Observation of nuclear forward scattering from ^{83}Kr in bulk and monolayer films

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The coherent nuclear forward scattering of synchrotron radiation from the 9.4-keV level of ^{83}Kr has been observed from bulk films and monolayer Kr adsorbed on exfoliated graphite.

I. INTRODUCTION

Mössbauer spectroscopy (MS) has been used extensively in a wide range of condensed-matter studies for over 30 years. Over the past ten years, various groups have shown the viability of Mössbauer spectroscopy using synchrotron radiation (SR), most notably nuclear forward scattering (NFS).[1] NFS is the time analog to the conventional transmission Mössbauer spectrum in which a time-resolved measurement is made of the decay of the nuclear state populated by a SR pulse.

Most Mössbauer studies (both conventional and NFS) have been performed with the ^{57}Fe isotope, while relatively little conventional MS has been performed with ^{83}Kr. Nevertheless, studies were undertaken approximately 20 years ago, focusing on a lower-than-expected Lamb-Mössbauer factor (the probability that a resonantly absorbed gamma ray is reemitted from the nucleus without recoil) later shown to be the result of source effects.[2] At approximately the same time, investigations of physisorbed inert gases (including Kr) were performed.[3] This body of research has revealed a rich phase diagram for monolayer and multilayer Kr. Features such as an incommensurate-commensurate transition at submonolayer coverages and multilayer reentrant melting have been reported.[4,5] To date, Mössbauer spectroscopy has not been used to study these systems. With this technique it is in principle possible to investigate the boundaries and character of the liquid-solid transitions by measurement of the Lamb-Mössbauer factor as it differs significantly from zero only for solids.

^{83}Kr is a favorable candidate for SR-excited NFS, as the resonance cross section and lifetime are comparable to those of ^{57}Fe, with a lower transition energy nearly ideal for current x-ray SR sources. In addition, if one is interested in performing MS with ^{83}Kr, SR-excited NFS is an excellent tool in that it avoids introducing source effects that have significantly hampered such studies in the past.[2,6]

In a resonant scattering process, the resonantly absorbed photons are scattered on a time scale comparable to the lifetime(s) of the excited state(s) involved. In the case of a Mössbauer resonance, this time ranges from a few tenths of a nanosecond up to several microseconds. Thus it is possible, with a fast detector, to discriminate the delayed resonant scattering from the prompt nonresonant scattering. It is this fact that makes NFS measurements possible as the ratio of resonant to nonresonant scattered photons is at most 10^{-5} at current SR sources.

In a typical NFS measurement, highly monochromatic x rays are incident on a sample containing resonant nuclei. A fast detector with associated timing electronics is used to measure the time distribution of photons scattered from the sample relative to the SR pulses from the storage ring. Samples with a large nuclear-resonant thickness display a Bessel function modulation to the exponential decay of the excited nuclear state due to saturation in the resonant absorption. The resonant thickness is proportional to the areal density of resonantly absorbing nuclei which subsequently reemit photons with no recoil (i.e., the product of the number of resonant nuclei/cm^2 with the Lamb-Mössbauer factor). The Bessel function modulation can be derived by considering the nuclear index of refraction for the resonant nuclei, and has been covered in depth elsewhere.[7]

EXPERIMENT

All measurements were performed using natural Kr gas (i.e., ^{83}Kr constituted only 11% of the total amount of Kr used). The experiments were performed at the X12A beamline at the National Synchrotron Light Source in Brookhaven. The operating conditions were typically 70-mA ring current with a single bunch circulating in the storage ring (a period was 567 ns). A Si (111) channel-cut premonochromator absorbed nearly all the incident power, and a Si (733) channel-cut monochromator reduced the bandwidth of the diffracted beam to approximately 50 meV. The intensity incident on the sample was approximately 7×10^7 Hz. An avalanche photodiode from Advanced Photonix coupled to a Phillips Timing Pick-Off Pre-Amp (Model 6955) detected the forward-scattered photons. The rest of the timing system is similar to those described previously.[1]

RESULTS AND DISCUSSION

The first experiment was performed to demonstrate the possibility of observing NFS from Kr. Bulk samples of Kr were grown by vapor deposition of Kr gas onto a cold Be foil. The resonance energy was known only to $+/-10$ eV, so the monochromator was scanned over this range.[8] To locate the resonance, the number of photons falling into a time window (30–330 ns after detection of the prompt pulse) was integrated over 20-s steps.

Off resonance the count rate in this window was approximately 0.03 Hz, but on resonance this rate increased to approximately 2 Hz. A subsequent time-resolved measurement clearly showed the decay of the excited state (Fig. 1). In order to provide ourselves with a fiducial for locating the resonance, a second (733) crystal was inserted into the monochromatic beam while on resonance. The Bragg angle corresponding to this energy was found to be $83.373°+/-0.006°$ (at 25.8 °C), although no special effort was made to eliminate systematic errors in the measurement.

In previous studies of the Kr-on-graphite system, attention centered around the phase transitions occurring at nominal monolayer coverages.[4] It was of interest, then, to see whether NFS from Kr could be observed in the monolayer regime. A sample cell 20 mm in diameter $\times 30$ mm long was filled with exfoliated graphite. Volumetric isotherms were performed during which we observed layer-by-layer growth on the graphite substrate, and deduced the effective surface are for a monolayer coverage to be 20 m^2. For the subsequent NFS measurements, a monolayer coverage of Kr was used.

Two spectra were measured at sample temperatures of 10 and 55 K for approximately 3 h each (limited by the available beam time). Figure 2 shows the results of these measurements. One can clearly see the differences in the intensities and slopes of the two curves due to a decrease in the resonant thickness of the sample. On resonance, the observed count rates were 0.7 and 0.1 Hz, respectively (with the graphite substrate being approximately 50% transmitting). The spectra were fit using the equation for a sample with a single line (i.e., no hyperfine splitting):

$$I(t)=I_0(\chi/\tau)\exp(-\tau)|J_1(\sqrt{4\chi\tau})|^2 , \quad (1)$$

where τ is time in units of the natural lifetime. The resonant thickness χ is given by

$$\chi=\tfrac{1}{4}n\sigma_0 f , \quad (2)$$

where n is the number of resonant nuclei/cm^2, σ_0 is the absorption cross section at resonance, and f is the Lamb-Mössbauer factor.

The number of resonant nuclei in the solid phase is known to be constant from the phase diagram. The natural isotopic abundance of 11% was assumed. The spectra were fit from approximately 50 ns on due to dead time effects which are significant at earlier times. The results of the fitting procedure give $f=0.76+/-0.06$ at 10 K, which rapidly decreases to approximately $f=0.3+/-0.2$ at 55 K.

In summary, we have observed NFS from Kr not only in bulk films but also from a monolayer coverage on exfoliated graphite. From the Kr-on-graphite data, estimates of the Lamb-Mössbauer factor were obtained by fitting the data to the expression for NFS for an unsplit line. Recently, precision measurements of the Lamb-Mössbauer factor using NFS from ^{57}Fe have been performed.[9] The results of this study indicate that a large resonant thickness (say, $\chi>3$) aids the analysis by producing significant Bessel function oscillations in the observed spectra which depend sensitively on the value of f. In the data presented here, however, the thickness is relatively small ($\chi\sim 1.2$ at 10 K). By simply replacing the natural Kr gas in the present sample cell with isotopically enriched Kr, the resonant thickness is increased by approximately a factor of 7. We are currently investigating the use of such samples in studies to elucidate details in the Kr-on-graphite phase diagram by measurement of changes in the Lamb-Mössbauer factor as a function of temperature and coverage.

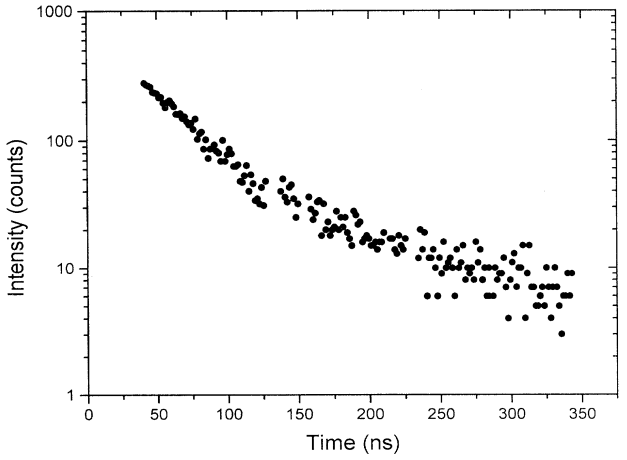

FIG. 1. Typical spectrum observed from Kr condensed on a Be foil at $T=10$ K. The total collection time for this spectrum was 3 h.

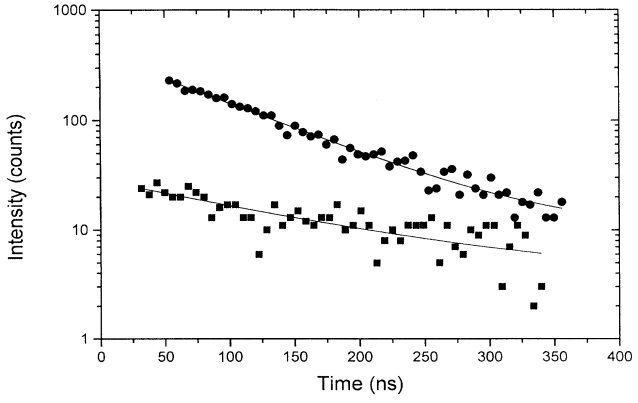

FIG. 2. Time spectra from monolayer Kr adsorbed on graphite at $T=10$ (represented by circles) and 55 K (represented by squares). The solid lines represent fits to the data. Collection time for each spectrum was approximately 3 h. Four-channel summing was used on each data set.

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