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Fast oxygen diffusion in bismuth oxide probed by quasielastic neutron scattering

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Abstract – We present the first, to our knowledge, study of solid state oxygen translational diffusion by quasielastic neutron scattering. Such studies in the past might have been precluded by relatively low diffusivities of oxygen anions in the temperature range amenable to neutron scattering experiments. To explore the potential of the quasielastic scattering technique, which can deduce atomic diffusion jump length of oxygen anions through the momentum transfer dependence of the scattering signal, we have selected the fastest known oxygen conductor, bismuth oxide. We have found the oxygen anion jump length in excellent agreement with the nearest oxygen-vacancy distance in the anion sublattice of the fluorite-related structure of bismuth oxide.

Key words: Oxygen diffusion; quasielastic neutron scattering.

1. Introduction

The δ -phase of bismuth oxide, Bi_2O_3 , which is stable between ca. 730°C and the melting temperature of ca. 825°C, is known for its highest reported ionic conductivity, on the scale of 1-3 S cm⁻¹. The 25 % oxygen deficiency compared to regular fluorite structure is associated with high mobility of oxygen in this compound [1, 2]. Along with other diffraction techniques, neutron diffraction has played a major role in extensive investigation of Bi_2O_3 δ -phase structure, due to a sizable neutron coherent scattering cross-section of oxygen. Various structural models proposed for the δ -phase differ on possible displacements of oxygen anion from the tetrahedral sites of 8c symmetry, and whether the oxygen vacancies are ordered, or disordered [3-27]. At the same time, little information is available on oxygen mobility in bismuth oxide, with the first oxygen tracer diffusion measurement reported only recently [28]. Here we report measurement of oxygen diffusivity in the δ -phase of Bi_2O_3 on the Angstrom length scale. The elementary anion diffusion jumps that we probe using quasielastic neutron scattering (QENS) underline the long-range macroscopic oxygen diffusivity, which on the greater length scale can be affected by nanoscopic structural non-homogeneities [29] and microscopic grain boundaries. QENS is commonly applied in studies of proton diffusion in solids (particularly proton-conducting oxides; see [30] for a recent review) and, much more rarely, diffusion of cations and anions in fast ionic conductors, but, to our knowledge, this may be the first QENS study of oxygen solid state translational diffusion. The only previous QENS study of oxygen mobility known to us probed localized rather than translational oxygen jumps [31]. One possible reason might be the common belief that very high temperatures are needed for oxygen diffusivities to enter the range readily

accessible to QENS (above ca. 10^{-11} m²/s). This is not a concern for Bi₂O₃, where oxygen diffusivities on the 10^{-9} m²/s scale have been reported in the δ -phase [28, 32]. Another possible reason for the lack of previous QENS studies of oxygen mobility might be the purely coherent neutron scattering cross-section of oxygen; the coherent QENS theory is much less developed than incoherent QENS theory. Nevertheless, the QENS data that we measured from Bi₂O₃ allow simple interpretation. We believe that various oxygen conductors might be amenable to diffusivity studies by QENS to measure not only the atomic scale diffusion coefficient but also the elementary diffusion jump length of oxygen in the lattice.

2. Experimental

Bi₂O₃ powder of 99.999 % purity was purchased from Sigma Aldrich. The powder was loaded in an open quartz sample holder with an inner diameter of 12.7 mm and a height of ca. 30 mm and mounted in a MICAS vacuum furnace, which controlled the temperature set points with an accuracy of better than a degree Celsius. Prior to measurements with neutrons, the sample mounted in the furnace was outgassed in vacuum at 300°C for 48 hours. This was necessary because oxide powders, either as received, or pre-annealed but even briefly exposed to atmosphere, tend to adsorb water that would completely dominate the scattering signal due to the very high incoherent neutron scattering cross-section of hydrogen [33, 34]. QENS experiment was performed on backscattering spectrometer BASIS [35] at SNS, ORNL, using newly commissioned set of Si(311) analyzer crystals that Bragg-reflect, at near-backscattering angle of 88°, neutrons of 3.273 Å wavelength (7.636 meV). In this operation mode, the spectrometer energy resolution, averaged over all scattering angles, is about 15 μ eV (FWHM), whereas the useful range of energy transfers is about ± 660 μ eV when the spectrometer choppers are set up for a symmetric incident neutron bandwidth at 60

Hz. Following outgassing procedure as described above, the data from the Bi_2O_3 sample was collected at ambient temperature and subsequently used as the resolution function. Then the sample was gradually heated up, until the scattering intensity integrated under the elastic line showed a drop indicative of the onset of rapid oxygen diffusion associated with the transition into the δ -phase (Figure 1). Although reduction of the elastic intensity with temperature is always observed (due to Debye-Waller thermal factors), onset of measurable diffusivity in the sample leads to much faster elastic intensity decrease with temperature. Below the phase transition the oxygen diffusivity is much too small to cause signal broadening beyond the elastic line. Above the phase transition the oxygen diffusivity causes signal broadening (quasielastic wings) at the expense of the elastic line intensity.

Figure 1. Temperature dependence of neutron elastic intensity scan (integrated over all Q values) for Bi_2O_3 that was outgassed before the measurement to remove surface water. A rapid drop above ca. 740 K is due to the onset of rapid oxygen diffusion (leading to scattering intensity redistribution from the elastic line into the quasielastic signal) associated with the transition into the δ -phase.

The sample was then measured from 750°C to 810°C, with 10°C temperature increment, to remain sufficiently below the melting point. The measurement time at each temperature point was about 6 hours. After the completion of the measurement, the sample was cooled down to the near ambient temperature to verify that no loss of the original scattering intensity occurred. Finally, the background spectrum measurement was performed using the empty quartz sample holder in the furnace at 810°C. Separate analysis of this background spectrum showed no QENS signal from the quartz sample holder at 810°C. This point is illustrated by Figure 2, where the background spectrum from the sample holder almost overlaps with the elastic fit component obtained independently from fitting the data without background subtraction; the quasielastic component of the fit is thus completely unrelated to the sample holder.

3. Results and discussion

Representative spectra collected at 810°C at a scattering momentum transfer $Q = 1.1 \text{ \AA}^{-1}$ are shown in Figure 2, along with the fitting curves. The conclusion, which holds for all temperatures and Q values, is that background spectra subtraction significantly reduces, but does not eliminate the elastic line near zero energy transfer. Thus, an elastic line with a variable spectral weight, $x(Q)$, needs to be included in the QENS data fits with the following model scattering function:

$$I(Q, E) = \left[x(Q)\delta(E - E_o) + (1 - x(Q))\frac{1}{\pi} \frac{\Gamma(Q)}{\Gamma^2(Q) + (E - E_o)^2} \right] \otimes R(Q, E) + (C_1(Q)E + C_2(Q))$$

(1)

Figure 2. QENS data and fits (as described in the text) of Bi₂O₃ at $Q = 1.1 \text{ \AA}^{-1}$ at 810°C . (a) Left panel: without subtracted background spectrum. (b) Right panel: with subtracted background spectrum. Grey symbols: data. Black solid line: overall fit. Black short-dashed line: elastic component. Black long-dashed line: quasielastic component combined with the linear background. Grey solid line in the panel showing data without subtraction (almost overlaps with the elastic fit component): background spectrum from the quartz sample holder at 810°C .

The fits of the scattering intensity, $I(Q, E)$, as a function of neutron energy transfer, E , are performed separately at each Q value, and include a superposition of elastic line (delta-function) with a Lorentzian quasielastic broadening term, convolved with the resolution function, $R(Q, E)$, and a linear background term, $(C_1(Q)E + C_2(Q))$. The variation of the peak position with respect to zero energy transfer, E_0 , allows for a small sample misalignment.

The fact that a separate elastic line was needed in the fits even after the background spectrum had been subtracted is remarkable in view of the following theoretical expression

for the diffusion of non-interacting (except for site blocking) lattice-gas species given by Hempelmann [36]:

$$S(\mathbf{Q}, E) = c(1 - c) \frac{1}{\pi} \frac{\Gamma^{CE}(\mathbf{Q})}{\Gamma^{CE}(\mathbf{Q})^2 + E^2} + c^2 \frac{(2\pi)^3}{V_c} \sum_{\mathbf{G}} \delta(\mathbf{Q} - \mathbf{G}) \quad (2)$$

Here c is the average occupancy of the sites. For the general case of the scattering signal dependence on the non-powder-averaged momentum transfer, $\mathbf{Q}$, the second term of this equation comprises the sum over all reciprocal lattice vectors, $\mathbf{G}$, normalized to the cell volume, V_c , thus representing Bragg peaks. Equation 2 can be spatially averaged over all directions, as appropriate for powders. At the Q values different from the Bragg peaks positions (in single crystals or powders), the scattering signal (the first term in Equation 2) should be a Lorentzian, or a powder-averaged Lorentzian superposition, of the linewidth described by Chudley-Elliott (CE) model, and there should be no elastic line. Integration of the first term in Equation 2 over E would yield diffuse Laue scattering for coherent scattering by a lattice with atoms randomly distributed [36]. The presence of the elastic line in the measured QENS spectra thus indicates some additional static disorder in the sample, which could be, e.g., due to Frenkel type interstitial defects, which are known in oxides [37, 38]. The elastic term in Equation 1 may be needed to account for the static disorder, and the background term in Equation 1 is also needed for fits, even though it decreases greatly following subtraction of the background spectra. The information of interest to us is derived from the quasielastic Lorentzian term in Equation 1. The linewidth of this Lorentzian term can be described by Chudley-Elliott jump diffusion model:

$$\Gamma(Q) = \frac{6\hbar D}{L^2} \left(1 - \frac{\sin(QL)}{QL} \right) \quad (3)$$

where $\hbar$ is reduced Planck constant, D is the diffusion coefficient and L is the diffusion jump length. Chudley-Elliott model in the form of a single Lorentzian with a linewidth described by Equation 3 is valid, strictly speaking, only for liquids, whereas for powders a proper

Figure 3. Linewidth of QENS signal (symbols) and its fits with Chudley-Elliott jump diffusion model over $0.5 \text{ \AA}^{-1} \leq Q \leq 1.7 \text{ \AA}^{-1}$ (solid lines) and $0.5 \text{ \AA}^{-1} \leq Q \leq 3.5 \text{ \AA}^{-1}$ (dashed lines). The fits of the linewidth over different Q ranges are explained in the text. (a) Left panel: without subtracted background spectrum. (b) Right panel: with subtracted background spectrum. The bottom graphs of each panel show the diffraction pattern of Bi_2O_3 collected using diffraction detectors of the BASIS; the first diffraction peak is at $Q = 1.9 \text{ \AA}^{-1}$.

numerical spatial averaging over the first term in Equation 2 would be required.

Nevertheless, a single-Lorentzian quasielastic term with a linewidth described by Equation 3 is commonly and successfully used to analyze jump diffusion in powders.

Figure 3 shows the $\Gamma(Q)$ obtained from the QENS data fits with Equation 1, which was, in turn, fitted with Equation 3. We have investigated systematically how the fit parameters vary when the data are fitted over variable Q range. With the minimum Q used for the fit always at $0.5 \text{ \AA}^{-1}$, the diffusion jump length, L , shows little variation until the maximum Q used for the fit reaches $1.9 \text{ \AA}^{-1}$ (the position of the first Bragg peak). Beyond that, the L varies in rather systematic manner as the maximum Q used for the fit is increased, until it reaches the maximum value of $3.5 \text{ \AA}^{-1}$.

The fit parameters for the fits over $0.5 \text{ \AA}^{-1} \leq Q \leq 1.7 \text{ \AA}^{-1}$ and $0.5 \text{ \AA}^{-1} \leq Q \leq 3.5 \text{ \AA}^{-1}$ are listed in Table 1 and 2, respectively. The nearest-neighbor distance between the partially oxygen-occupied tetrahedral sites in Bi_2O_3 is ca. $2.83 \text{ \AA}$, based on the δ -phase lattice parameter of $5.66 \text{ \AA}$ [39]. The fits for the $0.5 \text{ \AA}^{-1} \leq Q \leq 1.7 \text{ \AA}^{-1}$ range described in Table 1 yield the L values consistently close to the expected value of $2.83 \text{ \AA}$, irrespective of whether the background spectra were subtracted from the Bi_2O_3 data, or not. The deviations of the L values from the exact value of $2.83 \text{ \AA}$ could be attributed, in principle, to possible displacements of oxygen anion from the tetrahedral sites of $8c$ symmetry [3-27]. However, scatter in the data is more plausible explanation; e.g., the diffusion coefficient in Table 1 should increase systematically with temperature, which is true as the general trend, but not for each temperature data set. Besides, the diffusion coefficients listed in Table 1 exhibit systematic, but weak, sensitivity to the background spectra subtraction or lack thereof.

The situation is rather different for the data presented in Table 2. Background spectra subtraction makes a dramatic difference for the fitted values of both L and D . Irrespective of background subtraction, the diffusion jumps length obtained from $0.5 \text{ \AA}^{-1} \leq Q \leq 3.5 \text{ \AA}^{-1}$ fits is never close to the expected value of $2.83 \text{ \AA}$. It should be noted that we compare not the relative goodness of various diffusion models (the model is given by Equation 3), but rather the choice of the data sets (variable Q range and background treatment) to determine what data sets would give the expected value of the oxygen diffusion jump length.

Table 1. Oxygen jump length and *coherent* diffusivity determined from QENS measurements of Bi_2O_3 in the $0.5 \text{ \AA}^{-1} \leq Q \leq 1.7 \text{ \AA}^{-1}$ range. Standard deviation values are shown in parenthesis.

$T, ^\circ\text{C}$	Fits without background subtraction		Fits with background subtraction	
	Jump length, $\text{\AA}$	Diffusivity, $10^{-10} \text{ m}^2/\text{s}$	Jump length, $\text{\AA}$	Diffusivity, $10^{-10} \text{ m}^2/\text{s}$
810	2.76 (0.06)	29.87 (1.12)	2.84 (0.06)	27.01 (0.96)
800	2.84 (0.06)	29.89 (1.10)	2.91 (0.06)	26.99 (0.95)
790	2.87 (0.06)	29.65 (1.06)	2.92 (0.05)	26.33 (0.90)
780	2.64 (0.06)	25.02 (0.82)	2.70 (0.05)	22.30 (0.70)
770	2.74 (0.05)	25.86 (0.82)	2.82 (0.05)	23.44 (0.72)
760	2.66 (0.05)	22.81 (0.70)	2.73 (0.05)	20.59 (0.61)
750	2.76 (0.05)	23.59 (0.68)	2.82 (0.05)	21.21 (0.59)

Table 2. Oxygen jump length and *coherent* diffusivity determined from QENS measurements of Bi_2O_3 in the $0.5 \text{ \AA}^{-1} \leq Q \leq 3.5 \text{ \AA}^{-1}$ range. Standard deviation values are shown in parenthesis.

$T, ^\circ\text{C}$	Fits without background subtraction		Fits with background subtraction	
	Jump length, $\text{\AA}$	Diffusivity, $10^{-10} \text{ m}^2/\text{s}$	Jump length, $\text{\AA}$	Diffusivity, $10^{-10} \text{ m}^2/\text{s}$
810	3.21 (0.03)	39.86 (0.68)	2.09 (0.02)	17.22 (0.27)

800	3.22 (0.03)	38.73 (0.64)	2.07 (0.01)	16.31 (0.25)
790	3.23 (0.03)	36.69 (0.59)	2.04 (0.01)	15.50 (0.23)
780	3.21 (0.03)	35.88 (0.55)	2.07 (0.01)	15.40 (0.21)
770	3.19 (0.03)	34.16 (0.50)	2.12 (0.01)	15.60 (0.21)
760	3.21 (0.02)	33.77 (0.46)	2.05 (0.01)	13.93 (0.17)
750	3.24 (0.02)	32.99 (0.41)	2.07 (0.01)	13.58 (0.16)

There seems to be a consensus in the literature [32, 40-42] that oxygen jumps to one of the nearest unoccupied tetrahedral sites is the main diffusion mechanism in Bi_2O_3 , even though the most energetically favorable pathway between the tetrahedral sites may not necessarily lie along the $\langle 100 \rangle$ direction [42]. Therefore, we conclude that the parameters obtained from the $0.5 \text{ \AA}^{-1} \leq Q \leq 1.7 \text{ \AA}^{-1}$ fits are not only largely insensitive to background handling, but also in agreement with the oxygen diffusion mechanism proposed in the literature. While the earlier suggestions were based on modeling, the current study provides the first experimental verification of the oxygen diffusion jump length in the δ -phase of bismuth oxide.

For the fits involving higher Q values, above $1.7 \text{ \AA}^{-1}$, we believe that strong sensitivity to background handling and lack of agreement with the expected values of L is a consequence of the Bragg peaks affecting the spectra beginning at $Q = 1.9 \text{ \AA}^{-1}$. The bottom graphs in Figure 3 demonstrate the presence of at least four Bragg peaks in the accessible Q range. They cannot be reliably subtracted from the spectra and affect the data through the strong Bragg scattering. **Neither of the two sets of fits presented with the dashed lines in Figure 3 with the parameters listed in Table 2 is thus trustworthy.** Instead, the maximum Q values used in the fits of $\Gamma(Q)$ should be limited to a value below the first Bragg peak. This

explains our choice of the $0.5 \text{ \AA}^{-1} \leq Q \leq 1.7 \text{ \AA}^{-1}$ range for the trustworthy fits in in Figure 3.

The present data analysis does not indicate whether reliable QENS data fitting for other systems can be extended into the Q range affected by the Bragg peaks, or not. At the same time, we have demonstrated that the Q range below the first Bragg peak can be successfully used for accurate analysis of QENS data.

The diffusion coefficients obtained in the trustworthy fits and listed in Table 1 seem to exceed the value of ca. $10 \times 10^{-10} \text{ m}^2/\text{s}$ assigned in the literature [28, 32] for the δ -phase prior to melting. Even though one work reports merely the simulation-based value of D (linked to conductivity) [32] and the other reports macroscopic measurements of D in the pelletized powder samples [28], the discrepancy by a factor of 3 with the Angstrom-scale diffusivity would be too high. To clarify this apparent discrepancy, we recall that, due to the exclusively coherent neutron scattering cross-section of oxygen, here we measure the coherent, not tracer [28, 32], diffusion coefficient. As pointed out by Hempelmann [36], the $\Gamma(Q)$ of the coherent scattering is insensitive to the site occupancy (the parameter c in Equation 2), whereas the corresponding $\Gamma(Q)$ of the incoherent scattering, associated with single-particle tracer diffusivity, equals the $\Gamma(Q)$ of the coherent scattering only in the limit of very low site occupancy. Otherwise, the $\Gamma(Q)$ of the incoherent scattering is reduced due to site blocking, proportional to the $(1-c)$ factor [36]. For randomly oxygen-occupied tetrahedral sites of Bi_2O_3 , $c = 0.75$, and four-fold reduction of the tracer diffusion coefficient compared to the corresponding coherent scattering value can be expected. Therefore, the tracer diffusion value that we would have measured (if oxygen scattered neutrons purely

incoherently) would be ca. $7 \times 10^{-10} \text{ m}^2/\text{s}$ at 810°C . It is this value that should be compared with the tracer diffusivity of ca. $10 \times 10^{-10} \text{ m}^2/\text{s}$ suggested in the literature.

Finally, we present Arrhenius plot of the diffusivity in Figure 4 using all the diffusivity data from Table 1 and 2. The diffusion activation energy values are obtained as follows: $E_a = (45.0 \pm 5.8) \text{ kJ/mol}$ for $0.5 \text{ \AA}^{-1} \leq Q \leq 1.7 \text{ \AA}^{-1}$ without background spectra subtraction; $E_a = (44.8 \pm 5.6) \text{ kJ/mol}$ for $0.5 \text{ \AA}^{-1} \leq Q \leq 1.7 \text{ \AA}^{-1}$ with background spectra subtraction; $E_a = (29.2 \pm 2.6) \text{ kJ/mol}$ for $0.5 \text{ \AA}^{-1} \leq Q \leq 3.5 \text{ \AA}^{-1}$ without background spectra subtraction; $E_a = (34.2 \pm 2.4) \text{ kJ/mol}$ for $0.5 \text{ \AA}^{-1} \leq Q \leq 3.5 \text{ \AA}^{-1}$ with background spectra subtraction. The trustworthy data obtained from the $0.5 \text{ \AA}^{-1} \leq Q \leq 1.7 \text{ \AA}^{-1}$ fits suggest diffusion activation energy of ca. 0.47 eV. This is more than twice the value of 0.2 eV estimated from the tracer diffusion measured in the pelletized powder samples [28].

Figure 4. Arrhenius plot obtained using diffusivity data in Table 1 and 2.

Even though the authors cautioned [28] that the value of 0.2 eV may be associated with a significant error due to the limited temperature range of the measurement, we attribute the

apparent discrepancy mainly to the fact that our QENS measurement probes elementary diffusion jumps, not affected by grain boundaries and other structural features. QENS experiment is not sensitive to the morphology of the sample, whereas macroscopic tracer diffusion measurement is sensitive to the sample morphology, which may in general lead to significant discrepancy between microscopic and macroscopic diffusivity measurements, due to, e.g., surface diffusion in the sample. The unique strength of QENS is due to its sensitivity to the atomic scale diffusion coefficient and especially the elementary diffusion jump length.

4. Conclusion

Despite the limitations imposed by the Bragg peaks, the presence of which seems to distort the data fits, we consistently obtained the diffusion jump length in agreement with the tetrahedral-tetrahedral site distance in the δ -phase of Bi_2O_3 (2.83 Å) from the QENS data collected below the first Bragg peak. The diffusion activation energy of 45 kJ/mol (0.47 eV) was obtained from the trustworthy data fits, and the diffusivity value renormalized to the single-particle tracer diffusion was ca. $7 \times 10^{-10} \text{ m}^2/\text{s}$ at 810°C. We emphasize that QENS is the only experimental technique capable of measuring directly the spatial characteristics of diffusion processes on Angstrom length scale, such as diffusion jump length. The current work is the first study known to us that applies QENS for probing oxygen translational diffusion in solids. The QENS signal line width was measured on the energy scale exceeding some 100 μeV . Given the μeV energy resolution of the modern neutron backscattering spectrometers, one can expect that oxygen diffusivities that are lower (at the maximum accessible measurement temperature) by up to two orders of magnitude compared to oxygen diffusivity in Bi_2O_3 in the 740°C-825°C temperature range can be studied by QENS. Even in the same temperature range, there are several compounds with anticipated oxygen diffusivity

within 2 orders of magnitude from the value measured for bismuth oxide in this work [28]. Increase of measurement temperature to ca. 1500°C, which is fairly routinely attained in neutron scattering experiments, may bring many more oxygen compounds to the measurable diffusivity range of ca. 10^{-11} m²/s and above. Finally, we propose that even lower oxygen diffusivities might be measurable by neutron spin-echo spectrometers, which would additionally benefit from the completely coherent neutron scattering cross-sections, as exhibited by oxygen.

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