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Pressure induced charge order collapse in Fe_2OBO_3

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Abstract. The effect of pressure on the charge order in the mixed-valence Fe_2OBO_3 has been investigated using ^{57}Fe Mössbauer spectroscopy at pressures up to 30 GPa in diamond anvil cell experiments. Above 16 GPa only signatures of electron hopping, $Fe^{2+} \Leftrightarrow Fe^{3+}$, where "$\Leftrightarrow$" represents the hopping between the different ionic charge states are discerned. Analysis shows that the hopping frequency is of the order of MHz (~100 nanosecond time scale), that is, in a time window to which the Mössbauer spectroscopy technique is particularly sensitive. The fluctuation signatures persist upon further pressurization to ≈ 30 GPa at 300 K. The frequency lies in the range of 2–4 MHz upon increasing pressure. The charge order collapse initiated by external pressure was found to be reversible upon decompression to ambient conditions.

1. Introduction

Site-centered charge ordering (CO) refers to the spatial localisation of charge carriers on atomic sites with a certain periodicity, resulting in valence electrons localising and giving rise to mixed-valence superstructures within crystal lattices. This may occur in strongly correlated systems as a mechanism to minimize the repulsive energy between valence electrons at the expense of their kinetic energy [1]. The condensation of charge into distinct states or valences (also called a Wigner crystal [2]) invokes the concept of ionic charge order, in which valence states take on integer values. Until recently the concept of ionic charge order in metal oxides has been under doubt because valence separation into distinct charge states does not take on integer values, even in the case of well-studied Fe_3O_4 (magnetite), which is the first CO compound to be discovered. Recent work has then found evidence of a superstructure in iron oxoborate, Fe_2OBO_3, with a valence separation, $Fe^{(2+\delta)+}$ — $Fe^{(3-\delta)+}$, near to integral values, where $\delta \leq 0.2$ [3]. This makes Fe_2OBO_3 the archetypal ionic CO compound.

Fe_2OBO_3 belongs to a family of homometallic oxoborates with a warwickite crystal structure. The structure is characterised by one-dimensional ribbons of edge sharing FeO_6 octahedra, stacked along the *a*-axis direction. The ribbons are connected by corner sharing octahedra and trigonal-planar BO_3

groups, defining non-equivalent crystallographic sites (referred to as Fe (1) and Fe (2)) in the FeO_6 octahedra (see figure 1 (a)).

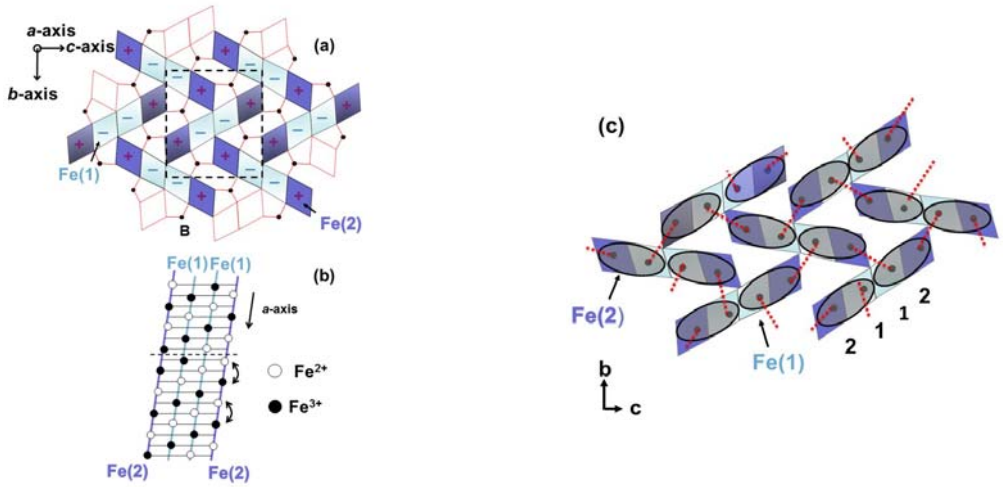


Figure 1 (Colour online): (a) Crystal structure of Fe_2OBO_3 adapted from Attfield et. al. [1]. In the *b*-*c* plane this can be represented as Fe (2)-Fe (1)-Fe (1)-Fe (2) edge-sharing octahedra within a ribbon, where Fe (1) and Fe (2) indicate structurally distinct iron octahedral sites that make up such four-chain ribbons. The "+" and "-" signs refer to antiparallel magnetic moments in the magnetically ordered phase. (b) Ribbon in the CO phase comprised of chains of four edge-sharing FeO_6 octahedra that extend infinitely along the crystallographic *a*-axis. (c) Dimerisation in the orthorhombic structure of Fe_2OBO_3, depicted by the ellipses. The red dotted lines show the possible paths in which electron hopping can occur.

Fe_2OBO_3 undergoes an orthorhombic-monoclinic structural phase transition at T_{CO} = 317 K, with a concomitant charge delocalization. These structural and electronic changes are attributed to site-centered CO, manifested as a Fe^{2+} and Fe^{3+} mixed-valence state [1, 4]. In this scenario the CO involves the localisation of the extra down-spin electron in a t_{2g} orbital of the Fe^{2+} cation (t_{2g}^4 e_g^2). The CO in this case is stabilised in the monoclinic structure.

^{57}Fe Mössbauer spectroscopy has shown that below 270 K (monoclinic unit cell, $P2_1/c$), the Fe^{2+} and Fe^{3+} are equivalently distributed in crystallographically distinct sites. Above 400 K (orthorhombic unit cell, *Pmcn*), the semi-valent state $Fe^{2.5+}$ representing dynamic charge carriers or electronic hopping is present exclusively. In between 270 K – 400 K, there is co-existence of Fe^{2+}, Fe^{3+} and $Fe^{2.5+}$ [5]. In the temperature range 270 K − 400 K, there exists the so-called intermediate phase [6], which is characterized by an incommensurate CO super structure due to the geometrical frustration occurring in the system. The intermediate phase was shown to undergo resistive switching where application of an electric field induces a change in the resistance. This ability to tune the resistance is thought to be related to mobility of charge carriers in this temperature region [7].

An analogy to this temperature-dependent study is our recent x-ray powder diffraction pressure-dependent study of the structural properties of Fe_2OBO_3 [8]. Analysis of the in-situ XRD data indicates that, starting at ≈ 6 GPa, the ambient pressure $P2_1/c$ monoclinic structure gradually transforms into the high pressure *Pmcn* orthorhombic phase, and at 22 GPa the phase transition is

complete. Moreover, the unit cell was found to be more compressible along the *a*-axis (10% over the pressure range up to 30 GPa) compared to the other directions in the unit cell which have a 3% compressibility over the same pressure range. The change in volume for the $P2_1/c \rightarrow Pmcn$ phase transition is limited to 1% and this therefore suggests the bulk moduli of the two structures are commensurate.

Our previous ^{57}Fe Mössbauer spectroscopy studies involving the application of external pressure (P) on an Fe_2OBO_3 have led to a an extension of the magneto-electronic temperature-pressure phase diagram (not shown in this publication; the detailed phase diagram can be found in ref. [9]). On the basis of the analysis of the Mössbauer data it was revealed that (i) the site-centered CO collapse is initiated at ≈ 11 GPa at 300 K; at $P \geq 16$ GPa, *only* electron hopping processes on the time-scale of the Mössbauer effect (10^{-7} s) were discerned (this was typified by asymmetric relative intensities and hyperfine parameters values intermediate to that of Fe^{2+} and Fe^{3+}, that is, the intermediate valence state $Fe^{2.5+}$); (ii) suppression of CO and magnetic ordering below 115 K at $P \geq 16$ GPa. Thus in the CO phase the magnetic transition temperature T_M does not increase or rise beyond the ambient pressure value of $T_M = 155$ K.

This study is a continuation of our previous work [9] with a particular focus on the pressure range 16–30 GPa so as to make a quantitative assessment of the electron dynamics. We present a detailed analysis of the high pressure electronic state of Fe in Fe_2OBO_3 using ^{57}Fe Mössbauer spectroscopy as a probing technique of the Fe ion valence. We show that electron hopping frequency increases doubles, from 2 to 4 MHz in the pressure range 16–30 GPa. This , less than one order of magnitude, increase in the hopping frequency is also reflected in the Mössbauer line shape that shows no major discernable change over an extensive pressure range spanning 14 GPa. The high pressure orthorhombic (space group, *Pmcn*) phase is found to be reversible to the ambient monoclinic (space group, $P2_1/c$) phase, where the CO is stabilised.

2. Experimental details

A sample of natural ^{57}Fe abundance (2%) was used in this work. Details of the synthesis can be found in a previous work [4]. The composition and magnetic properties of the samples at ambient pressure were confirmed by conventional powder x-ray diffraction (XRD) and Mössbauer spectroscopy (MS). For MS studies the sample was encapsulated in a 250 μm cavity of a pre-indented Re gasket of thickness 30 μm in a Merrill-Basset diamond anvil cell (DAC). Re also served as a collimator for the 14.4 keV Mössbauer resonance γ-rays. Daphne 7373 oil was used as the pressure transmitting medium (PTM) and ruby fluorescence served as a manometer.

Mössbauer studies were carried out with a 10 mCi ^{57}Co (Rh) point source in transmission geometry. The typical collection time of a single spectrum was ≈ 72 hours. All the spectra were analysed using an innovative fitting model, as described in the following section [10]. Hyperfine parameters were obtained by fitting theoretical sub-spectral curves to experimental data with Lorentzian line shapes to de-convolute Fe phases in the spectrum. Prior to analysis each spectrum was folded with its mirror image and, where necessary, adjacent channels subsequently added. The purpose of this was to remove geometrical base-line distortions and to reduce the signal-to-noise ratio in the final data set to be used for analysis.

3. Results and Discussion

Room temperature Mössbauer spectra of Fe_2OBO_3 in the range 16–30 GPa are shown in figure 2 (a). Their line shape is indicative of electron hopping processes occurring within the time sensing window

of the Mössbauer effect, ~10^{-7} s [11-13]. There is a marked disappearance of the right most resonant absorption lines (high velocity side) in the ambient pressure spectra with increasing pressure, see figure 2 (a) and (b) for a visual comparison. Marked changes in spectral features were rationalized as an electronic hopping process between sites of different valence state; in the case of Fe_2OBO_3, $Fe^{2+} \Leftrightarrow Fe^{3+}$ in the high pressure regime [9], indicative of a complete CO collapse.

The fitting model adopted for the fluctuating valence state is markedly different from previous works [5, 8]. The model implemented here describes electron hopping relaxation in a paramagnetic powder using the theory proposed by Blume [11, 12]. From the fitting parameters characterising the lineshape, we were able to extract the isomer shift and primarily the hopping frequency of electrons in this dynamical process. The isomer shifts quoted in this work for the $Fe^{2.5+}$ (electron hopping) are an average of the Fe^{2+} and Fe^{3+} valences.

Each spectrum was fitted with a single hopping component, which has been superimposed to the corresponding experimental spectrum in figure 2 (a) (red solid line). There are two possible routes for the electron hopping to occur; inter-ribbon, between Fe^{2+} and Fe^{3+} sites on adjacent ribbons, or intra-ribbon, within the same ribbon (see figure 1(c)). Hence the MS spectrum can be expected to be composed of two components. Our approach of using a single fitting component offers the safest route because MS cannot easily discriminate between different hopping paths, involving similar hopping frequencies, but can only reveal the valence state as being static or fluctuating (intermediate between two states) when the electron processes are within the time window of the Mössbauer effect (10^{-7} s).

It is apparent that there are no marked or drastic changes in the spectral line shape over the pressure range spanning a range of 14 GPa, indicating that no new electronic phase change occurs and that the hopping persists up to 30 GPa.

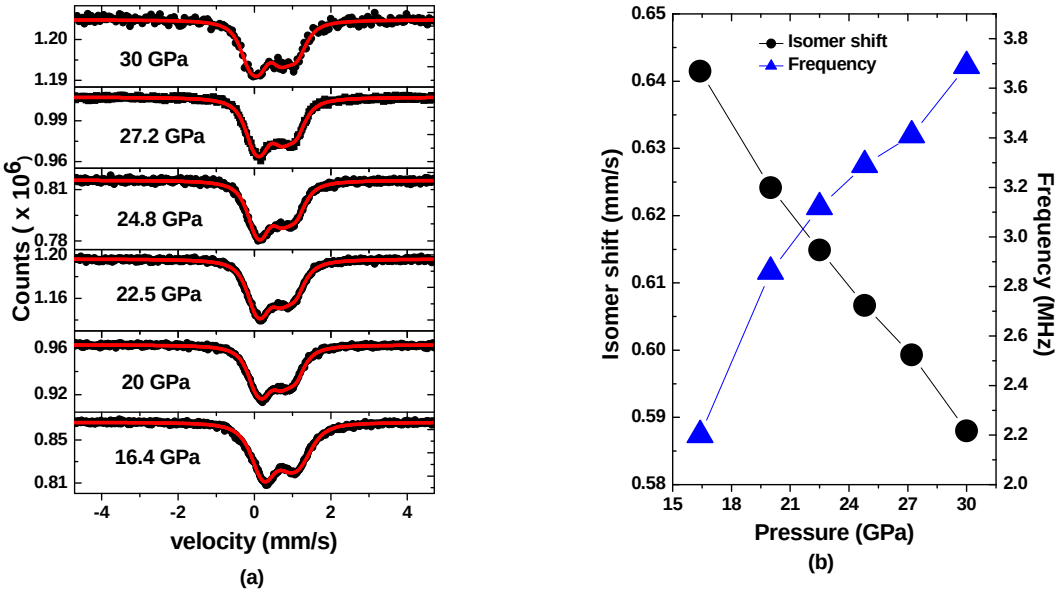


Figure 2 (Colour online): (a) Mössbauer spectra recorded at pressure from 16.4 GPa to 30 GPa. The solid red lines represent the fit to the experimental data (in black). (b) IS and frequency plotted as function of pressure in the range 16-30 GPa. The values of the IS are quoted with respect to α-Fe. The black coloured circles are data points and the lines joining the points are intended as a guide to the eye.

Figure 2 (b) shows a combined plot of the isomer shift (IS) and hopping frequency as a function of pressure, as retrieved from the fitting to the experimental data. The values of the IS are intermediate between those normally associated with Fe^{2+} and Fe^{3+}. This supports the notion that the charge carriers are confined in a lattice dimerised bond, between Fe^{2+}-Fe^{3+} pairs, see figure 1 (c). Our previous work on the structural properties of Fe_2OBO_3 shows that the unit cell is more compressible along the *a*-axis compared to other axes [8]. It is therefore expected that such a lattice distortion will favour a spontaneous Peierls-type dimerisation along the *a*-axis compared to other crystallographic directions and such paths are conducive to charge transfer, that is, electron hopping. The values of the IS also decrease with pressure, which is attributed to the *s*-electron density increasing near the Fe nucleus. The IS is a function of *s*-electron density, ρ_s, at the nucleus.

The pressure dependency of the hopping frequency shows a 70% increase between 16 GPa and 30 GPa. Application of pressure causes the inter-atomic distances to decrease and hence an increase in pressure is expected to promote the $Fe^{2+} \Leftrightarrow Fe^{3+}$ electron exchange, from the increase in orbital overlap. Resistivity studies done by our group infer that there is a site-centered to bond-centered insulator transition in Fe_2OBO_3 above 16 GPa, i.e. a Wigner crystal to a dimer-Mott insulating state transition [8].

The high pressure CO collapse was found to be reversible upon releasing pressure to ambient conditions, see figure 3 below. Distinct signatures of Fe^{3+} and Fe^{2+} indicating CO are again retained at $\approx$ 0.3 mm/s and $\approx$ 2 mm/s respectively. This therefore means the high pressure orthorhombic phase is reversible to the monoclinic low pressure phase.

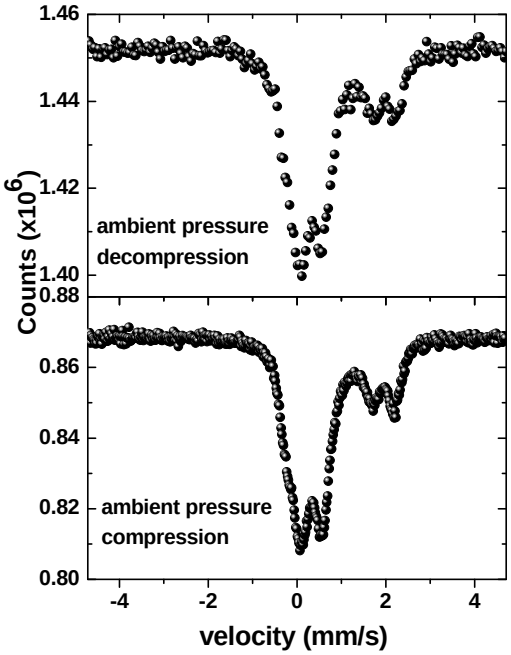


Figure 3. The ambient pressure spectra for the compression and decompression runs. The very good similarity between these two spectra shows that the low pressure monoclinic ($P2_1/c$) site-centered CO phase is recovered after decompression.

4. Conclusions

In summary, we used ^{57}Fe Mössbauer spectroscopy at room temperature to probe the nature of site-centered CO in Fe_2OBO_3 by applying external pressure. Our analysis of the MS spectra above 16 GPa, where such site-centered CO is disrupted, show an average valence of $Fe^{2.5+}$ as the IS values are intermediate to that normally associated with Fe^{2+} and Fe^{3+}, indicating electron hopping relaxation. The electron hopping persists up to 30 GPa, on the time-scale of the Mössbauer effect, with frequencies on the order of MHz (~100 nanoseconds). The site-centered CO disruption was found to be reversible, with Wigner crystallisation (CO) being re-established upon decompression to ambient conditions.

Acknowledgements

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