

# A spherical electrostatic spectrometer for surface Mössbauer studies

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The construction and operation of an ultrahigh-vacuum spherical electrostatic spectrometer for surface Mössbauer studies is reported. Data are presented which suggest that the recoil-free fraction at room temperature of very thin oxide layers on the surface of an iron foil is low.

## INTRODUCTION

The purpose of this paper is to present details of a high-transmission spectrometer for Mössbauer spectroscopy with energy resolution of the conversion electrons. We also discuss the potential of such devices for depth-selective surface analysis.

The recoil-free resonant absorption of gamma rays by Mössbauer nuclei is followed by their de-excitation, which takes place by either the reemission of gamma rays, or x rays, or internal conversion electrons accompanied by Auger electrons. Most of the Mössbauer experiments involve the detection of gamma rays transmitted through an absorber, which has provided a wealth of information relating to the bulk properties of solids.<sup>1</sup> However, a second mode exists involving the detection of electrons. This method has the advantage of smaller backgrounds, and since the escape depth of the emitted electrons is much smaller than that of gamma rays and x rays, the method is much more surface sensitive.<sup>2</sup> For the most widely used <sup>57</sup>Fe Mössbauer isotope, the surface layer probed is about 250 nm thick if all the electrons are detected with no attempt at energy resolution, and use of this mode has also yielded a wealth of information.<sup>2</sup> However, the inelastic mean free path of electrons in the solid state is small,<sup>3</sup> being of the order of  $15\sqrt{\text{KE}} \text{ \AA}$  if the electron kinetic energy (KE) is measured in keV, and the amount of energy lost in the average inelastic collision is typically 15–20 eV. Thus, if the conversion or Auger electrons are energy selected to restrict detection to the “no-loss” electrons, the surface sensitivity can be greatly enhanced.<sup>4</sup>

This apparently simple experiment has only been exploited to a limited extent until now because of the enormous loss in integrated signal intensity as a result of the energy selection. Restriction of the conversion electrons to a 1% bandpass is likely to reduce the total signal by a factor of about 100, even if the electron-energy analyzer transmits 100% of the electrons emitted in a  $4\pi$  solid angle. Indeed, a typical analyzer for x-ray photoelectron spectroscopy, with an energy resolution of about 0.01% and a transmission of about 0.1% of  $4\pi$ , would reduce the signal by a factor of nearly  $10^6$ . Because the average electron-energy loss per collision is so high, the crucial factor in choice of an electron analyzer for Mössbauer spectroscopy is in fact the transmis-

sion, and not the energy resolution. This is especially true for studies of the first monolayer(s) of a surface without the influence of contamination.

Various types of electrostatic analyzers have been used (a list is given in Ref. 4; the latest electrostatic Mössbauer system is described in Ref. 5), and the highest transmission (13% of  $4\pi$ ) is probably that of a spherical spectrometer constructed by Yang *et al.*<sup>6</sup> The energy resolution of all constructed electrostatic spectrometers is comparable, although their transmission differs significantly. There are, however, few reports in the literature which allow one to assess the rate of data acquisition and the feasibility of, for instance, true depth profiling experiments using energy-selective conversion electron Mössbauer spectroscopy. It is this need which we attempt to treat here. The Mössbauer system constructed is an ultrahigh-vacuum system with a spherical electrostatic analyzer similar to that of Yang *et al.*<sup>6</sup> and with the possibility of performing measurements between liquid-nitrogen and room temperatures. We will illustrate its use with spectra from <sup>57</sup>Fe-enriched Fe samples and discuss the limitations of such measurements.

## I. SYSTEM DESCRIPTION

The operating principles of an electrostatic spherical analyzer have been demonstrated a long time ago.<sup>7,8</sup> The main result is the calibration equation  $E_0 = e\Delta V / (R_0/R_1 - R_1/R_0)$ , where  $E_0$  is the pass energy and  $\Delta V$  is the potential difference between the inner and outer spheres, whose radii are, respectively,  $R_1$  and  $R_0$ . When these radii are chosen properly, i.e., not too small and sufficiently separated, the resolution  $R$  and the transmission  $T$  depend only on the exit angle  $\chi$  of the analyzer. An angle  $\chi = 0$  would correspond to electron orbits traversing the full  $180^\circ$ . For a point source these relations are  $R \equiv \Delta E/E = (\chi/4)^2$  and  $T = \chi/4$  (fraction of  $4\pi$ ). The maximum escape angle  $\alpha$  of the electrons relative to the surface plane is given by  $\sin \alpha = \chi/2$ .

The main limitation on the choice of construction parameters is the overall size of the spectrometer, which has to fit into an ultrahigh-vacuum (UHV) system. We chose, therefore,  $R_0 = 150.5$  mm and  $R_1 = 116.0$  mm. The optimum exit angle then is  $\chi = 30^\circ = 0.52$  rad. This means that

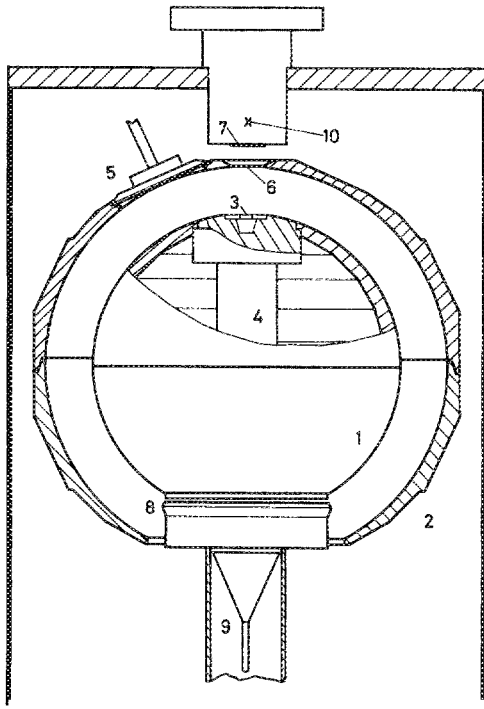


FIG. 1. Schematic view of the electrostatic spherical analyzer. (1) Inner sphere, (2) outer sphere, (3) sample holder, (4) cold finger, (5) sample access port, (6) Al window, (7) Be window, (8) adjustable slit, (9) channeltron, and (10) Mössbauer source position.

the analyzer constant  $e\Delta V/E_0$  is 0.527. The theoretical limits on  $R$  and  $T$  (for a point source) are  $R = 1.7\%$  and  $T = 13\%$  of  $4\pi$ . The maximum escape angle for the electrons to be detected is  $\alpha = 15^\circ = 0.26$  rad. This means at the same time that the effective probing depth relative to perpendicular escape angles is smaller by a factor of 0.26, which is important for surface analysis. For a disk source with a radius of 5 mm, the actual resolution reduces to  $R = 2.1\%$ .<sup>6</sup>

A schematic view of the spherical analyzer is presented in Fig. 1. Photographs of the actual surface Mössbauer spectrometer are presented in Fig. 2. As can be seen, both the inner and outer spheres are almost completely closed to assure high uniformity of the dispersive electric field. The spheres were preformed of nonmagnetic austenitic stainless-steel RVS316Ti (Technische Handelsonderneming "Muyser B.V.", Postbus 35, 2860 AA Berg Ambacht, The Netherlands) and then further worked to reduce weight and increase sphericity. The inner sphere is made of two halves that were first welded together with a rather deep weld and only then turned on a lathe to the required sphericity. This procedure, although not common practice in UHV work, resulted in a connection without any detectable leaks. Also, this weld was tested to be nonmagnetic. The sphere can be filled with liquid nitrogen. The sample to be investigated is placed at the pole of this sphere on a copper sample holder to prevent radiation from the Mössbauer source hitting any

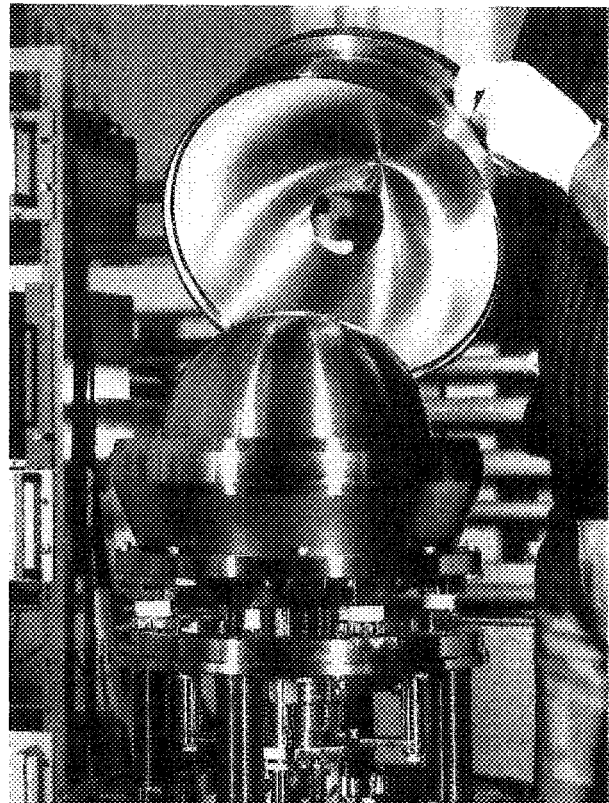
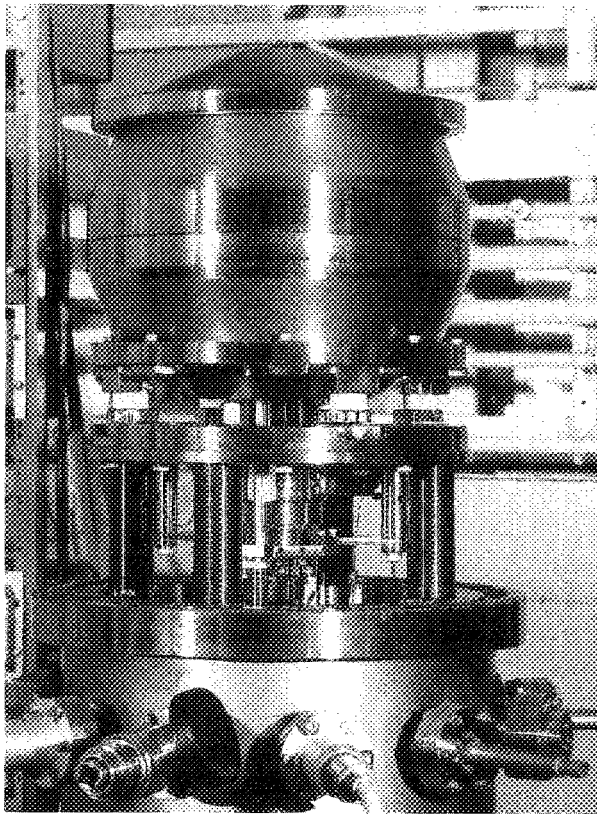


FIG. 2. Photograph of the actual surface Mössbauer spectrometer: (a) fully mounted; (b) top of outer sphere removed.

stainless-steel parts, with consequent emission of electrons from Fe in the steel. By means of a massive copper "cold finger" extending into the liquid-nitrogen reservoir, the sample can be cooled to 77 K.

The outer sphere, whose top is demountable, has a "window" at the top to let the radiation from the Mössbauer source reach the sample. To minimize field inhomogeneities, this window is covered with a thin aluminum foil. The same holds for the sample access port in this sphere. Normally this port is closed with a lid. To change samples and for *in situ* sample preparation, this lid can be retracted and the sample can be picked up from its measurement position.

The slit at the exit of the analyzer is movable and can be adjusted to obtain the optimum resolution versus transmission or to increase the transmission (at the cost of resolution). The inner sphere has a small lip at this point. This is to prevent entrance into the electron counter of low-energy (secondary) electrons that might skim over the surface of the sphere. The slit can be set at a variable potential to improve the field pattern at the exit stage of the analyzer. Behind the slit a single-channel electron multiplier with a very wide (50-mm-diam) entrance cone<sup>9</sup> is mounted to detect the electrons.

The Mössbauer source is mounted on a transducer outside the UHV system for ease and safety of operation. A vacuum-tight beryllium window welded to a UHV flange (by Electrofusion Corporation, 25 Constitution Drive, Menlo Park, CA 940425) allows the radiation to pass. The source-to-sample distance is chosen to be 7 cm. A shorter distance, even with the source penetrating the outer sphere of the analyzer, would have been possible and would have increased the radiation intensity at the sample. Apart from field inhomogeneities, a shorter distance would cause distortion of the usual Lorentzian line shape in the Mössbauer spectra due to geometric effects,<sup>10</sup> which, however, one might find acceptable in view of the intensity problems described later.

The spherical analyzer is mounted in a custom-built bakable UHV system (Varian) pumped with 120- $\ell$ /s ion getter pumps and a 1000- $\ell$ /s liquid-nitrogen-cooled Ti sublimation pump to a base pressure of about  $10^{-10}$  Torr. The high voltages applied to the outer sphere, the slit, and the sample can be controlled by a microprocessor system that is also used as a multichannel analyzer and controller for the Mössbauer spectrometer. Velocity calibration is achieved using a Michelson interferometer.<sup>11</sup>

## II. SYSTEM OPERATION

The ion pumps used introduced unacceptable noise at the channeltron due to charged-particle emission, which could only slightly be reduced by inserting a mesh or a baffle on a small potential between the pumps and the analyzer. With the ion pumps on, the noise was typically 500 c/s at  $10^{-7}$  Torr and 50 c/s at  $10^{-9}$  Torr. Therefore, during measurements, the ion pumps were switched off and only the Ti sublimation pump was used. Occasional pumping with the ion pumps, with the measurement interrupted, was sufficient to keep low the level of light residual inert gases that are not pumped by the sublimation pump.

In order to measure the energy spectrum of internal conversion and Auger electrons emitted in the decay of the 14.4-keV state of <sup>57</sup>Fe, a 60- $\mu$ Ci source, prepared by electrodeposition of <sup>57</sup>CoCl<sub>2</sub> on an aluminum plate, was placed at the sample position. The spectrum is shown in Fig. 3. All expected conversion and Auger peaks are visible down to the smallest energies. The energy resolution of the 7.3-keV *K*-conversion peak is 3.5%, which is slightly larger than the expected value. This might be due to contamination of the surface of the sample. The experimental analyzer constant is 0.51 and is close to the expected value of 0.527. Note the high inelastic background level just above the *LXY* Auger peak.

To test the performance of the system, <sup>57</sup>Fe Mössbauer spectra of two samples were recorded at room temperature. The first was a 100-nm Fe film (enriched to 95% in <sup>57</sup>Fe) on an Al substrate prepared in an ultrahigh vacuum (during evaporation of <sup>57</sup>Fe onto Al, the pressure rose to  $10^{-8}$  Torr). This sample had been exposed to air for many weeks, so that one would expect it to be covered with an oxide layer. The Mössbauer spectrum of this sample [Fig. 4(a)] measured with a 10-mCi <sup>57</sup>Co (Rh) source and with the spectrometer set at the *K*-conversion electron energy shows only the six-line Zeeman pattern due to alpha-iron, which is surprising in view of the sample history. The fitted parameters [isomer shift (relative to the source)  $\delta = -0.104(2)$  mm/s and hyperfine magnetic field  $H = 329.5(0.9)$  kOe] correspond indeed to  $\alpha$ -Fe.<sup>12</sup> It should be stressed that the base line corresponds to only 3890 counts and the effect is high.

The second sample was in the form of 12.7  $\mu$ m Fe foil (enriched in <sup>57</sup>Fe to 95%). It was cleaned in UHV by Ar sputtering and then transferred, via air, to the Mössbauer spectrometer. Control x-ray photoelectron (XPS) measurements of this sample indicated that it was covered with about 10–15 Å of Fe oxides during the Mössbauer experiment. The foil Mössbauer spectrum measured with a 60-mCi <sup>57</sup>Co (Rh) source and with the spectrometer set at the *K*-conversion electron energy [Fig. 4(b)] clearly shows the presence at the surface not only of Fe metal, but also of Fe oxide contaminants. To determine these contaminants, the Mössbauer spectrum was fitted to three subspectra: two Zeeman patterns [patterns  $\beta$  and  $\gamma$  in Fig. 4(b)] characterized by parameters  $\delta_i$  and  $H_i$  ( $i = 1, 2$ ) and one doublet [pattern  $\alpha$  in Fig. 4(b)]

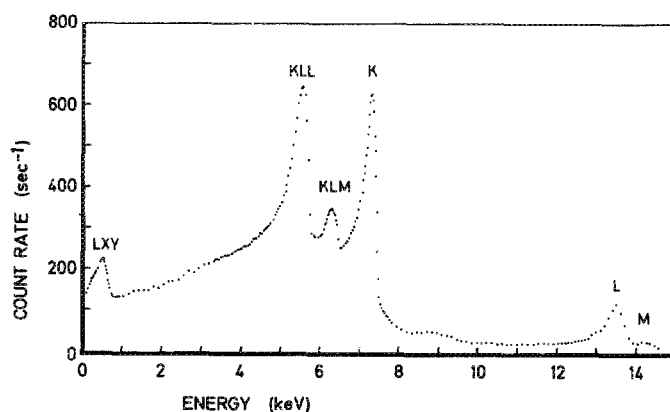


FIG. 3. Energy spectrum of electrons emitted from <sup>57</sup>Co  $\beta$  source (<sup>57</sup>CoCl<sub>2</sub> electrodeposited on Al), showing the *K*, *L*, and *M* conversion electrons, as well as the *KLL* and other Auger electrons.

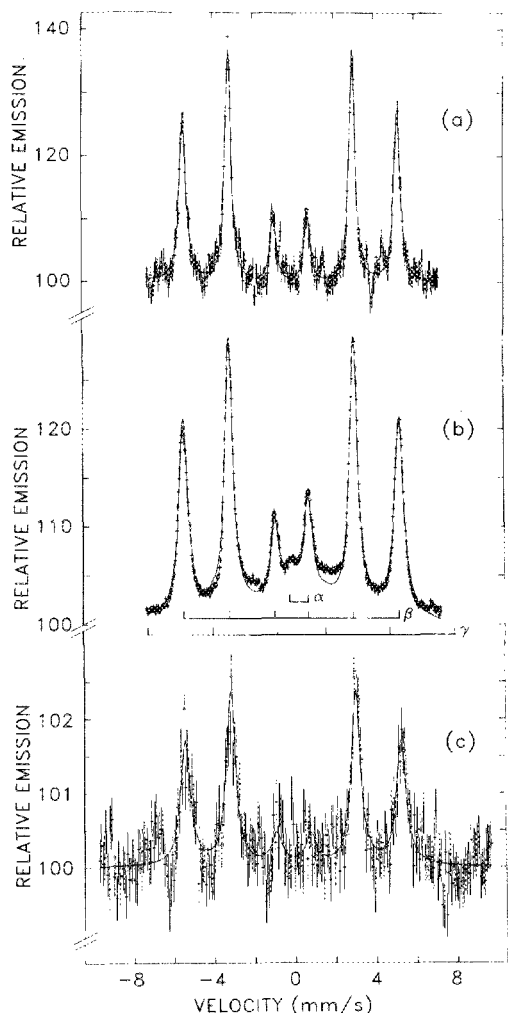


FIG. 4.  $^{57}\text{Fe}$  Mössbauer spectra of a 100-nm Fe film enriched in  $^{57}\text{Fe}$  to 95% on an Al substrate [(a)], and of a 12.7- $\mu\text{m}$  Fe foil enriched in  $^{57}\text{Fe}$  to 95% [(b) and (c)]. The spectra (a) and (b) were measured using Fe  $K$ -conversion electrons, and for spectrum (c) the  $LXY$  Auger electrons were used. The solid line is a least-squares computer fit, as described in the text. The vertical bars indicate statistical error. The pattern designated  $\beta$  is that of  $\alpha$ -Fe. The  $\alpha$  and  $\gamma$  patterns are due to  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ , respectively.

characterized by parameters  $\delta_3$  and quadrupole splitting  $\Delta$ . Their values are  $\delta_1 = -0.106(3)$  mm/s,  $H_1 = 330.4(0.8)$  kOe,  $\delta_2 = 0.621(35)$  mm/s,  $H_2 = 470.6(5.5)$  kOe,  $\delta_3 = 0.265(33)$  mm/s, and  $\Delta = 0.913(102)$  mm/s. The first set of parameters corresponds to  $\alpha$ -Fe.<sup>12</sup> The second set of parameters is compatible with that of  $\text{Fe}_3\text{O}_4$ .<sup>13</sup> The parameters of the doublet correspond to ferric iron ions and are most probably due to the presence of small  $\text{Fe}_2\text{O}_3$  particles at the surface.<sup>14</sup> We thus conclude that the surface of the second sample is covered with iron oxides, most probably  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . However, the signal due to oxides is only a few percent of the total.

The spectrum of the second sample measured with an electron energy set at 550 eV ( $LXY$  Auger peak in Fig. 3) is shown in Fig. 4(c). In spite of its relatively low signal-to-noise ratio, there is clearly no contribution from the oxides, and the parameters of the observed Zeeman pattern [ $\delta = -0.102(6)$  mm/s,  $H = 331.0(1.3)$  kOe] are due to a  $\alpha$ -Fe. This is a very surprising result, since by using  $LXY$

Auger electrons one would expect an enhancement of the oxide contribution to the spectrum (see also Sec. III).

### III. DISCUSSION

We have constructed and operated an instrument for Mössbauer spectroscopy based on the principle of energy selection of the conversion electrons in order to assess the potential of this technique. We find, as expected, that the low intensity of the spectrum is a severe problem. Count rates at the peak  $KLL$  Auger or  $K$ -conversion energies were typically 0.08 counts per second with (a) 95% enriched  $^{57}\text{Fe}$  samples, (b) a 50-mCi source, and (c) a 70-mm source-sample distance.

The count rates might realistically be improved by a factor of 3–4, by increasing the activity of the Mössbauer source, and by a further factor of about 4 if the source-sample distance were reduced to 35 mm. The latter is, of course, at the cost of broadening of the Mössbauer spectrum due to the finite sample size and geometric factors. Such increases would not be sufficient to compensate for the decrease by a factor of about 50 in the signal from natural Fe in, for instance, steels due to the low abundance of  $^{57}\text{Fe}$  (2.14%). We thus conclude that the applications of a spectrometer such as ours to commercial steels have limited potential, unless more effective detection methods can be conceived e.g., use of position-sensitive detectors.

A surprising feature of the spectra show in Fig. 4 is the low intensity of features due to oxides. The electrons analyzed have low take-off angles  $\alpha$  with respect to the surface. At the  $K$ -conversion energy the electron inelastic mean free path is of the order of 50 Å and the mean escape depth of the electrons is  $50 \sin \alpha$  Å. Even if we assume an unrealistically high mean take-off angle of about  $20^\circ$ , the mean inelastic escape depth is less than 20 Å. The first sample [Fig. 4(a)] had been exposed to air for a considerable time and should have been heavily oxidized (it would not fit into our XPS spectrometer for a definitive test). The second sample was shown by XPS to be covered by an oxide film of about 15 Å thick, so that nearly half of the signal was expected to arise from oxides, instead of only a few percent, as observed [Fig. 4(b)]. We also observe no enhancement of the surface oxide contribution when the Mössbauer effect is monitored using the low-energy  $LXY$  Auger electrons [Fig. 4(c)].

Our failure to observe a Mössbauer signal commensurate with the amount of oxide layers on Fe samples is in agreement with the results of Belozerskii *et al.*<sup>15</sup> However, Staniek *et al.*<sup>16</sup> certainly did observe a spectral contribution from surface oxides, and variation of the surface oxide signal strength with chemical history of the sample clearly has to be further investigated. We see two possible explanations for the low intensity from the surface oxides. First, the top oxide layer may be nonresonant, i.e., the recoil-free fraction of this layer could be close to zero at room temperature for some oxides. This could be a result of, for instance, very small oxide crystallite size and weak coupling to the mass of the bulk material. Alternatively, the Mössbauer signal could be smeared out due to extreme chemical and morphological disorder in the surface layer. While the second explanation may not be so attractive because Mössbauer spectra of disor-

dered systems have been measured, little is known about the degree of disorder in ultrathin surface oxide layers, and it may be extremely high.

It is clearly of fundamental interest that the Mössbauer signal from thin oxide layers and bulk Fe is variable and not directly related to the concentration of Fe atoms in the environments. However, this variability would be disastrous for any applications in surface analysis and nondestructive depth profiling.

Finally, we note that one of the potentially most appealing features of Mössbauer spectroscopy with conversion electrons was the possibility to use the different information depths for Fe *KLL* and *LXY* Auger electrons. However, we find that the *LXY* Auger peak excited by resonant absorption of gamma rays has only approximately 15%–20% of the intensity in the peaks due to the Fe *KLL* Auger or the *K*-conversion electrons. Furthermore, this *LXY* peak sits on a background due to *KLL* and *K* electrons which were created deep in the solid and lost most of their energy during transport to the surface. This background, which will resonate with the signal due to the bulk, is more intense than the *LXY* signal itself. It reduces the surface contribution of the signal at the *LXY* energy by a factor of about 2.5. Clearly, exploitation of the *LXY* surface sensitivity requires a difference spectrum between the signal at the *LXY* energy and at slightly higher energies, which further exacerbates the problem of the low signal strength.

In view of the factors discussed above, we perceive the future of Mössbauer spectroscopy based on energy selection of the conversion electrons to lie in fundamental studies of surface magnetism and chemical bonding at well-defined surfaces, of the sort attempted by Korecki and Gradmann.<sup>5</sup> For these studies it will be necessary to take all possible measures to maximize the signal. It will also be necessary to improvise good, *in situ* sample-preparation facilities. Finally, great care will be necessary to ensure the best possible vacuum because of the very long counting times.

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<sup>1</sup>P. Gütlich, R. Link, and A. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry*, Vol. 3 of *Inorganic Chemistry Concepts* (Springer, Berlin, 1978).

<sup>2</sup>W. Keune, *Hyp. Inter.* **27**, 111 (1986).

<sup>3</sup>M. P. Seah and W. A. Dench, *Surf. Int. Anal.* **1**, 2 (1979).

<sup>4</sup>T. Toriyama, K. Asano, K. Saneyoshi, and K. Hisatake, *Nucl. Instrum. Methods B* **4**, 170 (1984).

<sup>5</sup>J. Korecki and U. Gradmann, *Hyp. Inter.* **28**, 931 (1986).

<sup>6</sup>T.-S. Yang, B. Kolk, T. Kachnowski, J. Trooster, and N. Benczer-Koller, *Nucl. Instrum. Methods* **197**, 545 (1982).

<sup>7</sup>R. H. Ritchie, J. S. Cheka, and R. D. Birkhoff, *Nucl. Instrum. Methods* **6**, 157 (1960).

<sup>8</sup>R. D. Birkhoff, J. M. Kohn, H. B. Eldridge, and R. H. Ritchie, *Nucl. Instrum. Methods* **8**, 313 (1960).

<sup>9</sup>Galileo Electron Optics Corp., model 4716.

<sup>10</sup>J. J. Bara and B. F. Bogacz, *Mössb. Eff. Ref. Data J.* **3**, 154 (1980).

<sup>11</sup>B. F. Otterloo, Z. M. Stadnik, and A. E. M. Swolfs, *Rev. Sci. Instrum.* **54**, 1574 (1983).

<sup>12</sup>J. G. Stevens, in *Handbook of Spectroscopy*, edited by J. W. Robinson (CRC, Boca Raton, FL 1981), Vol. III, pp. 403–528.

<sup>13</sup>B. J. Evans and Lu-San Pan, *J. Appl. Phys.* **61**, 4352 (1987).

<sup>14</sup>W. Kündig, H. Bömmel, G. Constabaris, and R. H. Lindquist, *Phys. Rev.* **142**, 327 (1966).

<sup>15</sup>G. N. Belozerskii, C. Bohm, T. Ekdahl, and D. Liljequist, *Nucl. Instrum. Methods* **192**, 539 (1982).

<sup>16</sup>S. Staniek, T. Shigematsu, W. Keune, and H.-D. Pfannes, *J. Magn. Magn. Mater.* **35**, 347 (1984).