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A new approach to the analysis of short-range order in alloys using total scattering

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ABSTRACT

In spite of its influence on a number of physical properties, short-range order in crystalline alloys has received little recent attention, largely due to the complexity of the experimental methods involved. In this work, a novel approach that could be used for the analysis of ordering transitions and short-range order in crystalline alloys using total scattering and reverse Monte Carlo (RMC) refinements is presented. Calculated pair distribution functions representative of different types of short-range order are used to illustrate the level of information contained within these experimentally accessible functions and the insight into ordering which may be obtained using this new method. Key considerations in the acquisition of data of sufficient quality for successful analysis are also discussed. It is shown that the atomistic models obtained from RMC refinements may be analysed to identify directly the Clapp configurations that are present. It is further shown how these configurations can be enhanced compared with a random structure, and how their degradation pathways and the distribution of Warren-Cowley parameters, can then be used to obtain a detailed, quantitative structural description of the short-range order occurring in crystalline alloys.

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1. Introduction

1.1. Background and context

The effects of short-range order on physical properties have long been noted in a variety of alloys systems. Thermodynamic discontinuities [1] in nickel chromium alloys, along with observed anomalies in electrical resistivity [2,3] have led to the description of a Komplex (K-) state containing a different order to that expected for a random solid solution. Similarly, changes in magnetic properties, such as an increase in the observed spin wave stiffness of Ni₃Mn [4] provide evidence for short-range ordering. In addition, short-range order has been shown to influence dislocation motion [5,6] and has been observed in a number of systems used for structural applications, including nickel superalloys [7]. In spite of this influence on numerous materials properties, the study of

short-range ordering in alloy systems has been largely abandoned over the last 20 years or so. This is due mainly to the lack of experimental evidence available from conventional diffraction experiments and the difficulties associated with the calculation of the ordering parameters from the diffuse scattering observed in single crystal experiments.

In this paper, a methodology is presented by which total scattering techniques may be used for the direct observation of short-range order in crystalline alloy systems. Simulated supercells based on the face-centred cubic (fcc) structure, containing various types and degrees of short-range order, are used to explore the information content of pair distribution functions, which are experimentally accessible through Fourier transformation of total scattering data. The atomistic models that may be obtained from the analysis of such experimental data can be used to provide quantitative information about the types of short-range order present, and approaches by which this can be achieved are discussed.

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1.2. Total scattering

Standard diffraction experiments, particularly of powder samples, derive structural information from the characteristic Bragg pattern [9]. Inherently, this analysis is based on the long-range average structure of the material and information on the short-range ordering that may be present in the system is lost in the averaging. The study of amorphous materials, which by definition lack the long-range order that leads to Bragg peaks, motivated the development of the total scattering technique, in which the Bragg and diffuse scattering from a sample are measured and analysed simultaneously. The technique has, more recently, been applied with great success to study many crystalline and disordered-crystalline systems [10] providing insight into the local information through analysis of deviations from the average structure. The basic scattering function for neutrons [11] is given as:

$$S(Q) = \frac{1}{N} \sum_{ij} b_i b_j \exp(iQ \cdot [r_i - r_j]) \quad (1)$$

where i and j are atomic labels, r the instantaneous position of an atom, b the atomic scattering length, N the number of atoms and Q the magnitude of the scattering vector \mathbf{Q} i.e. the momentum transfer of the incident radiation. An equivalent expression for X-rays can be derived, replacing the neutron scattering length b with the Q -dependent atomic form factor. For a periodic crystal this equation simplifies to the Bragg condition. In the case of an amorphous glass this may be written as:

$$S(Q) = \frac{1}{N} \sum_{ij} \bar{b}_i \bar{b}_j \frac{\sin(Q|r_i - r_j|)}{Q|r_i - r_j|} \quad (2)$$

Separating the self-scattering components:

$$S(Q) = \frac{1}{N} \sum_i \bar{b}_i^2 + \frac{1}{N} \sum_{i \neq j} \bar{b}_i \bar{b}_j \frac{\sin(Q|r_i - r_j|)}{Q|r_i - r_j|} \quad (3)$$

which can be recast in the form:

$$S(Q) = F(Q) + \sum_i c_i \bar{b}_i^2 \quad (4)$$

where c_i is the concentration of species i and the total scattering function, $F(Q)$, is given by:

$$F(Q) = \rho_0 \int_0^\infty 4\pi r^2 G(r) \frac{\sin Qr}{Qr} dr \quad (5)$$

in which ρ_0 is the average density of the structure and:

$$G(r) = \sum_{ij} c_i c_j \bar{b}_i \bar{b}_j (g_{ij}(r) - 1) \quad (6)$$

where the $g_{ij}(r)$ terms are the partial pair distribution functions. The function $G(r)$ is often known as the pair distribution function (PDF). The inverse Fourier transform of Eq. (5), used for the calculation of a PDF, is given by:

$$G(r) = \frac{1}{(2\pi)^3 \rho_0} \int_0^\infty 4\pi Q^2 F(Q) \frac{\sin Qr}{Qr} dQ \quad (7)$$

Alternative normalisations of the PDF are sometimes used for

convenience, to emphasise specific features of the function related to the properties and length-scales of interest. A full description of the other formulations of the PDF has been provided by Keen [12]. Unless otherwise stated, the terms $G(r)$ and PDF are used interchangeably here.

The partial PDFs are described mathematically as:

$$g_{ij}(r) = \frac{n_{ij}(r)}{4\pi r^2 \rho_i} \quad (8)$$

where $n_{ij}(r)$ is the number of atoms lying within r and $r+dr$, and $\rho_i = c_i \rho_0$, where ρ_0 is the density of the substance and c_i the concentration of species i . Critically, this description is as applicable to periodic crystals as to amorphous materials.

The PDF, by definition, is a weighted histogram of the distribution of distances between atoms in the structure. A peak in the PDF will indicate the average distance of one atom relative to another; its width being dependent on the distribution of the inter-atomic distances (thermal vibration or static displacements) and its area being governed by the number and scattering length of the correlating atoms.

As is apparent from Eqs. (5) and (7), the PDF and $F(Q)$ are effectively different representations of the same information (both contain the local structural information lacking in the Bragg peaks alone). Here the PDF is considered, as it is intuitively understandable as a visual representation of the local structure, but an equivalent analysis could be achieved through consideration of the $F(Q)$.

Whilst other local structural probes exist, such as EXAFS and NMR spectroscopy, they are of limited use for the analysis of short-range order in alloys systems, owing to the fact that ordering information for a large number of coordination shells can be extracted from a PDF, whilst EXAFS and NMR provide information for only the first couple of shells.

It is straightforward to achieve a qualitative understanding of the information provided by a PDF, however producing structural models is more involved. There are two popular approaches. The first, often known as ‘small-box’ modelling, utilises tools such as PDFgui [13], and is analogous to Rietveld refinement though the models are constrained by the PDF instead of the Bragg diffraction pattern. This technique is not well suited to the characterisation of short-range order in alloys since it produces a crystallographic description of a structure (i.e. one that comprises cell parameters, thermal parameters, fractional site occupancies), albeit one that is biased towards the local, rather than the average, structure. The second, a ‘large-box’ modelling technique using the reverse Monte Carlo [14] algorithm, is arguably better suited for the analysis of ordering in alloy systems as it is unconstrained by symmetry and produces large (>10,000 atom) models that provide the ability to probe the ordering across appropriate length scales.

1.3. The reverse Monte Carlo technique

Traditionally, analysis of total scattering data involves visual inspection of the scattering functions and the use of peak fitting to obtain information about the arrangement of the first one or two coordination shells. It is also common to use molecular dynamics or hard-sphere Monte-Carlo to calculate structural models, from which theoretical total scattering functions can be calculated and compared with the observed data. Analysis of the system is then possible only if the two are found to be in good agreement. The tuning of initial potentials to create a structural model that more accurately reflects the data is theoretically possible, but the direct effect of the potentials on the diffuse scattering is often difficult to quantify and the process of fine-tuning is laborious. To this end, the

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