Water Dynamics in Controlled Pore Silica Glasses

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Abstract. Water in porous silica glass is a suitable system for investigating the effect of confinement on translational diffusion. These systems are important because of their relevance in catalytic and separation processes. Here quasi-elastic neutron scattering experiments at room-temperature-on-water-filled-controlled-pore glasses with radius of 15, 24 and 32Å, are presented and analyzed using the random-jump diffusion model. Both the average residence time and the mean jump distance increase with decreasing pore radius.

1. INTRODUCTION

No liquid has been as extensively studied as water. Experiments using techniques such as Raman, infrared absorption, inelastic and quasi-elastic neutron scattering, x-ray and computer molecular-dynamics (MD) simulations have been performed in the supercooled regime, where the effects due to hydrogen bonding are dominant [1]. Analysis of the dynamical behavior demonstrates that hydrogen bonds play a crucial role in water [2]. However, of recent interest is understanding modifications to its bulk behavior when water is placed in a confined geometry [3]. This situation occurs in a large variety of important contexts such as mining, corrosion inhibition, enzymatic activity, and functions of membranes and food conservation. In addition, the structure and dynamical properties of confined water have been considerably studied due to their relevance in the understanding of chemical reactions in catalysis and separation process in micropores such as vycor glass, silica gel and nafion.

Investigations of the dynamics of water molecule confined in different geometries reveal a slowing down of the translational motion compared to bulk water [4]. Recent MD simulations on TIP4P water confined in cylindrical pore built inside a SiO_2 glass indicate that the H-bond distribution through the pore is strongly distorted and that a number of non H-bonded (interstitial) neighboring molecules must be present [5]. This suggests that the main effect of confinement is to disturb the orientational arrangement of molecules to such an extent that a continuous network of bonds is not favored up to distances from the interface of the order of 8 Å. The MD results are in qualitative agreement with experimental findings on water confined in Vycor glass [6]. Two factors are to be considered in the case of confined water: (1) the effects of hydrophilic and hydrophobic surfaces on interfacial water and (2) how the dynamics of the hydrogen bond network changes due to the volume of confinement. Water in porous silica glass is a suitable system for investigating the effect of confinement on the translational diffusion. In this paper quasi-elastic (QE) neutron scattering experiments at room temperature on water-filled controlled-pore glasses (CPG) with radius of 15, 24 and 32Å are reported. CPG is a total porous borosilicate glass with a very narrow size distribution about a mean radius.

2. EXPERIMENTAL

The QE experiments were performed using the time-of-flight spectrometer QENS at the Intense Pulsed Neutron Source at Argonne National Laboratory. Unique constant-energy focusing of the graphite analyzer crystal arrays provides high resolution (~90 μeV) for quasi-elastic and low-energy inelastic scattering, while maintaining high data rates. Three spectra were recorded for each angular setting of the spectrometer corresponding to three different momentum transfers, Q. Data from up to four settings of the instrument were analyzed corresponding to 0.57 $Å^{-1} < Q < 2.54$ $Å^{-1}$. Data were

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PHONON DENSITY OF STATES IN EPITAXIAL FE/CR(001) SUPERLATTICES

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Abstract

Incoherent nuclear resonant absorption of synchrotron radiation at the 14.413 keV nuclear resonance of ^{57}Fe was employed to measure directly the Fe-projected (partial) phonon density of states (DOS) in epitaxial [Fe(8.7ML)/Cr(8ML)]$_{200}$ superlattices and alloy films MBE-grown on MgO(001). Isotopically depleted ^{56}Fe was used which gives no resonance signal. 0.7 monolayers (ML) thick ^{57}Fe-probe layers (1 Å) of 95.5% enrichment were placed either at the ^{56}Fe-on-Cr interfaces or at the center of the ^{56}Fe layers, thus providing us a nuclear resonance signal from different places in the films. In addition, we prepared an epitaxial film which contains only a 1-Å-thick ^{57}Fe submonolayer in Cr(001) and no ^{56}Fe layers. Moreover we prepared a 7000-Å-thick epitaxial $^{57}Fe_{0.03}Cr_{0.97}$(001) alloy film. The measurements were performed at 300 K with 2.3 meV energy resolution around 14.413 keV. The phonon DOS of the center site was found to be very similar to that of bulk bcc Fe. Compared to the center site, the DOS of the other samples show distinct differences. In particular, longitudinal vibrations of Fe atoms are suppressed at the Fe/Cr interfaces.

1. Introduction

Knowledge of the phonon density of states (DOS) is essential for our basic understanding of lattice vibrations. Extensive investigations of phonons in semiconducting superlattices have revealed novel phenomena, such as folding, confinement and interface modes [1]. For metallic multilayers (MMLs), on the other hand, only few reports of folded [2] or confined [3] phonons exist. Knowledge of vibrational properties of MMLs is highly desirable, also because their electronic properties may be affected by phonons [4]. In the present work inelastic nuclear scattering of X-rays from the 14.413 keV nuclear resonance of ^{57}Fe [5-7] was used to measure directly the Fe-projected phonon DOS in Fe/Cr(001) superlattices and epitaxial FeCr(001) alloy films.

2. Experimental and sample characterization

The following types of Fe/Cr films (labeled FeCr1 - FeCr4, respectively) were epitaxially grown in UHV at 160 °C by molecular beam epitaxy (MBE) on MgO(001) substrates carrying a 50Å Cr buffer layer, which was grown at 670 °C:

FeCr1: MgO(001)/Cr(50Å)/[^{56}Fe(4ML)/^{57}Fe(0.7ML)/^{56}Fe(4ML)/Cr(8ML)]$_{200}$,

FeCr2: MgO(001)/Cr(50Å)/[^{57}Fe(0.7ML)/^{56}Fe(8ML)/Cr(8ML)]$_{200}$,

FeCr3: MgO(001)/Cr(50Å)/[^{57}Fe(0.7ML)/Cr(8ML)]$_{200}$,

FeCr4: MgO(001)/Cr(50Å)/[$^{57}Fe_{0.03}Cr_{0.97}$(001)], 7000 Å thick,

The pressure during growth was $< 7 \cdot 10^{-10}$ mbar. Samples FeCr1 and FeCr2 were superlattices with (001) orientation. 0.7 monolayer (ML) thick probe layers (1 Å) of 95.5 % enriched ^{57}Fe were artificially placed either at the ^{56}Fe-on-Cr interfaces (FeCr2) or in the center of the ^{56}Fe layers (FeCr1), thus providing a nuclear resonance signal either from this Fe/Cr interface (FeCr2) or from the Fe-film center (FeCr1). Isotopically depleted ^{56}Fe was used, which gives no nuclear resonance signal. In addition, we prepared an epitaxial film (FeCr3) which contains no bcc-^{56}Fe layers, but only 0.7-ML-thick ^{57}Fe probes embedded on both sides between 8-ML-thick Cr(001) layers. The fourth sample was a 7000-Å-thick epitaxial $^{57}Fe_{0.03}Cr_{0.97}$(001) single layer alloy film (FeCr4), that film was prepared in UHV by thermal co-evaporation of high-purity Cr and ^{57}Fe, under the same conditions as the other samples.

Fig. 1 shows high-angle (Θ-2Θ) X-ray diffraction (XRD) patterns of our samples. Samples FeCr1 and FeCr2 exhibit two symmetrical superstructure-satellite peaks around the main Cr/Fe(002) Bragg reflection. This demonstrates the high-quality superlattice structure of these samples. XRD patterns (Fig. 1) of samples FeCr3 and FeCr4 show a(002) Bragg reflection as expected and confirm the epitaxial (001) orientation both samlpes.

The inelastic nuclear resonant absorption experiments were performed at the undulator beamline 3-ID of SRI-CAT at the Advanced Photon Source. The method of inelastic nuclear resonant absorption of 14.4136 keV X-rays is selective to the ^{57}Fe resonant isotope and provides the Fe-projected (partial) phonon DOS rather directly with a minimum of modelling [6]. Details of the technique are described in ref. [5-7]. The monochromatized synchrotron radiation was incident onto the thin films under a grazing angle of ≈ 4 mrad and had an energy bandwidth of 2.3 meV. The energy was tuned around the 14.413 keV nuclear resonance of ^{57}Fe. The measurements were performed at 300 K with collection times of ~ 10 h to ~24 h per spectrum.

3. Results and Discussion

The measured normalized data (not shown), i.e., the resulting phonon excitation probabilities per unit of energy, commonly feature a dominant elastic peak in a narrow energy range around the nuclear transition energy and side bands at lower and higher energy due to phonon annihilation and phonon creation, respectively [5-7]. The partial phonon DOS were extracted from the measured excitation probabilities by using the procedure described in ref. [6].

The partial phonon DOS of our Fe/Cr-samples show distinct differences with each other (Fig. 2). The phonon DOS of the center site (FeCr1) is found to be very similar to that of bulk bcc Fe [6], exhibiting peaks near 23 and 28 meV (transverse phonons) and 36 meV (longitudinal phonons). The phonon DOS of the other samples are different. Compared to the phonon DOS of the center site (FeCr1), the DOS peak of the interface site (FeCr2) near 36 meV is remarkably reduced in intensity, while the lower energy feature (near 23 and 26 meV) is notably enhanced. Moreover the lower energy double peak structure for the center side starts to change to a single peak structure at the interface. The suppression of the longitudinal atomic vibrations and the enhancement of the transverse atomic vibrations at the interfaces is even more pronounced in sample FeCr3, where only 0.7-ML-thick ^{57}Fe probes are on both sides in contact with 8-ML-thick Cr(001) layers. Sample FeCr3 exhibits clearly a rather strong single peak at lower energy (near 23 meV). The evolution of this 23 meV DOS peak is even more pronounced for the epitaxial 3 at.% ^{57}Fe-Cr alloy film (sample FeCr4). This peak shares features of a local vibrational mode of Fe in the Cr matrix. Nevertheless, there is still a weak peak observable near 36 meV for this sample.

The observed similarity of the DOS for bulk bcc Fe and sample FeCr1 (center side) demonstrates that phonon confinement (if it exists at all) within 8 ML thick bcc-Fe films embedded between Cr layers is not detectable in the DOS. As a possible explanation for the reduction of the 36-meV peak intensity at the interface (sample FeCr2 and FeCr3) one should notice that its position nearly coincides with the deep minimum at ~ 34 meV in the bulk-phonon DOS of Cr [9]. Because of this gap in the phonon DOS of Cr, longitudinal phonons near 36 meV are partially suppressed at the Fe/Cr interface. An inspection of phonon dispersion curves of bulk Fe and Cr shows that this suppression affects longitudinal [00ζ] phonons of Fe near the H point of the Brillouin zone [9]. Concerning the enhancement of the lower-energy DOS feature at the interface should notice that qualitatively the number of Cr neighboring atoms around one ^{57}Fe probe atom increases from sample FeCr1 to sample FeCr4. The peak intensity in the phonon DOS near 23

meV correlates qualitatively with the number of Cr neighbors. A localized Fe phonon mode near 23 meV seems to develop with increasing number of Cr neighbors.

Summarizing, we have demonstrated that inelastic nuclear resonant absorption of the 14.4136 keV ^{57}Fe-nuclear transition is sensitive for measuring the Fe-projected vibrational density of states in thin films, multilayers and isotopically-enriched buried interfaces.

Acknowledgments

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Figure captions

Fig. 1: High-angle (Θ-2Θ) X-ray diffraction patterns of multilayers FeCr1, FeCr2 and FeCR3, and alloy film FeCr4. (Cu-K_α-radiation)

Fig. 2: Fe-projected phonon density of states (DOS) of Fe/Cr(001) samples labeled FeCr1 (○) (signal from center of Fe layers), FeCr2 (▲) (interface signal), FeCr3 (◇) (1 Å ^{57}Fe embedded on both sides in Cr) and FeCr4 (■) ($^{57}Fe_{0.03}Cr_{0.97}$ alloy film). The phonon DOS obtained from a bulk-Fe sample (●) is shown for comparison.

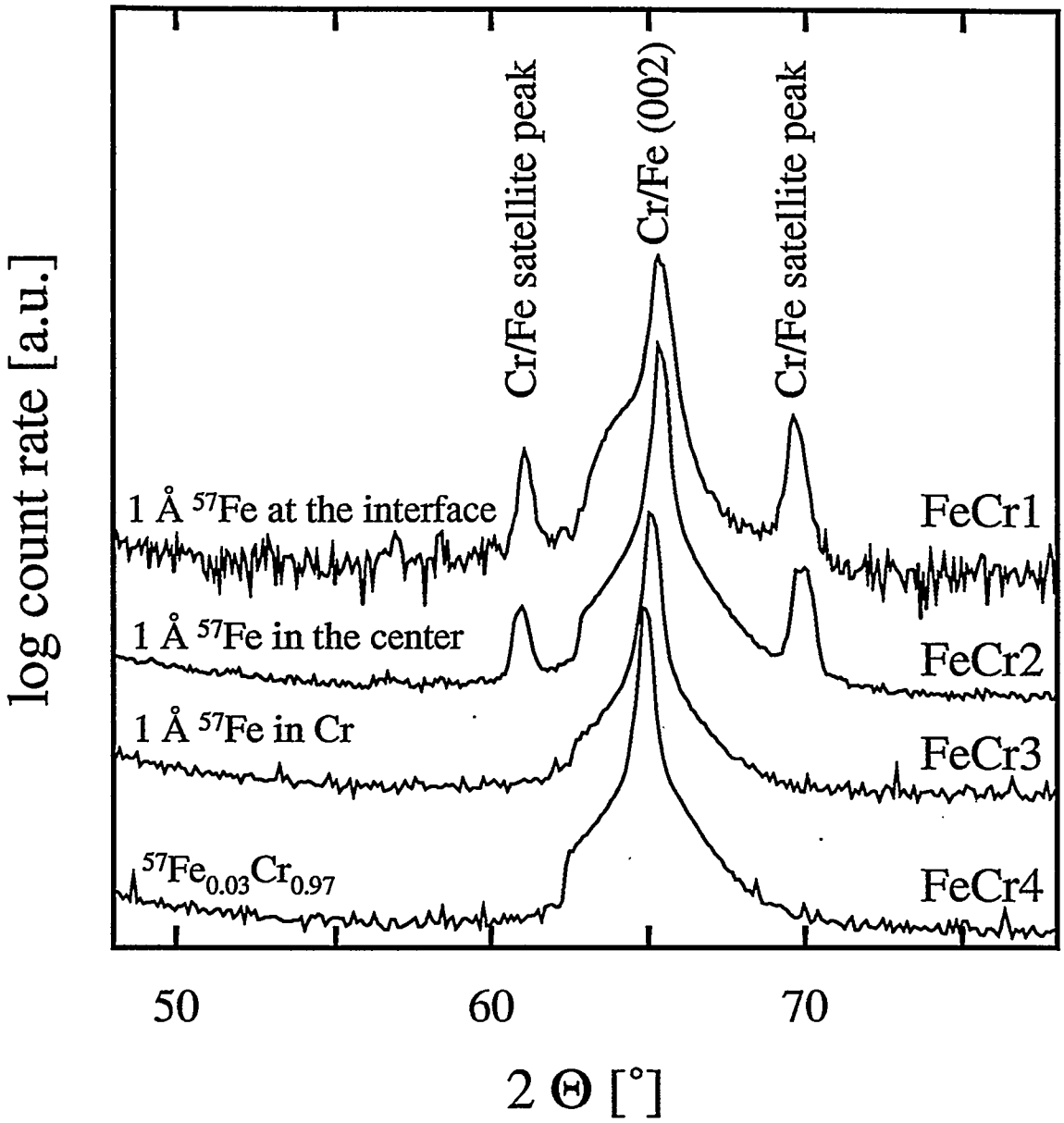
log count rate [a.u.]
Cr/Fe satellite peak
Cr/Fe (002)
Cr/Fe satellite peak
1 Å ^{57}Fe at the interface
FeCr1
1 Å ^{57}Fe in the center
FeCr2
1 Å ^{57}Fe in Cr
FeCr3
$^{57}Fe_{0.03}Cr_{0.97}$
FeCr4
50
60
70
2 Θ [°]

Fig.1

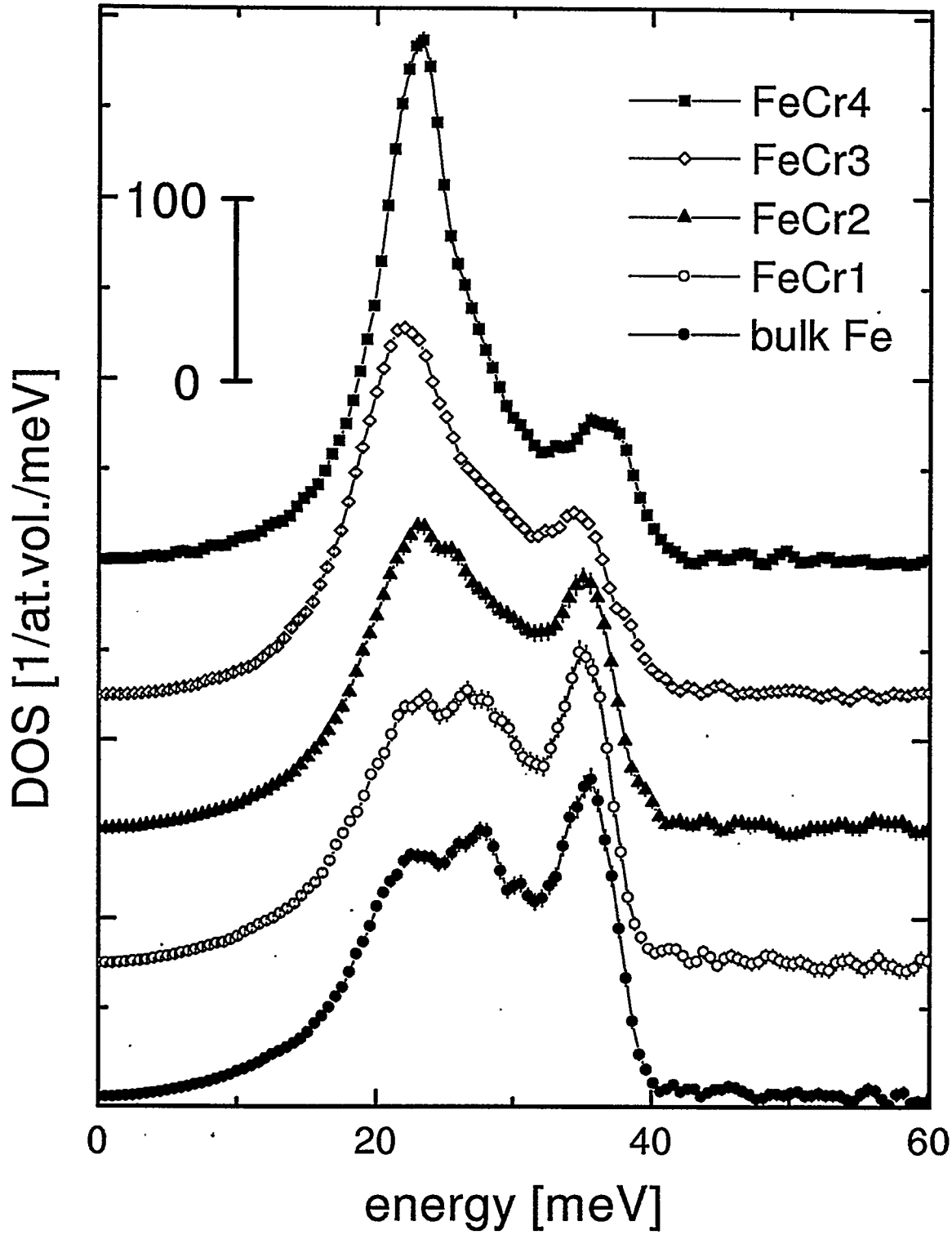
FeCr4
FeCr3
FeCr2
FeCr1
bulk Fe
100
0
DOS [1/at.vol./meV]
0
20
40
60
energy [meV]

Fig.2