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Neutron diffraction on amorphous iron powder

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Neutron-diffraction experiments have been carried out on amorphous iron powder prepared from the ultrasonic irradiation of $Fe(CO)_5$. The structural information from the shape of the radial distribution function is consistent with the random-packing-model (RPD) calculations previously made for films of amorphous iron. The atomic magnetic moment of iron in the amorphous bulk phase has been obtained and its value is close to that of liquid iron. A comparison is made between the present μ_{Fe} value and those previously extracted by extrapolation from the concentration dependence of the binary $Fe_{(1-x)}B_x$ metallic glasses.

INTRODUCTION

As our understanding of the physical properties and structure of crystalline elements and compounds has increased, substantial interest has arisen in the homologous materials in amorphous phases. As a consequence, in the last two decades, both theoretical and experimental studies have been devoted to the nature of the amorphous state and to the understanding of its physical properties, often in comparison with their crystalline counterpart.

While some elemental materials may be obtained in both crystalline and amorphous solid phases[1] and in the liquid state, it has been very difficult to produce amorphous metals. We now have available extensive data, thoroughly reviewed by Chen,[11] on liquid metals and also many theoretical proposals on noncrystalline solid metals; however, very few experimental results are available on amorphous metals, at present, mainly because of the great difficulties encountered in producing solid amorphous metals. Among them, not only for its fundamental interest but also for practical applications, experimental data about the transition metals in the amorphous state and, particularly, for amorphous iron are highly desirable.

Recently, a sonochemical synthesis of amorphous iron has been performed through the ultrasonic irradiation of the volatile iron pentacarbonyl $[Fe(CO)_5)]$.[2] We have now obtained neutron-diffraction data to delineate the structure and magnetic properties of this material.

EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

Samples of amorphous iron power, used here for neutron-diffraction experiments, were prepared sonochemically.[2] Bulk elemental analysis determined that the iron powder contained by weight 2% hydrogen, 3% carbon, and 1% oxygen. Neutron-diffraction measurements were carried out on the 7C2 spectrometer on the hot source of the reactor Orphee of the Laboratory Leon Brillouin at Saclay. The sample consisted of 500 mg of iron powder under inert atmosphere in a cylindrical, tight closed, vanadium cell. The use of a monochromatic neutron beam with a 0.7-Å wavelength provided us with a momentum transfer range from 0.3 to 16 $Å^{-1}$, large enough to obtain an accurate pair correlation function $g(r)$ by Fourier transform. Measurements have been carried out at temperatures of 30, 100, 170, and 220°C and, further, again at 30°. During the run at 170°C, where the differential scanning calorimetry (DSC) curve[2] exhibits a first peak, the sample began to show crystalline features in the diffractograms, and after 15 h at 200°C the diffraction pattern was mainly of crystalline type.

A typical diffraction pattern before crystallization, at $T=30°C$, is shown in Fig. 1 (curve a). The general features of the diffraction pattern, in which sharp peaks are absent, confirming previous[2] x-ray data demonstrates the amorphous nature of the sample. From the chemical test, a contribution was expected from the form factor of the residual hydrogen in a wide range of the explored Q.

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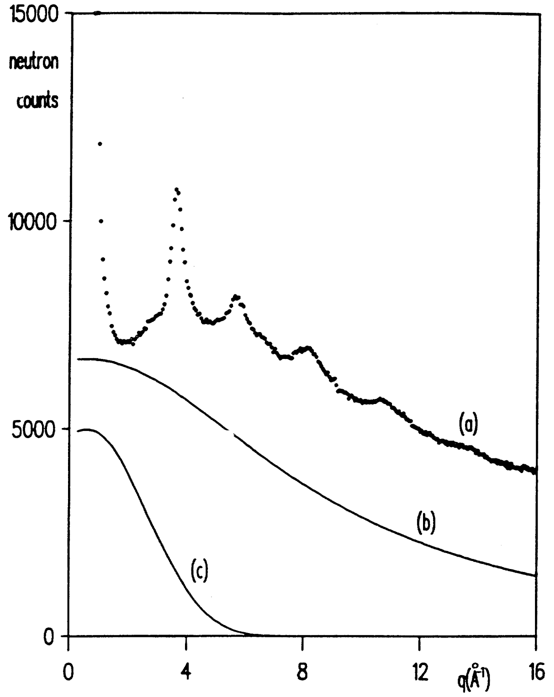

FIG. 1. (a) Diffraction intensity pattern $I(q)$ of amorphous iron powder at $T=30°C$; (b) hydrogen form factor, and (c) magnetic form factor. The scale of curve (c) has been expanded ten times.

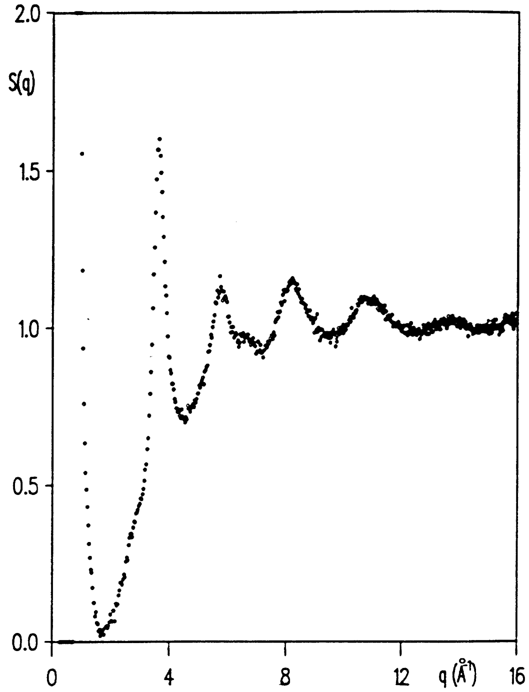

FIG. 2. Structure factor, $S(q)$, of amorphous iron powder at $T=30°C$.

The solid line in Fig. 1 (curve b) shows properly the shape of this form factor used in the data reduction.

Because the sample exhibits clear amorphous character and the ferromagnetism of iron takes place from the crystalline ordering of its atoms, macroscopic effects of coupling between the magnetic moments of neutrons and sample was not expected. Moreover, a residual magnetic moment, like that shown by analogous experiments on the liquid phase,[3] could persist in the amorphous state of iron giving rise to a magnetic form factor like that shown in Fig. 1 (curve c).[4]

Taking into account weighted quantities of these two contributions, at $T=30°C$, one gets the structure factor $S(q)$ shown in Fig. 2. The corresponding pair correlation function $g(r)$, obtained from it by Fourier transform, is given in Fig. 3. The structural information that comes out from Figs. 1 and 2 is summarized in Table I.

Data reduction has been carried out following the classical method of Paalman and Pings[5] for the absorption correction by the furnace, the container, and the sample itself. The multiple scattering correction has been done following the Blech and Averbach[6] procedure. The residual hydrogen contribution, a few atomic percent, has been removed. It consisted of the smooth decrease, as a function of the momentum transfer, of the incoherent inelastic scattered intensity and was evaluated following a procedure due to Chieux *et al.*[7]

The column designated "0th"' in Table I refers to a peak which is generally absent in previous neutron-diffraction curves on binary metal-metalloid metallic glasses. Its presence, in our sample, comes from the contribution of some Fe-O or FeC bonds due to the residual oxygen or carbon. The average Fe(III)-O distance, as obtained by other authors,[8] is just 1.86±0.06 Å, giving the attribution to Fe-O bonds more likely. From measurements performed at the various temperatures, the

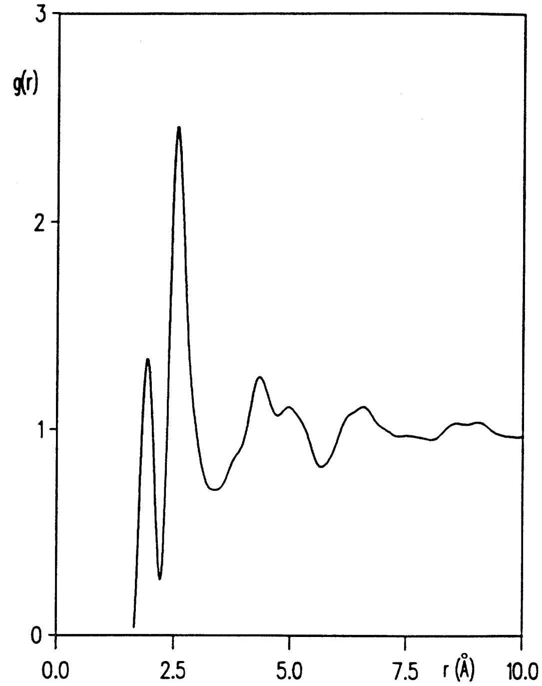

FIG. 3. Radial distribution function, $g(r)$, of amorphous iron powder.

TABLE I. Comparison of the peak position in $s(q)$ and $g(r)$; coordination number and magnetic moment, between liquid and bulk amorphous iron. Symbols refer to ($^\wedge$) liquid (Ref. 3); (*) this work. Values of the second peak position in the radial distribution function from this work correspond to the two subpeaks in which it is split.

	0th peak	1st peak	2nd peak	3rd peak
Structure factor (A^{-1})		2.07$^\wedge$	5.48$^\wedge$	7.95$^\wedge$
		3.05*	5.22*	7.71*
Radial distrib. func. (A)		2.58$^\wedge$	5.07$^\wedge$	
	1.93*	2.56*	4.34*; 4.96*	
Coord. number		9.5$^\wedge$		
		8.7$^\wedge$ 0.5		
Magn. moment		$1.2\mu_B^\wedge$		
		$1.4\mu_B^*$		

features of this peak are temperature dependent. Its relative contribution increases with temperature indicating iron oxidation with temperature-dependent kinetics.

A discussion on the structure of amorphous iron must be done in comparison with the results in crystals, liquid, and glassy thin film. This last can be particularly useful because of the existence of previous diffraction data[9] and further structural analysis done by Ichikawa.[10] He noted a subpeak in the second peak of the radial distribution function, as we have in our RDF at 30°C, that is present in many amorphous transition metals. Table II summarizes the ratios of distances as measured by Ichikawa on thin film and by ourselves in the present work on powders of amorphous iron.

Ichikawa suggested a dense random-packing model (RDP), in which the structure is built by "serially and densely piling up regular or slightly distorted tetrahedra around an assumed seed cluster." As it can be seen in Table II, the ratios of distances result in good agreement between the film and amorphous iron powder, suggesting an analogous hypothesis on its structure.

THE MAGNETIC MOMENT

The knowledge of the magnetic moment of amorphous iron is one of the open problems in the physics of glassy metals, particularly in the relationship between topological disorder and magnetic properties of materials that, in normal conditions, would be ferromagnetic.

Because of the unavailability of amorphous iron the problem has been approached by extrapolating data of atomic magnetic moment μ_{Fe} from $\mathrm{Fe}_{1-x}\mathrm{B}_x$-type metallic glasses achieved by various techniques.[11] The glass-forming range of these glasses is between 9 and 28 at. % of Boron percentage and μ_{Fe} has been determined as a function of the boron concentration. The experiments by Hasegawa and Ray[12] and by Fukamichi *et al.*[13] support a linear dependence of the atomic magnetic moment against the boron concentration (mainly at low x), with an extrapolated value for the glassy iron ($x=0$) of about $\mu_{\mathrm{Fe}}=2.24\mu_B$ in melt-spun ribbon. Webb *et al.*[14] and Bushow and van Engen[15] got an analogous linear shape in thin films. Hiroyoshi *et al.*[16] and Luborsky *et al.*[17] obtained a completely different behavior of magnetic moment versus the boron concentration in melt-spun ribbons. Rather than linear, their curves showed a parabolic shape with a maximum around 17% of boron. Almost the same features have been observed by Bayreuther *et al.*[18] on thin films, suggesting an extrapolated value μ_{Fe} between 1.2 and $1.7\mu_B$. In 1985, Cowlam and Carr[19] compared all these experiments. Fitting the second type results with a parabolic dependence they achieved $\mu_{\mathrm{Fe}}=1.7\mu_B$ as extrapolated value for the amorphous iron. Unfortunately Lauriat did not calculate the magnetic moment from his neutron-diffraction experiment on ex-carbonyl amorphous iron prepared by electric discharge[20] leaving the controversy unresolved until now. The extrapolation to the amorphous iron of the $\mu_{\mathrm{Fe-Bo}}$ values relates fundamentally to the effect of topological disorder on ferromagnetic coupling. If the value of μ_{Fe} for amorphous iron were close to that of crystalline α-Fe ($2.24\mu_B$), then the coupling would be unaffected; on the other hand, if μ_{Fe} were close to that of liquid iron ($1.2\mu_B$), then the exchange interaction would be lost.

Recent magnetometer measurements of sonochemically synthesized amorphous iron[21] give an effective μ_{Fe} of $1.6\mu_B$ at 20 kOe and a corrected value of $1.7\mu_B$ for the true saturation moment. This is in reasonable agreement with the result of our neutron-diffraction studies which gives $1.4\mu_B$. The magnetic moment obtained from the neutron-diffraction data is subject to some error. In accounting for the form factor from hydrogen impurities, systematic uncertainties may have been introduced into the magnetic moment evaluation. The form factor for hydrogen has a very high incoherent cross section which decreases smoothly with increasing inelastic momentum transfer, whereas the form factor for iron decreases much more quickly due to the large spatial extension of its d orbitals. Another source of error in the magnetic moment determination is the presence of small-angle neutron scattering in the range 0.3–1 A^{-1} (Figs. 1 and 2), which reflects some medium-range order in the sample (10–100 A, which is also the size of the clusters of iron that agglomerate to form this amorphous powder[2]). It must be emphasized, however, that both the small-angle scattered intensity and the incoherent inelastic contribution of hydrogen can be easily separated as their variations, as a function of the momentum transfer, are quite different from that of the magnetic form factor, as shown in Fig. 1.

TABLE II. Ratio of distances of the second, third, and fourth peaks to that of the first one in $g(r)$ in noncrystalline iron.

	Liquid[a]	Film[b]	Bulk[c]
r_2'/r_1	1.83	1.67	1.69
r_2''/r_1		1.96	1.94
r_3/r_1	2.67	2.51	
r_4/r_1	3.49	3.38	

[a] Reference 3.
[b] Reference 10.
[c] This work.

Concerning the hydrogen contribution, (b), its decrease, from about 7000 down to about 2000 counts, in the same unit of the plot (a), expands over all the experimental momentum transfer range 0.5–16 A^{-1}. A precise fitting of the hydrogen content, first estimated to 2% in weight, has been done in order to obtain a constant mean value of the structure factor of the Fig. 2, between 6 and 16 A^{-1}, where the hydrogen scattering is the only decreasing contribution. Such a procedure allows us to perform this correction within a 1% error bar in the intensity. The scaling factor for the subtraction of the magnetic contribution (curve c, magnified by ten in Fig. 1) has been then estimated to be about 500 counts for the zero limit of the momentum transfer, by assuming that the structure factor of iron (Fig. 2) must be close to zero at the flat minimum of the curve (a), between 1.5 and 2 A^{-1}. The deviation due to the small-angle intensity term is quite negligible in this range, while the magnetic form factor is still decreasing very slowly. The uncertainty on the magnetic moment is therefore between 5 and 10%, which clearly distinguishes the amorphous from the crystalline state of iron, but leaves less clear the difference with the liquid state. Polarized neutron scattering may resolve this issue and further experiments are planned.

The results of our work, from which we achieve $\mu_{\mathrm{Fe}}=1.4\mu_B$ from direct experiments on amorphous iron, agree with the previsions of the parabolic dependence of magnetic moment versus Boron concentration in the binary iron-boron metallic glasses. Moreover, it falls close the value measured for the liquid and it is reasonably consistent with the close similarity between the features of the amorphous and liquid phases.

CONCLUSIONS

Neutron-diffraction data have been obtained from samples of amorphous iron powder prepared sonochemically. The structural information from the radial distribution function is consistent with a random-packing model and is similar to that of thin amorphous films. The magnetic moment μ of amorphous iron, determined by the analysis of neutron-diffraction data, is significantly below that of crystalline iron and in agreement with some extrapolation made from iron-boron amorphous alloys.

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