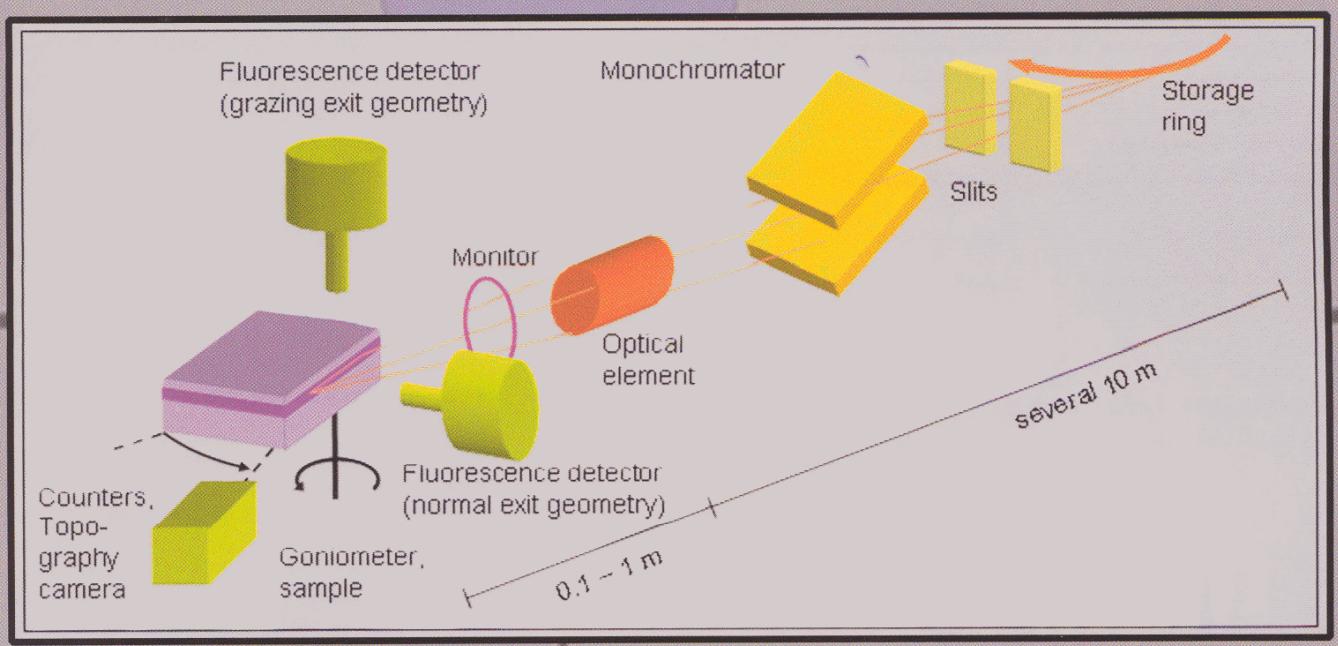
SRN

Synchrotron Radiation News
May/June 2004 • Vol. 17, No. 3

X-ray Standing Waves



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Spectroscopic Characterization of Buried Interfaces Using Soft X-ray Standing Waves

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Introduction

Buried solid-solid interfaces are ubiquitous in nanoscience and nanotechnology, and their properties are thus becoming more important in many areas of application, for example in magnetic read heads, magnetic data storage devices, and semiconductor logic devices. Due to the continuous shrinkage of the various layers and elements in these devices into the nanometer range, the thickness of the interfaces and their degree of roughness, as well as the variation across them of composition, of the chemical and magnetic states of their various constituents, and of the detailed valence electronic structure, all represent important microscopic properties that can strongly influence macroscopic properties such as electrical conductivity and magnetism.

Perhaps the most powerful method at present for studying buried interfaces is scanning transmission electron microscopy (STEM), but this requires sectioning and thinning of samples, and so cannot be considered to be non-destructive. With energy loss spectroscopy (ELS), STEM can however provide spectroscopic information that is roughly equivalent to X-ray absorption spectroscopy (XAS) as to element distributions and chemical states across interfaces, with the best instruments at present yielding energy resolutions of a few tenths of eV. However, the degree of magnetic information in this type of measurement is limited, and the resulting XAS-like spectra must sometimes be interpreted more or less in a fingerprint mode to identify chemical states.

Turning to the various synchrotron radiation techniques, we note that some sensitivity to buried interfaces can be achieved by going into combinations of X-ray incidence angle and photon energy (e.g. near resonances) in which the radiation is selectively reflected at a buried interface, rather than at the outermost surface. Such photon in/photon out measurements have permitted determining both chemical and magnetic roughnesses at buried interfaces [1]. However, if we now turn to the powerful set of measurements involving photon in/electron out, as e.g. core and valence photoemission or measurements based on secondary electron yields, the small electron escape depths imply a high degree of surface sensitivity that makes the direct observation of buried-interface properties difficult. In some cases, chemical shifts of features in photoemission or X-ray absorption at the interface can permit deconvoluting them [2], but this procedure cannot be relied upon for all cases.

We here discuss a new method for spectroscopically characterizing buried interfaces using soft X-ray standing waves that permits much more quantitatively analyzing compositions, chemical and magnetic structure, and electronic structure [3, 4]. Although we will illustrate the method for a system of interest in thin-film magnetism (the Fe/Cr interface that exhibits giant magnetoresistance), the method should be much more broadly applicable to other classes of sample. We will also discuss here only the use of photoemission as the relevant measurement, but expanding the method to involve soft X-ray emission also represents a very promising direction for future study, as discussed later.

Probing buried magnetic interfaces with soft X-ray standing wave spectroscopies

The basic idea of this method is to grow the sample to be studied on top of a high-quality synthetic multilayer mirror of the type used in many SR optical systems, and to use this mirror to generate a strong soft X-ray standing wave (SW) inside the sample [3]. Combining this with the often-used idea of growing the sample in a variable-thickness wedge form permits effectively scanning the standing wave through the sample by translating the sample along the wedge direction under a reasonably well focused exciting X-ray beam whose dimensions are much less than the wedge length [4, 5]. Experimental geometry for studying the Fe/Cr interface is illustrated in Figure 1. The multilayer in Figure 1 is made up of 40 bilayers of B_4C and W (although many other pairs of materials are possible), with a period of 40 Å. The radiation is incident at the first-order Bragg angle, as defined by $\lambda_x = 2d_{ML} \sin \theta_{inc}$, which for the energy of 825 eV at which the measurements to be discussed have been carried out, is about 11°. The reflectivity R is then calculated to be roughly 5%. (It is not necessary to measure reflectivity in the soft X-ray regime for these spectroscopic measurements, although the multilayer is always first characterized by measuring its hard X-ray reflectivity.) Since a standard analysis of standing wave formation further indicates that the fractional modulation of the standing wave strength as measured by the square of its electric field will be given by roughly $4\sqrt{R}$, a 5% reflectivity implies a strong ±45% modulation relative to the incident wave field strength. The standing wave period as judged via the square of its electric field will also be equal to the multilayer period. The wedge form of

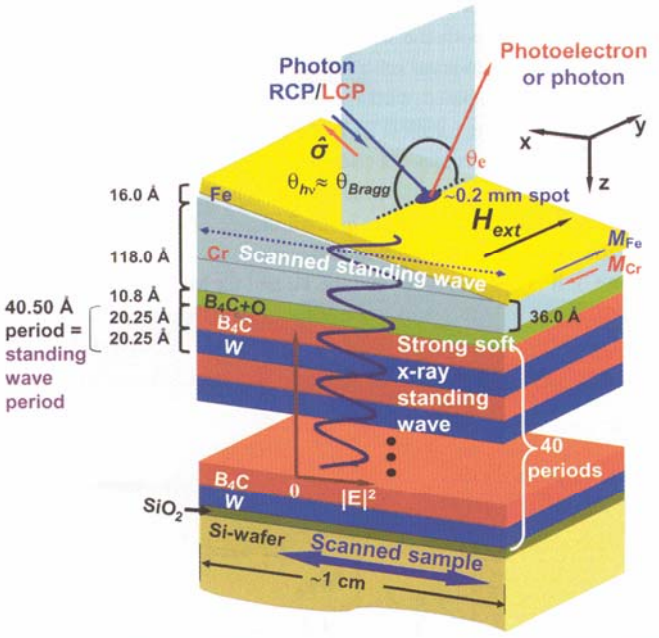

Figure 1: Basic geometry of an experiment combining soft X-ray excitation of photoemission (or in future experiments also X-ray emission) with a wedge-shaped bilayer sample grown on a multilayer-mirror standing wave generator (SWG) so as to selectively study the buried interface between Fe and Cr. Scanning the sample position along the x axis effectively scans the standing wave through the interface. [From ref. 4.]

the bilayer Fe/Cr sample, which was about 10 mm in length, combined with the small X-ray spot of about 0.1 mm in width then permits scanning the standing wave through the interface simply by translating the sample along the *x* direction in Figure 1.

Important to note here is that, by creating a standing wave of a few nm in period, we can probe structures of the order of nanometers, and with resolutions that we will show to be only fractions of a nanometer. We note also that, in one prior study, standing waves created by soft X-rays in the ~1 keV range have been used to study crystals that inherently have layer spacings in the few-nm regime [6]. By comparison, most configurations of harder X-ray standing wave measurements produce standing waves of too-small periods to selectively study interfaces between layers with typical spacings of nanometers, although some studies have used either grazing incidence reflectivity [7] or reflectivity from similar multilayers [8] to achieve nm-scale standing-wave periods.

We now consider some specific illustrative results for this particular Fe/Cr sample. In Figure 2, we show the variation of the *Cr 3p/Fe 3p* intensity ratio with both incidence-angle variation (left panel—a more standard type of "rocking curve" measurement, although rocking curves are usually plotted based on reflectivity) and sample-position variation (right panel). Either of these variations is expected to move the standing wave with respect to the interface, and it is clear that the form of the ratio-based rocking curve depends strongly on sample position, and that the phase of the modulation of the ratio changes with a change in X-ray incidence angle. These data have been analyzed using a specially-written computer program due to Yang [9], which includes all relevant X-ray optical (XRO) effects, as well as photoelectric cross sections and inelastic escape depths. Fitting these experimental results with the simple two-parameter linear model shown at left in Figure 3 for the variation of Fe and Cr compositions with depth (the depth at which the interface begins and the thickness over which the composition goes from 100% Fe to 100% Cr) yields via a trial-and-error search the values shown at left in the figure. The mean interface depth of 12.8 Å + 6.8/2 Å = 16.2 Å so determined is in excellent agreement with that expected from the thickness monitor during deposition, and the interface thickness of 6.8 Å is also consistent with a separate measurement on a similar sample using STEM. These simple core-level photoemission measurements thus im-

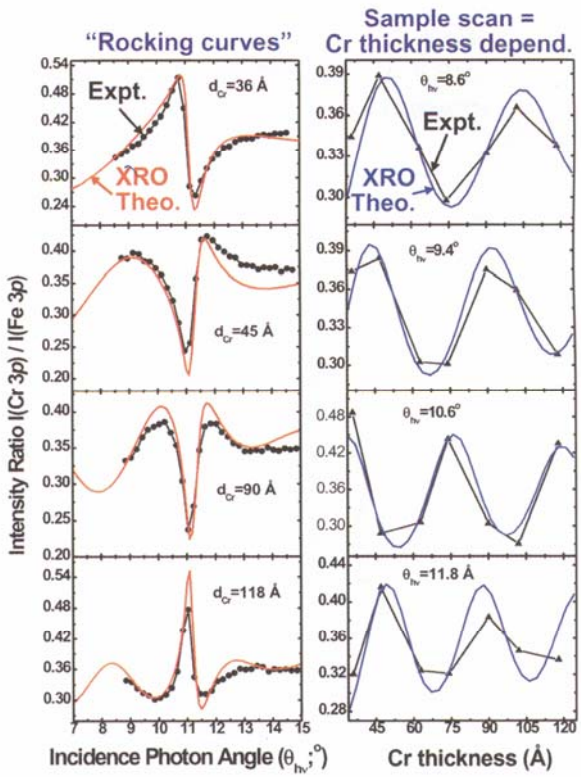

Figure 2: The ratio of the Cr 3p and Fe 3p intensities from the sample in Fig. 1 is plotted as a function of the incidence angle of the 825 eV soft X-rays (a sort of "rocking curve") for different sample positions along the x-direction in Fig. 1 (left panel), and as a function of the sample position for different incidence angles (right panel). [From ref. 4.]

mediately illustrate the ability of this method to non-destructively determine interface depths and composition profiles.

Beyond this, if the top Fe layer is magnetized, it is now possible to make use of magnetic circular dichroism (MCD) in core photoemission to determine the magnetization profiles of both Fe and Cr. Note that Cr is normally antiferromagnetic and thus should not show any MCD signal. Some results of this type are shown in Figure 4, where *Fe 2p* and *Cr 2p* spectra excited by right-circular polarized radiation (blue curves) and left-circular polarized radiation (red curves) yield reproducible and different MCD effects (black difference curves) for two special positions of the standing wave with respect to the interface: position *B* with the SW maximum at the interface and position *C* with its minimum at the interface. It is well known that such spin-orbit-split spectra ($j = \ell \pm 1/2 = 3/2$ and $1/2$ for the $2p$ cases here) will exhibit magnetic circular dichroism effects, with the basic origin being the effective exchange splitting of the various m_j sublevels in each j state due to the sample magnetization, combined with the polarization-dependent photoemission matrix elements for these m_j sublevels. A simple theoretical explanation of these effects appears elsewhere [10], but since the systematics of them are very well established, even with no theoretical analysis, we can easily sees that Cr exhibits a small degree of ferromagnetic order near the interface (point B) which decreases away from the interface (point C). It is also apparent that the Fe and Cr MCD effects show opposite tendencies at the two SW positions (Fe is weaker at position B, Cr is stronger). Furthermore, from the fact that the Fe MCD is first positive, then negative, on crossing the *Fe* $2p_{3/2}$ edge, whereas Cr shows the

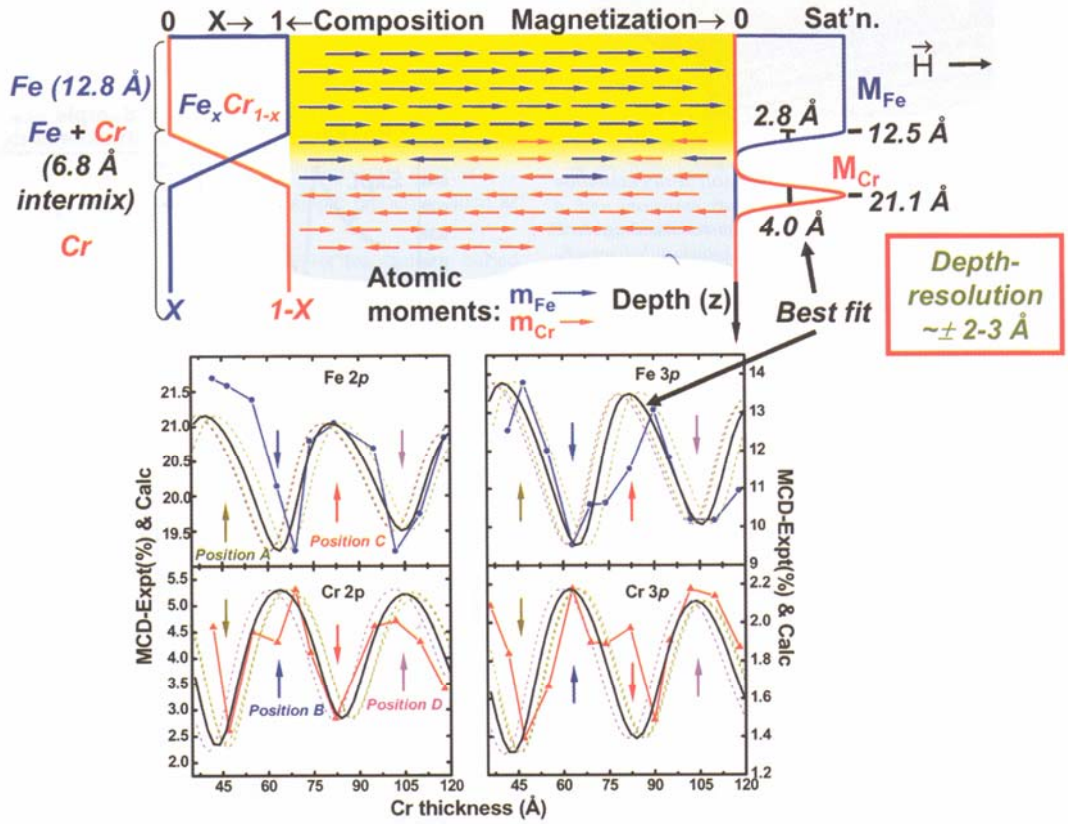

Figure 3: (Upper panel) The Fe/Cr interface quantities that have been derived from an analysis of standing-wave-excited photoemission results: at left are the concentration profiles, assumed to be linear in fitting the data of Fig. 2; at right are magnetization profiles, assumed to be gaussian in fitting the magnetic circular dichroism data in the lower panel. (Lower panel) Magnetic circular dichroism data for Fe 2p and 3p, as well as Cr 2p and 3p photoemission as a function of standing wave position relative to the Fe/Cr interface. Theoretical curves are shown for the best fit (solid line) as well as for typical variations of the magnetization parameters of about 3 Å away from this.

opposite variation, we can conclude that the Cr magnetization is opposite to that of Fe, as schematically shown by the arrows in Figures 1 and 3. Note here that the small X-ray incidence angle of only about 11° implies via the geometry in Figure 3 that these data are sensitive primarily to the in-plane (y) magnetizations of both species. Going beyond this analysis at the two positions B and C, the MCD of both species can be measured in detail as a function of standing-wave position, and with redundancy by looking at both the $2p$ and $3p$ levels, yielding the oscillatory data shown at the bottom of Figure 3. Analyzing these data with the same computer program, but now including the radiation polarization effects, via two-parameter gaussian models as shown at right in Figure 2 finally yields a determination of the magnetization profiles of both Fe and Cr through the interface. The Fe magnetization is found to decrease just as its composition begins to fall from 100%, going to zero at the bottom of the compositional interface. The oppositely oriented Cr magnetization on the other hand appears to be only about one atomic layer in thickness, and to be situated just below the interface.

The information thus determined for this ferromagnetic-antiferromagnetic interface is thus of relevance for understanding its giant magnetoresistance. In subsequent work, a multilayer structure of relevance to magnetic tunnel junction behavior has also been successfully studied using this SW + Wedge sample approach [11]; for this case, chemical shifts of the core levels of the various components and valence-band densities of states have provided further important information. Overall, this work illustrates the ability to non-destructively probe chemical composition, chemical and magnetic state, and valence electronic structure through an interface, with energy resolutions in the 0.1 eV range and making use of all of the physical effects present in photoelectron spectra (chemical shifts [11], multiplet splittings [4], valence densities of states [11]).

Future prospects

Looking to the future of such studies, we illustrate several possibilities in Figure 5. We first consider changes in the basic way the experiment is carried out. Other pairs of materials can be used for the multilayer mirror, including some that can be grown epitaxially, thus permitting the growth of epitaxial samples as well. The multilayer period (which as noted is equal to the standing wave period) can be reduced to 25–30 Å,

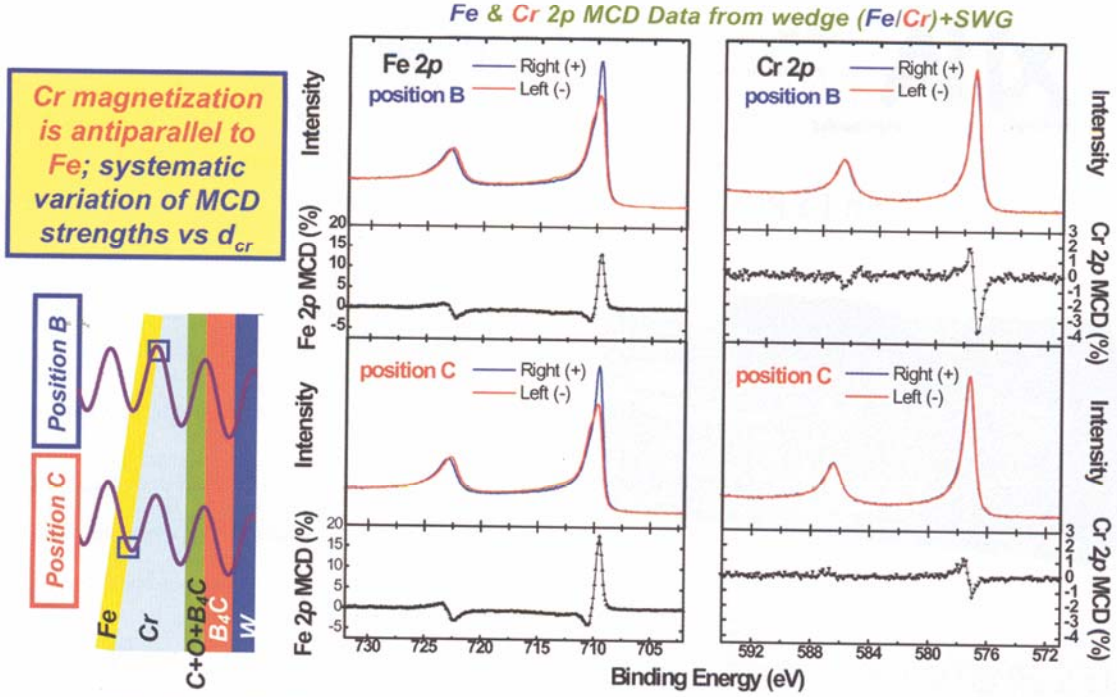

Figure 4: Fe 2p and Cr 2p photoelectron spectra obtained with right-circular and left-circular polarized radiation and at two sample positions corresponding to having the standing wave maximum at the interface (position B) and the minimum at the interface (position C). The difference of these two polarizations is the magnetic circular dichroism (MCD), which in turn measures the net magnetization of Fe and Cr. From the form and magnitudes of these curves, it is evident that Cr is magnetized anti-parallel to Fe, and that the Cr and Fe signals vary in different ways as the standing wave moves through the interface. More detailed data as a function of standing wave position are shown in the lower panel of Figure 3.

if not smaller, thereby increasing the precision with which vertical distances can be determined. The photon energy can be lowered while still maintaining a sufficiently high reflectivity to carry out standing wave experiments, thus permitting measurements with higher energy resolutions and leading for a given multilayer period to higher Bragg angles and thus in MCD measurements more sensitivity to the perpendicular (z) component of magnetization. Finally, if instead of photoelectron emission, soft X-ray emission is detected by a suitable spectrometer, the depth profile of the emitted photons will follow much more closely the profile of the standing wave, since the attenuation lengths for X-rays are much greater than those for electrons. This should permit more accurate determinations of various depth profiles [5].

Some possible future areas of application are also shown at right in Figure 5. These include various multilayer structures of interest in magnetism and semiconductor technology, self-assembled monolayers or other nanoparticles deposited on surfaces, and finally, in conjunction with laterally resolving (x, y) spectromicroscopes [2], the possibility of adding more quantitative information on the third (z = vertical) dimension in images.

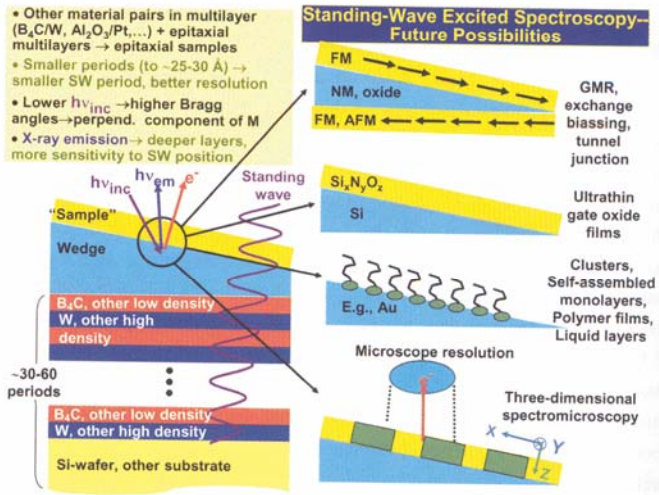

Figure 5: Some possible future directions for such standing-wave excited spectroscopy, including both variations on the experimental methodology (upper left panel) and the type of system to be studied (right panel).

To be sure, all of these ideas carry with them the requirement of growing the sample on top of a multilayer mirror, thus preventing studies of certain types of system and limiting any kind of annealing or heat treatment to temperatures over which the mirror is stable, but even in view of this, there appear to be considerable future possibilities for applying this approach to a range of buried interface studies. ■

Acknowledgments

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Science and Engineering Division, U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and by IBM Almaden Research Center.

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