



Magnetic and structural properties of amorphous transition metals and alloys

R. Bellissent^a, G. Galli^{b,*}, T. Hyeon^c, P. Migliardo^a, G. Parette^b, K.S. Suslick^c

^a *Laboratoire Leon Brillouin, CEN Saclay, 91191 Gif-sur-Yvette cedex, France*

^b *Dipartimento di Fisica and INFN, Universita di Messina, P.O. Box 55, 98166 Santagata, Messina, Italy*

^c *School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 S. Mathews Avenue, Urbana, IL 61801, USA*

Abstract

In this paper a neutron scattering study of local order and magnetic properties of the $\text{Fe}_{1-x}\text{Co}_x$ amorphous system is presented. A wide momentum transfer range has been used for studying local order. The better resolution associated with higher neutron wavelengths provided one with a description of the magnetic contribution measured with and without an applied magnetic field. Preliminary results are also reported on recent SANS measurements, which provide better insight on the magnetic properties and the structure and size of the powder grains.

1. Introduction

Amorphous transition metals exhibit unusual magnetic properties, and the relationship between the local order in such materials and their magnetic behavior remains poorly understood. Until recently it had been impossible to make amorphous monatomic transition metals or alloys in bulk. As a result, previous studies have been nearly exclusively of metal-main group element covalent-type alloys. Recently, gram quantities of amorphous iron and amorphous iron-cobalt alloy powders were produced from sonochemical decomposition of volatile organometallic precursors such as $\text{Fe}(\text{CO})_5$ or $\text{Co}(\text{CO})_3(\text{NO})$ [1-5]. Sonochemistry arises from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. The implosive collapse of bubble generates localized hot spot;

temperature of ~ 5000 K and pressure of ~ 1800 atm, with cooling rates that exceed 10^9 K/s [2]. The extremely high cooling rates are largely responsible for the formation of amorphous materials.

We report now new results on the structural and magnetic properties of sonochemically prepared binary alloys of Fe and Co obtained by neutron diffraction experiments carried out in a wide range of exchanged momentum. The entire set of data can be interpreted in terms of the random packing model for the pure metals and distorted tetrahedral structure for the alloys. The magnetic response, analyzed in terms of the magnetic cross-section, suggests ferromagnetic behavior, which is in accord with the direct magnetic susceptibility data [5].

2. Experimental procedure

Because the sonochemical reactions take place mostly inside the cavitation bubbles in a liquid, a

* Corresponding author. Tel.: +39-90 391 478; fax: +39-90 601 007.

good precursor must have a substantial vapor pressure. $\text{Fe}(\text{CO})_5$ and $\text{Co}(\text{CO})_3(\text{NO})$ were chosen because of their high vapor pressure and acceptable thermal stability. A solution of $\text{Fe}(\text{CO})_5$ and $\text{Co}(\text{CO})_3(\text{NO})$ in dry decane was irradiated at 0°C with a high-intensity ultrasonic probe for 3 h under argon. After irradiation, a black powder was formed, which was filtered and washed with dry pentane in the glove box. The composition of the Fe–Co alloys can be controlled simply by changing the ratio of solution concentrations of the precursors. All composition ranges can be produced by this method. After preparation, all samples were tested to ensure size homogeneity on the nanometer scale and consistent amorphism, as confirmed by electron beam microdiffraction and differential scanning calorimetry (DSC). After heat treatment under H_2 gas flow at 673 K for 2 h, all samples underwent crystallization, as demonstrated by X-ray diffraction and DSC. Local order measurements have been performed on the spectrometer 7C2 of Orphée Reactor of Laboratoire Léon Brillouin at Saclay (France).

3. Results and discussion

Using these samples we were able to study local order of $\alpha\text{-Fe}$ [3] and, more recently, $\alpha\text{-Fe}_{1-x}\text{Co}_x$ [4]. The measured structure factors that correspond to the five studied compositions ($x = 0, 0.25, 0.5, 0.75$ and 1) are shown in Fig. 1. It must be noted that the large difference between Co and Fe scattering length for thermal neutrons give the Fe contribution a dominant role in these total structure factors, especially for Fe concentrations exceeding 25%. The pair correlation function obtained by Fourier transform of the corresponding structure factors are shown in Fig. 2. These data show that there is a large difference between the amorphous state and the liquid state local order. The structure of the liquid iron is reasonably well described in terms of hard sphere packing [7] while the structure of the amorphous one is much closer to a random packing of tetrahedral units [8]. Thus the local order of amorphous iron seems to be based on a strongly anisotropic bonding, which is quite different from the corresponding liquid. While such behavior appears quite surprising for a metallic

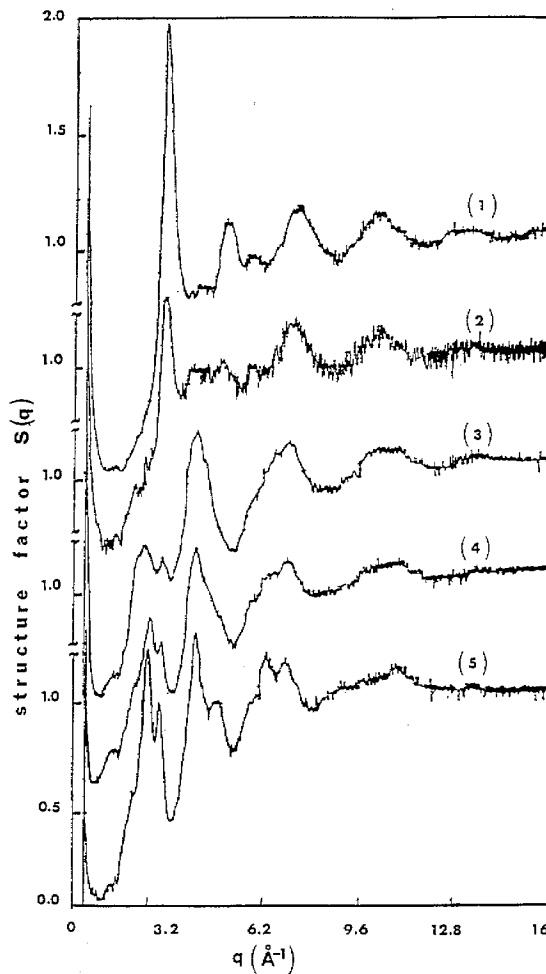


Fig. 1. Total structure factor $S(q)$ for pure $\alpha\text{-Fe}$ (1), $\alpha\text{-CoFe}_5$ (2), $\alpha\text{-CoFe}$ (3), $\alpha\text{-Co}_5\text{Fe}$ (4), and pure $\alpha\text{-Co}$ (5).

system, it is common among transition metal cluster compounds and extended solids [9].

All the amorphous $\text{Fe}_{1-x}\text{Co}_x$ alloys studied show magnetic scattering in the low momentum transfer range ($0.4 < q < 5 \text{ \AA}^{-1}$). The presence of magnetic scattering can be deduced from the limiting value of the structure factor, which is much larger than the expected compressibility contribution. Normally, the magnetic contribution cannot be directly separated from the nuclear one by using a single diffraction experiment. However, the preliminary fitting using the form factor of amorphous iron [10] lead to the estimated value of $1.4\mu_B$ for the atomic magnetic

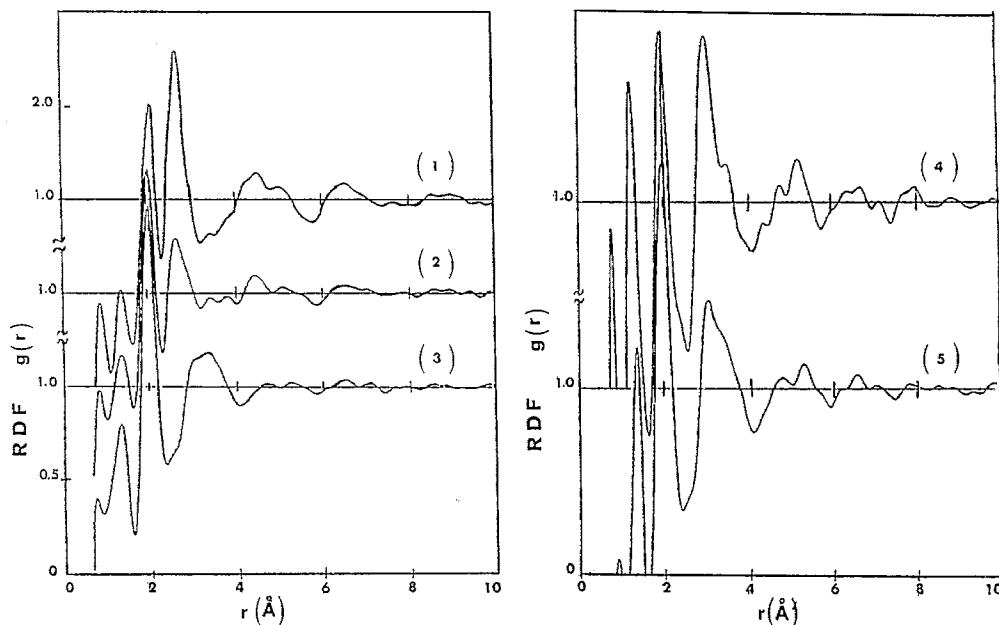


Fig. 2. Radial distribution function $g(r)$ for pure α -Fe (1), α -CoFe₅ (2), α -CoFe (3), α -Co₅Fe (4), and pure α -Co (5).

moment of α -Fe [3]. A better determination of this magnetic term and direct macroscopic magnetic measurements [5] of the alloys is needed and is underway. We have undertaken a new neutron diffraction experiment on the G61 spectrometer at the LLB that allows the detection of diffracted neutron at lower exchanged momenta. For a ferromagnetic system, the cross-section can be written as the following equation, when a magnetic field is applied perpendicular to the scattering plane:

$$\sigma_H = \sigma_N + \sigma_M. \quad (1)$$

Without a field, the cross-section is given as the following equation

$$\sigma_0 = \sigma_N + \frac{2}{3}\sigma_M. \quad (2)$$

We collected the diffraction spectra with and without an external magnetic field to give the paramagnetic cross-section $\sigma_M = 3(\sigma_H - \sigma_0)$. Preliminary results are reported in Fig. 3. The data reveal a near constant contribution to the momentum transfer range between 0.5 and 1.0 \AA^{-1} in addition to a strong increase of the intensity for smaller angles ($0.1 < q < 0.5 \text{\AA}^{-1}$). The occurrence of a magnetic structure factor having the same shape as the nuclear structure factor suggests ferromagnetic behavior,

which agrees with direct magnetic measurements. However, the calculated absolute value of the cross-section after normalizing with a vanadium probe is

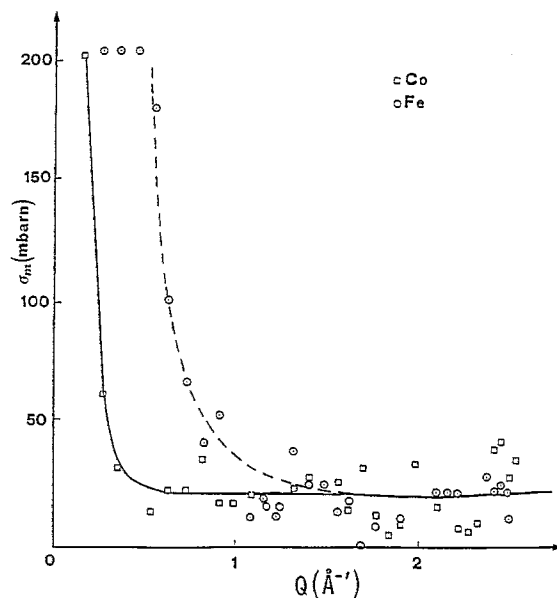


Fig. 3. Paramagnetic cross-section (σ_m) of pure α -Fe and α -Co versus momentum transfer, q , from elastic neutron scattering experiment.

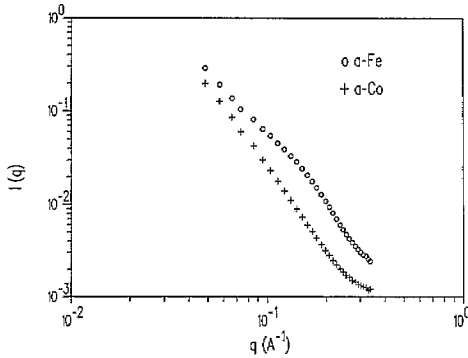


Fig. 4. Log of the scattered intensity $I(q)$ versus log of momentum transfer, q , from small angle neutron scattering (SANS) on α -Fe and α -Co.

25 mb at⁻¹ sr⁻¹, which is too high to support the hypothesis of ferromagnetic behavior. In fact, if we assume $1.4\mu_B$ for the magnetic moment of amorphous iron and 0.02 for the magnetic form factor of a ferromagnet, the expected value for the magnetic cross-section would be about 2 mb at⁻¹ sr⁻¹. By contrast, the assumption of paramagnetic behavior leads to a magnetic cross-section of 200 mb at⁻¹ sr⁻¹ for the form factor, which is quite close to 1 in the momentum transfer range. To clarify this point we have undertaken similar experiments on the PAXE small angle neutron scattering (SANS) spectrometer of the LLB at Saclay. Fig. 4 shows the preliminary data in a log-log scale for α -Fe and α -Co. The data indicate that the grain shapes for both samples cannot be immediately described in terms of the Guinier or Porod scattering law. The nanometer sized clusters [1] that make up these samples probably are responsible for an effective lower dimensionality of scattering for both the bulk and the surface.

4. Concluding remarks

Neutron elastic scattering data obtained from bulk amorphous iron, cobalt and their binary alloys have been presented. The results on the samples synthesized by sonochemical techniques reveal a dense

piling structure of slightly distorted tetrahedra around an assumed seed cluster. This structural model was originally proposed by Ichikawa [6] for pure amorphous metals. The binary Fe-Co alloys, whose structure is quite different from that of the corresponding liquid, can be rationalized in terms of distorted tetrahedra with some vacancies. The magnetic cross-section of α -Fe and α -Co as a function of the momentum transfer, q , behaves like the nuclear one. This result confirms the ferromagnetic nature of these materials. Finally, from SANS experiments, calculations concerning the grain surface and the compactness factor have been derived.

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References

- [1] K.S. Suslick, S.B. Choe, A.A. Cichowlas and M.W. Grinstaff, *Nature* 353 (1991) 414.
- [2] K.S. Suslick, M. Fang, T. Hyeon and A.A. Cichowlas, in: *Molecularly Designed Nanostructured Materials*, ed. K.E. Gonsalves (Materials Research Society, Pittsburg, PA, 1994).
- [3] R. Bellissent, G. Galli, M.W. Grinstaff, P. Migliardo and K.S. Suslick, *Phys. Rev.* B48 (1993) 15797.
- [4] R. Bellissent, G. Galli, T. Hyeon, S. Magazu, D. Majolino, P. Migliardo and K.S. Suslick, *Phys. Scr.* T57 (1995) 70.
- [5] M.W. Grinstaff, M.B. Salamon and K.S. Suslick, *Phys. Rev.* B48 (1993) 269.
- [6] M.W. Grinstaff, A.A. Cichowlas, S.B. Choe and K.S. Suslick, *Ultrasonics* 30 (1992) 168.
- [7] Y. Waseda and K. Suzuki, *Phys. Status Solidi* 39 (1970) 669.
- [8] T. Ichikawa, *Phys. Status Solidi* A29 (1975) 293.
- [9] J.K. Burdett, *Chemical Bonding in Solids* (Oxford University, New York, 1995).
- [10] C. Petrillo and F. Sacchetti, *Solid State Commun.* 74 (1990) 543.