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How to characterize disorder

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ABSTRACT

Researchers working on nuclear materials encounter disorder in the atomic structure all the time, usually caused by irradiation. The nature of disorder varies widely, from lattice defects to amorphous phase formation. Generally it is not easy to characterize the state of disorder with the accuracy necessary to elucidate the properties caused by structural disorder. However, owing to advances in the tools of characterization and rapid rise in computer power, significant progress has been made in characterizing structural disorder. We discuss how to describe and determine the structure and dynamics of disordered materials using scattering measurements and modeling. Lattice defects caused by irradiation usually has negative effects on properties, but glasses and highly disordered materials can be irradiation resistant, and could be useful as nuclear materials. Characterizing and controlling disorder is becoming an important endeavor in the field of nuclear materials.

1. Introduction

We know very well how to characterize the structure of crystals, for instance by diffraction experiments. However, a large part of materials we use are disordered, and even non-crystalline. When we face disordered materials we are much less optimistic in our capacity to characterize the structure, because the conventional methods of structural characterization do not work well. In fact just to describe the structure is difficult, because the terms such as "amorphous" or "disorder" provide only negative description. However, owing to recent advances in experimental tools, such as the advent of synchrotron-based radiation sources, and rapid growth in computing power, it is now possible to characterize the structure of disordered materials with considerable accuracy. In this article we discuss how to determine the structure and dynamics of highly disordered materials by scattering experiments, and how to describe disorder in the structure using newly introduced concepts, such as the atomic-level stresses.

In nuclear materials disorder is usually caused by irradiation. When a material is heavily irradiated at low temperatures it often becomes amorphous. We call it amorphous, rather than glass, because there is a subtle but important difference between a glass and an amorphous solid. A glass has a structure which was once in equilibrium at the temperature when the glass was frozen from a liquid. This temperature is called the fictive temperature, T_f, and characterizes the glassy state [1]. When a liquid is cooled very rapidly the structure becomes frozen, or arrested, at a relatively high temperature. So such a glass has a higher value of T_f, while a glass slowly cooled has a lower T_f. When a glass with a high T_f is annealed below the glass transition temperature, T_g, the structure relaxes and T_f is lowered. This process is called structure relaxation [2]. On the other hand if a glass-like solid does not have a well-defined fictive temperature, we call this solid amorphous. A solid classified as amorphous can be either highly defective nano-crystals or a glass with strongly heterogeneous local fictive temperatures.

Disorder caused by irradiation damage is usually harmful to the material. But it appears that materials with high degrees of structural and chemical disorder, such as glasses, may be more irradiation resistant, and thus certain types of disorder may be beneficial to the performance of nuclear material. In either case characterizing disorder with high accuracy will greatly facilitate research on nuclear materials.

We first describe the methods of determining the structure by diffraction and dynamics by inelastic scattering. However, the information obtained by scattering is about the two-body correlation in space and time, whereas the properties often depend on more collective atomic correlations. In order to elucidate the properties in terms of the structure computer modeling is becoming more popular. It is now relatively easy to perform simulation, such as molecular dynamics (MD) simulation, using widely available

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software packages. Unfortunately usually the analysis is done still at a relatively rudimental level. In order to describe and understand the models in a more effective and physically meaningful manner we introduce the concept of the local atomic structure and its description in terms of the atomic-level stresses which more directly connects the local structure to various properties.

2. Structural characterization by diffraction

The structure of a crystal is defined by lattice symmetry, the lattice constants, and a few atomic position parameters, which can be determined by diffraction experiments through the position and intensity of the Bragg peaks [3]. Any non-periodic components, such as structural disorder or thermal atomic vibration, produce diffuse scattering. Certain consequences of irradiation damage, such as local strains, can be evaluated relatively easily from careful measurement of the position and width of the Bragg peaks [3]. However, other damages at the atomic-level have to be evaluated through the study of the diffuse scattering, which is a more difficult undertaking [3]. In fact in the crystallographic structural analysis diffuse scattering is usually discarded as "background".

Liquids and glasses yield no Bragg peaks upon diffraction, and show only diffuse scattering. Therefore the diffraction measurement for liquids and glasses is quite demanding and more involved. Firstly the real background due to scattering not coming from the sample has to be accurately determined and subtracted from the data. Secondly in order to cover a wide range in the momentum transfer, $Q = |\mathbf{Q}|$, $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$, where $\mathbf{k}_i$ and $\mathbf{k}_f$ are the momenta of the probing particle before and after the scattering, a probe with high energy has to be used as discussed below. Thirdly, rigorous data reduction, including absorption correction and correction for incoherent scattering, has to be performed to obtain reliable results [4].

Fortunately the software for data reduction is widely available and the procedure for the measurement is well-established at the synchrotron X-ray facilities or at the pulse neutron facilities [4], so a user can obtain good results by applying for the beamtime to these facilities. Through such experiments one obtains the structure function, $S(Q)$, which is normalized to unity at large Q. The Fourier-transform of $S(Q)$ is the atomic pair-density function (PDF),

$$\rho_0 g(r) = \rho_0 + \frac{1}{2\pi^2 r}\int_0^\infty [S(Q) - 1]\sin(Qr)QdQ \qquad (1)$$

where ρ_0 is atomic number density [3,4]. Examples of $S(Q)$ and PDF are shown in Fig. 1 [5]. In Eq. (1) the integration has to be carried out to $Q \to \infty$, but in reality $Q < Q_{max} = 2k = 4\pi/\lambda$, because $Q = 2k \sin\theta = 4\pi \sin\theta/\lambda$, where $k = |\mathbf{k}_i| = |\mathbf{k}_f|$ for elastic scattering, λ is the wavelength of the probe, and θ is the diffraction angle. Therefore if Q_{max} is too small, high-Q portion of the data is left out in evaluating the PDF. This results in so-called termination error, and makes the PDF inaccurate [3,4]. Normally we need to choose the value of Q_{max} to be 30–35 Å^{-1}, in order to suppress termination error. For X-rays this limit corresponds to the X-ray energy of 30–35 keV (wavelength of 0.35–0.41 Å). Therefore the laboratory X-ray sources are totally inadequate; the energy of Cu K_α radiation is only 8 keV, and that of Mo K_α radiation is 17.4 keV. The use of synchrotron radiation is absolute necessity. By using X-rays with the energy over 100 keV and a two-dimensional detector the PDF can be determined with accuracy in a short time [4,6]. For neutron scattering the value of Q_{max} for thermal neutrons is about 12 Å^{-1}, so we have to use a synchrotron-based pulsed neutron source which provides ample intensity of epithermal neutrons with higher energies. The advent of the synchrotron-based radiation sources was crucial in transforming the PDF method from a semi-quantitative tool to a highly accurate experimental method. The data can be readily processed

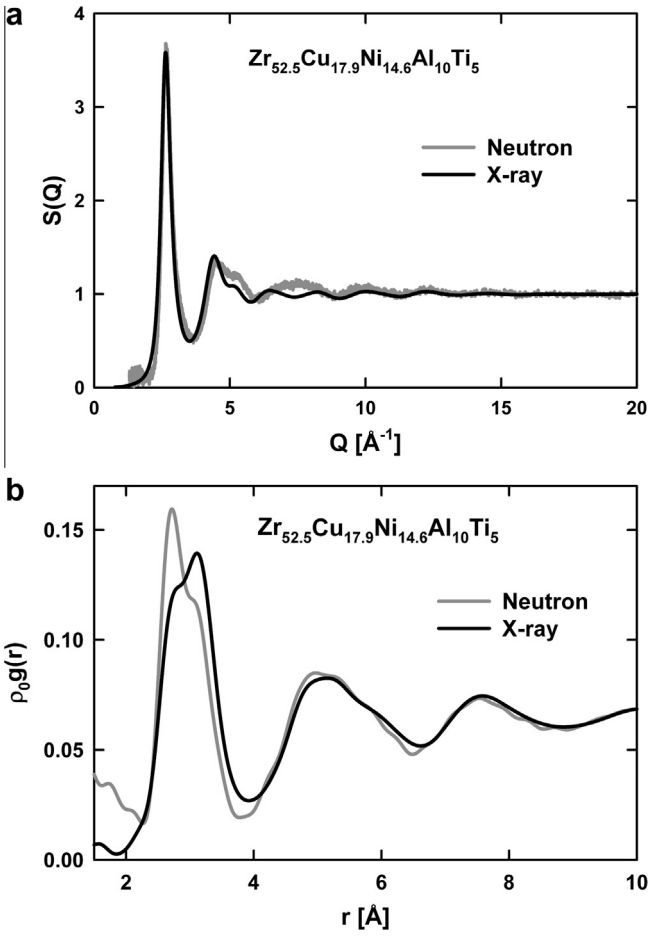

Fig. 1. (a) Structure function, $S(Q)$, and (b) PDF, $g(r)$, of amorphous Zr–Cu–Ni–Al–Ti alloy by X-ray and neutron diffraction [5].

using software such as PDFgetX [7] and PDFgetN [8], which can be downloaded from the source and are available at the facilities capable of obtaining the PDF.

Prior to this transformation of the PDF technique owing to synchrotron-based radiation sources, the method of extended X-ray absorption fine structure (EXAFS) was widely used as a local structural probe [9,10]. In the EXAFS method structural information is obtained through the diffraction of internally emitted photo-electrons excited by X-ray which produces oscillations in the energy dependence of the X-ray absorption coefficient. However, to interpret the EXAFS pattern, including the phase-shifts, we have to calculate the dynamics of photo-electrons by quantum–mechanical computation. Usually the electron–electron interaction is approximated using the density functional theory (DFT), but inelastic scattering and multiple scattering cannot be accurately estimated. Thus scattering from randomly displaced atoms is strongly attenuated. Consequently the coordination number (the number of the nearest neighbor atoms) in disordered system is underestimated in the EXAFS, and the information on the structure beyond the first nearest neighbors is strongly suppressed and not reliable. In contrast scattering of X-ray and neutron is weak enough to be accurately described by the Born approximation [3,4]. Thus the PDF can be determined up 200 Å or more depending on the Q resolution, allowing the determination of the short-range as well as medium-range structure (Fig. 2) [11]. Because the EXAFS measurement requires synchrotron radiation anyway, it is generally more advisable to use the PDF method than the EXAFS.

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