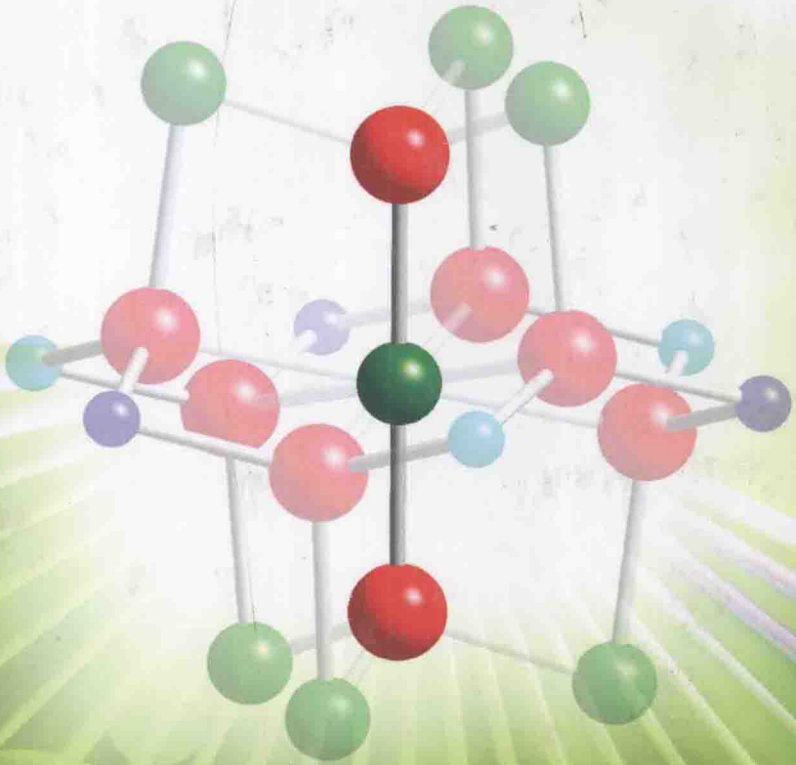
Inorganic Materials Series



Local Structural Characterisation

Editors
Duncan W. Bruce | Dermot O'Hare | Richard I. Walton

WILEY

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Edited by

Duncan W. Bruce
University of York, UK

Dermot O'Hare
University of Oxford, UK

Richard I. Walton
University of Warwick, UK

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Local Structural Characterisation

Inorganic Materials Series

Series Editors:

Professor Duncan W. Bruce
Department of Chemistry, University of York, UK

Professor Dermot O'Hare
Chemistry Research Laboratory, University of Oxford, UK

Professor Richard I. Walton
Department of Chemistry, University of Warwick, UK

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Inorganic Materials Series Preface

Back in 1992, two of us (DWB and DO'H) edited the first edition of *Inorganic Materials* in response to the growing emphasis on and interest in materials chemistry. The second edition, which contained updated chapters, appeared in 1996 and was reprinted in paperback. The aim had always been to provide chapters that while not necessarily comprehensive, nonetheless gave a first-rate and well-referenced introduction to the subject for the first-time reader. As such, the target audience was from first-year postgraduate students upwards. In these two editions, we believe our authors achieved this admirably.

In the intervening years, materials chemistry has grown hugely and it now finds itself central to many of the major challenges that face global society. We felt, therefore, that there was a need for more extensive coverage of the area, and so Richard Walton joined the team and, with Wiley, we set about working on a new and larger project.

The *Inorganic Materials Series* is the result, and our aim is to provide chapters with a similar pedagogical flavour to the first and second editions, but now with much wider subject coverage. As such, the work will be contained in several volumes. Many of the early volumes concentrate on materials derived from continuous inorganic solids. Later volumes, however, will emphasise methods of characterisation as well as molecular and soft-matter systems, as we aim for a much more comprehensive coverage of the area than was possible with *Inorganic Materials*.

We are delighted with the calibre of authors who have agreed to write for us and we thank them all for their efforts and cooperation. We believe they have done a splendid job and that their work will make these volumes a valuable reference and teaching resource.

DWB, York
DO'H, Oxford
RIW, Warwick
June 2013

Preface

Inorganic materials show a diverse range of important properties that are desirable for many contemporary, real-world applications. Good examples include recyclable battery cathode materials for energy storage and transport, porous solids for capture and storage of gases and molecular complexes that can be used in electronic devices. Some of these families of materials, and many others, were reviewed in earlier volumes of the *Inorganic Materials Series*. When considering the property-driven research in this large field, it is immediately apparent that methods for structural characterisation must be applied routinely in order to understand the function of materials and thus optimise their behaviour for real applications. Thus, 'structure–property relationships' are an important part of research in this area. To determine structure effectively, advances in methodology are important: the aim is often rapidly to examine increasingly complex materials in order to gain knowledge of structure over length scales ranging from local atomic order, through crystalline, long-range order to the meso- and macroscopic.

No single technique can examine all levels of structural order simultaneously, and the chapters presented in this volume deal with recent advances in important techniques that allow investigation of the structures of inorganic materials on the local atomic scale. Such short-range order is concerned with local atomic structure – the arrangement of atoms in space about a central probe atom – and deals with bond distances, coordination geometry and the local connectivity of the simple building units of a complex structure. It is often by studying this shortest of structural length scales that information about the underlying behaviour of a material can be deduced. The techniques employed are usually spectroscopic in origin, involving observation of the effect of interaction of an appropriate energy source with the substance being studied, which supplies information about the probe atoms' environments. It should be noted that these methods have no requirement for any long-range order (translational symmetry) and so can be applied equally to poorly crystalline, glassy, amorphous or heterogeneous systems, as well as to crystalline substances. Another consideration of any

characterisation study is the need to examine materials under real operating conditions in order to understand properly their function; here, spectroscopic, short-range probes of structure often provide the key.

Some of the techniques discussed in this volume may be familiar to the reader (such as NMR, EPR and XPS), but with recent advances broadening their applicability and making them available more routinely, it is timely to provide up-to-date overviews of their uses. Also included are techniques that require large-scale facilities, such as X-ray absorption spectroscopy (XAS) and inelastic neutron scattering (INS). With the investment by many countries in major facilities for X-ray and neutron science, such methods provide an important, and increasingly accessible, addition to the toolbox of techniques available to the scientist studying the structures of materials. We approached an international set of expert authors to write the chapters in this volume with the brief to provide an introduction to the principles of their technique, to describe recent developments in the field and then to select examples from the literature to illustrate the method under discussion. We believe they have done an excellent job in all respects and hope that the chapters provide a valuable set of references for those who wish to learn the principles of some important methods in the study of inorganic materials.

DWB, York
DO'H, Oxford
RIW, Warwick
June 2013

List of Contributors

Sharon E. Ashbrook School of Chemistry, University of St Andrews, St Andrews, UK

Daniel M. Dawson School of Chemistry, University of St Andrews, St Andrews, UK

Pieter Glatzel European Synchrotron Radiation Facility, Grenoble, France

John M. Griffin School of Chemistry, University of St Andrews, St Andrews, UK

Amélie Juhin Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), CNRS, Pierre-and-Marie-Curie University, Paris, France

Adam F. Lee Department of Chemistry, University of Warwick, Coventry, UK and School of Chemistry, Monash University, Melbourne, Australia

Tomasz Mazur Faculty of Chemistry, Jagiellonian University, Krakow, Poland

Philip C. H. Mitchell Department of Chemistry, University of Reading, Reading, UK

Piotr Pietrzyk Faculty of Chemistry, Jagiellonian University, Krakow, Poland

A. J. Ramirez-Cuesta Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA and ISIS Facility, Rutherford Appleton Laboratory, STFC, Oxford, UK

Zbigniew Sojka Faculty of Chemistry, Jagiellonian University, Krakow, Poland

Karen Wilson European Bioenergy Research Institute, School of Engineering and Applied Science, Aston University, Aston Triangle, Birmingham, UK

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1

Solid-State Nuclear Magnetic Resonance Spectroscopy

Sharon E. Ashbrook, Daniel M. Dawson and John M. Griffin
School of Chemistry, University of St Andrews, St Andrews, UK

1.1 OVERVIEW

Although solution-state nuclear magnetic resonance (NMR) spectroscopy is one of the most widely applied analytical tools in chemistry, providing a sensitive probe of local structure for systems ranging from small molecules to large proteins, it is only relatively recently that solid-state NMR has been able to provide information of a similar quality. The anisotropic (*i.e.* orientation-dependent) interactions affecting NMR spectra, which ultimately provide valuable information about structure, symmetry and bonding, are averaged in solution by the rapid tumbling motion of the molecules, resulting in simplified spectra from which information can be more easily obtained. In contrast, NMR spectra of solids remain broadened by these interactions, hindering the extraction of structural information. This broadening poses significant challenges both in the acquisition of high-resolution NMR spectra for solids and in their interpretation and analysis. However, in recent years considerable developments in hardware (*e.g.* increasing magnetic field strengths) and in software (*e.g.* improvements in computational simulations and analysis packages) have enabled solid-state NMR to

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develop to the point where it can play a central role in the atomic-level understanding of materials as diverse as zeolites, glasses, polymers, energy materials, pharmaceuticals and proteins.

The ability of NMR spectroscopy to probe the local atomic-scale environment, without any requirement for long- or short-range order, enables it to be used alongside more conventional diffraction-based approaches for the study of solids. The sensitivity of NMR to small changes in the local environment (and its element specificity) makes it an ideal approach for studying disorder in solids, be it positional or compositional, resulting in numerous applications to the study of glasses, gels and ceramics. NMR is also an excellent probe of dynamics, sensitive to motion over a wide range of timescales, depending upon the exact experiment used. However, despite this wealth of information, the interpretation of solid-state NMR spectra and the extraction of relevant structural detail remain a challenge. In recent years there has been growing interest in the use of computational methods alongside experimental measurement. While there has been a long tradition in quantum chemistry of the calculation of NMR parameters from first principles, much of the development has been focused on molecules (either in vacuum or in solution), rather than on the extended and periodic structures found in the solid state. Recent methods utilising periodic approaches to recreate the three-dimensional (3D) structure from a high-symmetry small-volume unit have found great favour with experimentalists, and are currently being applied to a wide range of different systems, helping to interpret complex NMR spectra, improve structural models and provide new insight into disorder and/or dynamics.

At first sight, the vast array of NMR experiments in the literature can seem daunting to the non-specialist; however they can be easily categorised by their overall aim. Many experiments are designed to improve resolution and/or sensitivity, typically through more efficient removal of anisotropic broadening – an enduring theme in solid-state NMR spectroscopy. Experiments have also been developed to measure the magnitudes of individual interactions, providing information on local geometry or symmetry, for example. Further experiments are concerned with the transfer of magnetisation between different nuclei, probing their through-bond or through-space connectivity. In many cases, the exact experimental detail is not of vital importance; it is more useful to understand the type of information available from a particular NMR spectrum and how it can be extracted. In this chapter, we will give an overview of solid-state NMR spectroscopy, focusing in particular upon its application to inorganic solids. We briefly introduce the theoretical

basis of the technique and the interactions that affect NMR spectra (and ultimately provide information). We describe the basic and routinely used experimental techniques, and the information that is available from solid-state NMR spectra. We then review the nuclear species most commonly studied and provide a range of examples of the application of NMR spectroscopy for a wide variety of materials, demonstrating the versatility and promise of the technique.

1.2 THEORETICAL BACKGROUND

A brief description of the theoretical basis of NMR spectroscopy is provided here. For a detailed description, see references [1, 2].

1.2.1 Fundamentals of NMR

Atomic nuclei possess an intrinsic spin angular momentum, **I**, described by the nuclear spin quantum number, I, which may take any positive integer or half-integer value. The projection of **I** onto a specified axis, arbitrarily the z-axis, is quantised in units of $m_I\hbar$, where m_I is the magnetic quantum number, and takes values between $+I$ and $-I$ in integer steps, leading to $2I + 1$ degenerate spin states. Nuclei with $I > 0$ possess a magnetic dipole moment, $\boldsymbol{\mu}$, related to **I** by the gyromagnetic ratio, γ, which is characteristic of a given nuclide. Therefore, $\boldsymbol{\mu}$ is quantised along the (arbitrary) z-axis in units of $\gamma m_I\hbar$. When an external magnetic field, B_0, is present, the axis of quantisation is defined and the degeneracy of the nuclear spin states is removed. The field-induced splitting of nuclear energy levels is known as the Zeeman interaction, with the Zeeman energy of a state, m_I, given by:

$$E_{m_I} = -\gamma m_I \hbar B_0 \tag{1.1}$$

as shown in Figure 1.1. Only transitions with $\Delta m_I = \pm 1$ are observable in NMR spectroscopy and, therefore, all observable transitions are degenerate, with a frequency:

$$\omega_0 = -\gamma B_0 \tag{1.2}$$

where ω_0 is the Larmor frequency, with units of rad s^{-1} (or $\upsilon_0 = \omega_0/2\pi$, in Hz). In a macroscopic sample at thermal equilibrium, nuclei occupy energy levels according to the Boltzmann distribution. The equilibrium

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