department, 3600 University St.  
Montreal, Quebec, H3A 2T8

We compare the effect of metalloid and metal alloying on the local structure of amorphous iron alloys. Data are presented on the quadrupole splitting and isomer shift measured above the magnetic ordering temperature for  $(\text{Fe}_{1-x}\text{Nd}_x)_{100-y}\text{B}_y$  ( $0 \leq x \leq 25$ ,  $5 \leq y \leq 20$ ). A common limit for  $x, y \rightarrow 0$  is obtained. No evidence for polymorphism in amorphous pure iron is found.

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### 1. INTRODUCTION

The extreme instability of amorphous pure iron precludes its preparation<sup>1</sup>. Attempts to understand its magnetic properties have therefore concentrated on extrapolation from series of amorphous alloys of the form  $\text{Fe}_{1-x}\text{M}_x$  containing small amounts (typically 10%) of impurities. For iron concentrations less than 90% at  $x$  the magnetic properties depend sensitively on the nature of the impurity: alloys with yttrium exhibit random non-collinear or asperomagnetic ordering below about 100K<sup>2</sup>, those with zirconium are also asperomagnetic but with higher ordering temperatures ( $\sim 250\text{K}$ ) while boron containing alloys are ferromagnetic with  $T_c$  as high as 750K<sup>4</sup>. As the iron concentration is increased beyond 90%, these distinctions are reduced. The ordering temperature of a-Fe-B alloys falls rapidly, and the spin structure in the ordered state of a-Fe-Zr alloys becomes progressively more random. Combining the results from these and other systems it is possible to extrapolate to the magnetic properties at the  $x = 100$  limit and to predict that pure amorphous iron would be speromagnetic (random non-collinear order with no net magnetisation) below a spin freezing temperature of  $\sim 150\text{K}$ <sup>3</sup>.

The validity of this approach has recently been called into question by the suggestion that alloys containing early transition metals or rare earths may be structurally distinct from those containing metalloids<sup>5</sup>. If this were the case, it would be unreasonable to expect alloy series to extrapolate to a common magnetic limit. The argument is based on results from a wide range of amorphous binary alloys which show that the quadrupole splitting (which is sensitive to the local atomic symmetry) appears to extrapolate to distinct limits depending on whether the alloy contains a metal (Ti, Hf, Zr, etc.) or metalloid (Ge, Si, B, etc.). Data on

the metalloid based systems are restricted, in room temperature measurements, to compositions with  $T_c < 300\text{K}$  to avoid the effects of magnetic order<sup>6</sup>. The maximum iron concentration studied was  $\sim 70\%$ , well short of the  $x=100$  limit, and in a region where the directional character of the Fe-metalloid bond, and the avoidance of metalloid-metalloid contacts leads to well defined short range order<sup>7</sup>. It is possible that this selective sampling of an uncharacteristic region is responsible for the observed differences.

We therefore undertook an investigation of a range of alloys of the form  $(\text{Fe}_{1-x}\text{Nd}_x)_{100-y}\text{B}_y$  ( $0 \leq x \leq 25$ ,  $5 \leq y \leq 20$ ) which allows us to compare the effects of metal and metalloid alloying. We made all measurements above  $T_c$  and were able to cover total iron concentrations from 60% to 88%.

### 2. EXPERIMENTAL METHODS

The alloys were prepared from the pure elements by induction melting and melt spinning under protective atmospheres as described elsewhere<sup>8</sup>. X-ray diffraction was used to confirm the absence of crystallinity. Samples for high temperature Mössbauer spectra were powdered, mixed with boron nitride and mounted between beryllium discs in a resistively heated oven. Oxidation was avoided by operating the oven in a dynamic vacuum of better than  $2 \times 10^{-4}\text{Pa}$  ( $10^{-6}$  torr) and selected samples were checked afterwards by X-ray diffraction for signs of crystallisation. Temperature control and homogeneity were better than  $\pm 2\text{K}$  during the measuring time. Mössbauer spectra were obtained on a conventional constant acceleration spectrometer with a 1GBq <sup>57</sup>CoPd source. Typical counting times of 20 hours yielded a baseline of  $5 \times 10^5$  counts. Least-squares fitting of two independent Lorentzian lines was used to obtain

isomer shifts ( $\delta$ ) and quadrupole splittings ( $\Delta$ ). Fitting a distribution of quadrupole splittings, with correlated isomer shifts gave better fits, but did not give different values. All isomer shifts are quoted relative to iron metal at room temperature.

3. RESULTS AND DISCUSSION

Fig 1 shows typical spectra for the  $y = 20$  series. The fitted values of isomer shift and quadrupole splitting are shown in Fig 2. Most samples were measured at 480K. Those with higher ordering temperatures were measured at the lowest temperature consistent with avoiding magnetic broadening (typically  $T_c + 20K$ ) and the values obtained were adjusted to  $480K$  using the measured values of  $d\delta/dT$  ( $-7.15 \pm 0.06 \times 10^{-4}$  mm/s/K) and  $d\Delta/dT$  ( $-1.00 \pm 0.07 \times 10^{-4}$  mm/s/K). Errors introduced by this procedure are of order  $2 \times 10^{-3}$  mm/s.

From Fig 2(a) it is clear that the addition of B and Nd have opposite effects on the value of  $\delta$ . Adding B leads to more positive values at a rate of  $\sim 4 \times 10^{-3}$  mm/s/%B, whereas Nd leads to a reduction in  $\delta$  at essentially the same rate. This reflects the difference between the Fe-B and Fe-Nd bonds. The large iron moments in  $a\text{-Fe}_{1-x}\text{B}_x$  alloys and the rapid destruction of the iron moment on alloying with Nd are also consequences of the bonding differences.

Replotting the data from Fig 2b in terms of total iron concentration (Fig 3) shows that, in the concentration range covered by this work, adding a metal or a metalloid has exactly the same effect on the local symmetry. For a given iron concentration, it does not matter what the composition of the remaining impurities is. Extrapolating the data in Fig 3 to 100% iron yields a value of  $0.33 \pm 0.04$  mm/s for the room temperature quadrupole splitting of amorphous pure iron, in perfect agreement with the value

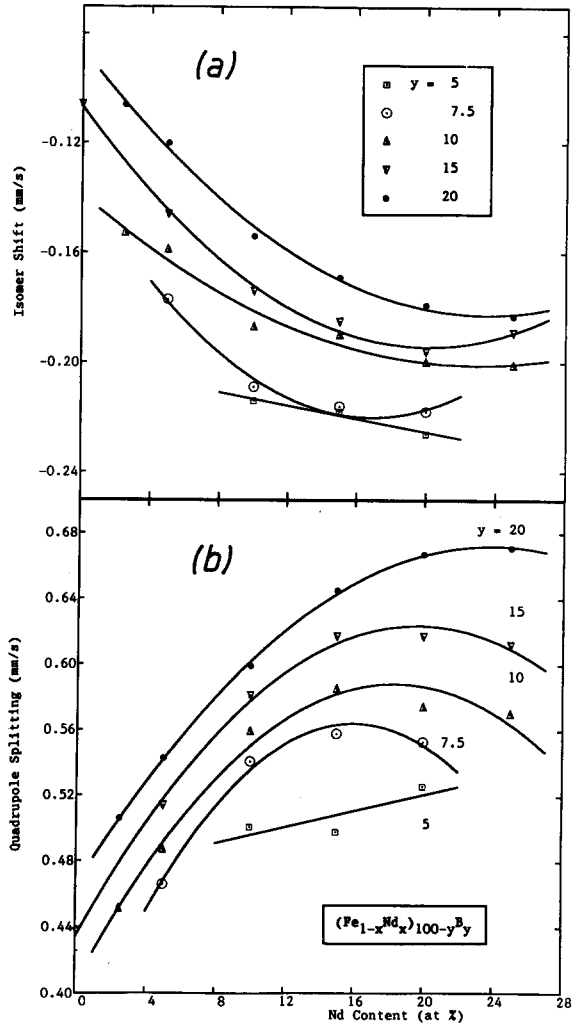


Fig. 2 (a) Isomer shift and (b) Quadrupole splitting for the five series of alloys, plotted against x. Values measured or adjusted to 480K.

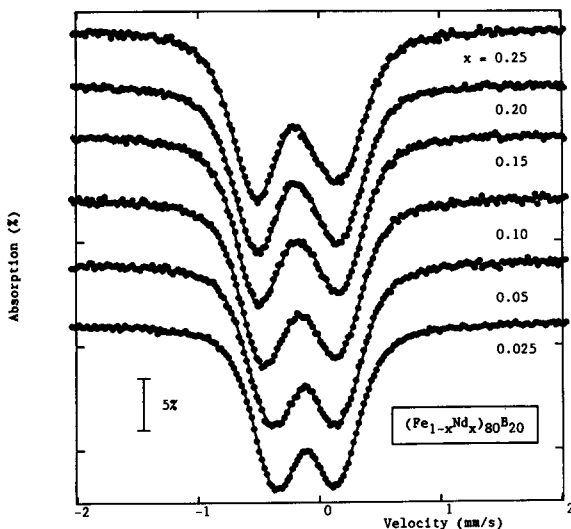


Fig. 1 Mössbauer spectra with fits for  $a\text{-}(\text{Fe}_{1-x}\text{Nd}_x)_{80}\text{B}_{20}$  measured above  $T_c$

of  $0.33$  mm/s obtained for iron-metal alloys<sup>6</sup>. Thus, the local atomic ordering in pure amorphous iron is independent of whether it is derived from metal-based or metalloid based alloys, and we may reasonably expect the magnetic properties also to extrapolate to a unique limit. The suggestion that the presence of metalloids in the amorphous alloy leads to different local order is based on data obtained too far from the iron-rich limit, in a region where the more directional nature of the iron-metalloid bond does lead to distinct local symmetry.

4. CONCLUSIONS

Comparison of the effects of B and Nd on the isomer shift shows evidence for the bonding differences which lead to the larger iron moments and higher ordering temperatures in Fe-

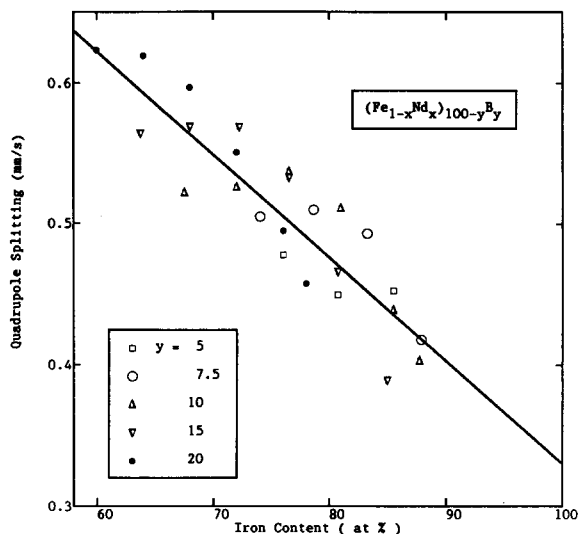


Fig. 3 Quadrupole splitting vs total iron concentration for all of the alloys in the study. Values are adjusted to 300K. Straight line is a least-squares fit.

metalloid alloys relative to Fe-metal systems.

The concentration dependence of quadrupole splitting in iron-rich amorphous Fe-Nd-B alloys over a wide composition range clearly indicates that iron-metal and iron-metalloid alloys extrapolate to a common structure limit at  $x =$

100. No evidence for polymorphism in amorphous pure iron was found.

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