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Mössbauer Spectroscopy by Scattered Electrons at 77 K

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A simple proportional counter has been designed for effective detection of low-energy electrons accompanying Mössbauer effect of the sample cooled at liquid nitrogen temperature (77 K). Pure helium gas, instead of Q gas (He+6% isobutane) usually used at room temperature, has been employed as a filling gas. Some features of the counter are described.

The penetration depth of electrons into a sample is much shorter than that of X-rays and γ rays with energies of the same order as the electrons. For example, in the case of ^{57}Fe Mössbauer measurements in the scattering geometry, the effective depth of a thin iron foil is the order of 10^3 Å for electrons accompanying Mössbauer effect, *i.e.,* 7.2-keV *K*-conversion electrons and about 5-keV Auger electrons emitted after the conversion process. On the other hand, the depth becomes the order of 1 μ for the scattered photons, *i.e.,* resonantly re-emitted 14.4-keV γ rays and 6.4-keV Fe *K* X-rays. We can, thus, find out a difference between the structure of a sample surface of the order of 10^3 Å and that as a bulk of the thickness more than 1 μ by comparing the two kinds of spectra; one is obtained by the scattered electrons and the other is by the scattered photons or by the 14.4-keV γ rays in the ordinary transmission geometry.

A proportional counter for detecting the scattered electrons was successfully designed by Swanson and Spijkerman[1~3] and also by our group.[4,5] With their proportional counters, more than 20% effect was easily obtained for an unenriched sample of stainless steel at room temperature. It was demonstrated that there exists a certain difference between the Mössbauer spectrum by the scattered electrons and that by the scattered X-rays for the samples of α iron and FeAl alloy.[5]

As a next step, it is interesting to extend this technique to the measurements at low temperature in order to obtain detailed information on the temperature dependence of Mössbauer parameters about the solid surface of the order of 10^3 Å. Following the previous works,[4,5] the proportional counter has been so improved that it can operate even at the temperature lower than that of liquid nitrogen (77 K).

The rare gas with the lowest atomic number, He, is usually used to detect low-energy electrons because of its insensitivity for X-rays and γ rays. In order to increase the mobility of electrons in the filling gas and surpress the self-discharge in the G-M region, a small amount of organic gases such as CO_2, CH_4, C_4H_{10} and CH_3OH is mixed in the He gas. Since quenching gases and other inpurities freeze on the counter wall at low temperature near 77 K and stain unfavorably the surface of a sample mounted inside the

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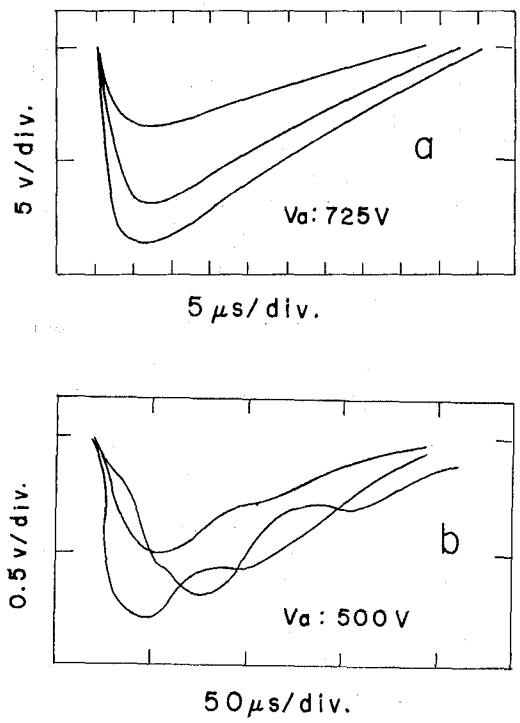

Fig. 1. Outputs signals from the counter. Pulse shapes of the preamplifier outputs when the counter is filled with Q gas and pure He gas are shown by figures a and b, respectively. V_a denotes the voltage applied to the anode wire.

counter, such a gas mixture is not available for the measurements at low temperature. In the present work, we have used pure ^{4}He gas as a filling gas.

The counter used in the present work is quite similar to the previous one;[4] it has a small sensitive volume consisting of a 4.5-mm thick Lucite frame with a square hole (14 mm × 14 mm). The anode is a 30-μ diam tungusten wire kept taut by a small steel spring. Aluminium is evaporated on inner sides of the frame to make it electrically conductive. One side of the hole is covered with a thin aluminium-evaporated Mylar film (1 mg/cm^2) while the other side is covered with a sample foil of unenriched Type 310 stainless steel to be studied.

Before Mössbauer measurements, filling the counter with pure ^{4}He gas or Q gas, we have examined its operation at various anode potentials. The sample in the counter was irradiated through the thin window film by collimated incident radiation from a Mössbauer source of about 1 mCi ^{57}Co diffused in copper. In this geometry, most of output signals from the counter are caused by electrons backscattered from the sample. The counter with Q gas operated in the proportional region at the anode potential ranging from 450 V to 650 V, while above 700 V it behaved as a G-M counter. When ^{4}He gas was used, the operating range became quite narrow; the proportional region was from 410 V to 440 V and its G-M region was at the voltages higher than 450 V. In Fig. 1 are shown the output signals from the counter with Q gas and with pure ^{4}He gas in the G-M region.

The risetimes of the signals from the ^{4}He counter ($\sim$15 μs) are much longer than those from the counter with Q gas ($\sim$2 μs). There appears very often pulses with zigzag shapes in outputs from the ^{4}He counter, as shown in Fig. 1b. Thus, output signals from the ^{4}He counter are a little unstable, but the counter is available for the Mössbauer measurements unnecessary for precise pulse-height analysis, as in the present work.

In order to cool the sample mounted in the counter at low temperature, we used a brass gas container specially designed, in which the counter was inserted, and then this container was mounted at the bottom of a cryostat. The entrance and exit windows of the container for incident radiation are 100-μ thick aluminium foils. The inside of the gas container is coated with a thin Lucite pipe of 0.5 mm thickness in order to reduce the unfavorable background counts due to electrons scattered from the brass wall. The signals from the counter feed to a coaxial cable of about 1 m in the cryostat through a hermetic seal connector soldered on the top of the container. This cable leads the signals to a charge-sensitive preamplifier mounted at the top of the cryostat through another hermetic seal connector. A phospher bronze bellow is used as a thermal conductor between the sample and the wall of the container. Indium wires of 1 mm diam are used as sealing materials to connect all components of the container and the cryostat. After the container was evacuated to a pressure of 10^{-4} torr and was warmed up to 80°C for about one day, pure ^{4}He gas of one atmosphere was led in it through 3-mm diam copper tube welded at the bottom of the container. The ^{4}He gas was sealed in the container by wrenching the inlet tube and soldering on its section.

We found that the output gain of the signals from the ^{4}He counter changes considerably at room temperature; the pulse height of the signal becomes gradually lower and almost saturates to about one tenth of the initial height after about one day. This may be caused by the outer gases from the counter assembly. To improve this problem, it may be helpful to use a container with larger volume and to bake it for a longer period than in the present case. Mössbauer measurements at room temperature were performed one day after ^{4}He gas was sealed off in the container. Nevertheless, we could not avoid a slight gain decrease of output signals of about 5% per day. When the counter assembly is cooled at 77 K, most of impurity gases in the container are trapped. This results in a sudden increase of the output gain. In order to count appropriate electron signals, we had to adjust a setting of the voltage applied to the anode wire and also the lower discriminator of a pulse-height analyzer at every run with a different temperature. The applied voltage was 480 V for the measurements at 300 K and 410 V for that at 77 K.

Mössbauer spectra of Type 310 stainless steel obtained at 300 K and 77 K by the scattered electrons are shown in Figs. 2a and 2b, respectively. The measuring period to get these spectra was about 120 hours. For comparison, the spectra obtained in the transmission geometry are also shown in Figs. 2c (at 300 K) and 2d (at 77 K). Detailed analysis of these spectra will be given elsewhere.

The present technique may be extended to the measurement at liquid helium temperature (4.2 K), as ^{4}He gas of one atmosphere at room temperature keeps gaseous state even at 4.2 K. Therefore, the counter with ^{3}He gas, as suggested in the previous work,[5] is not necessary at 4.2 K. The measurement at 4.2 K is now in progress.

The pulse with a zigzag shape in the outputs from the present pure ^{4}He counter may

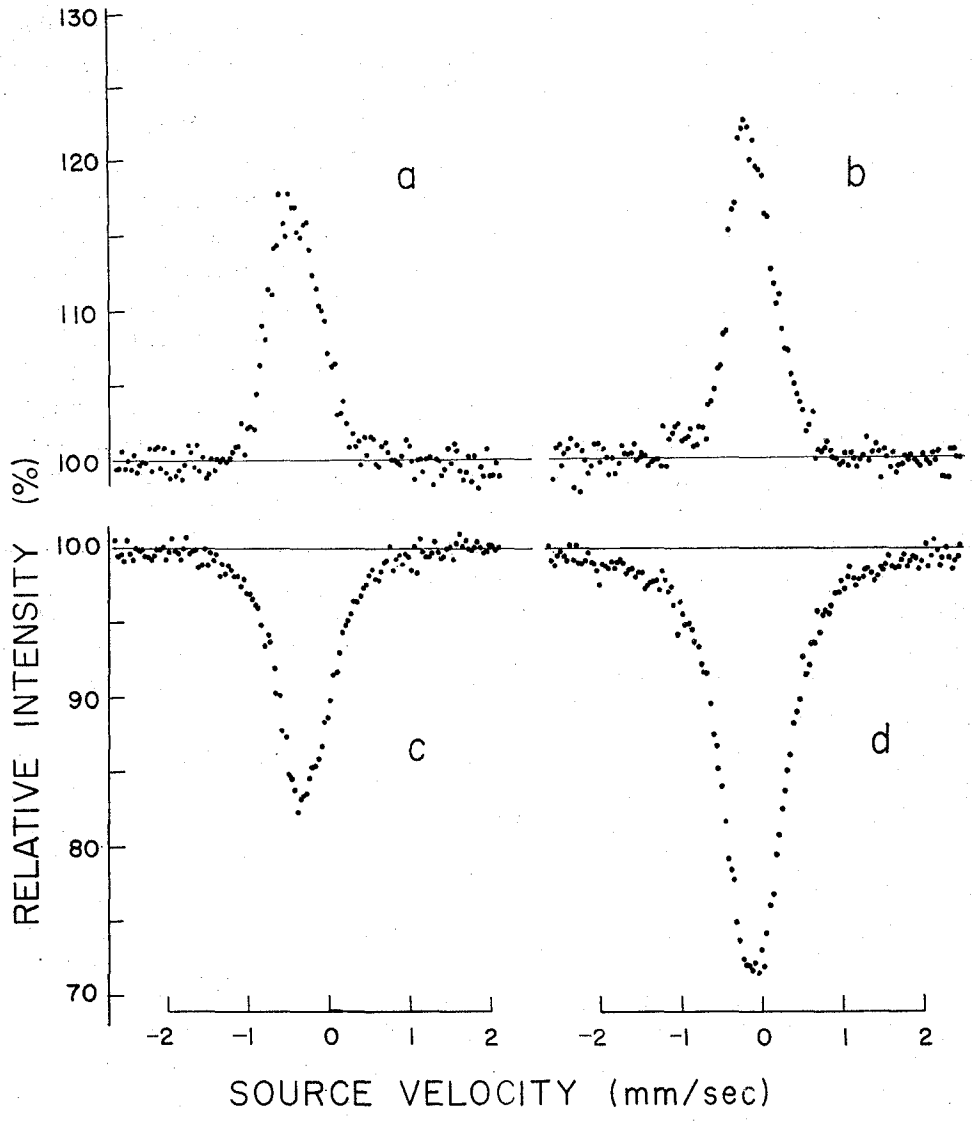

Fig. 2. Mössbauer spectra of Type 310 stainless steel. Spectra a and b are obtained by the present scattering method at 300 K and at 77 K, respectively. For comparison, spectra by the ordinay transmission method are shown by the figures c (at 300 K) and d (at 77 K).

be due to high-energy electrons created by the photoeffect or Compton scattering of 122-keV γ rays from the ^{57}Co source. These high-energy electrons leave rather long ionization tracks in the counter and collide with the counter wall several times to result in secondary electron emissions. Since the mobility of electrons in pure helium is much smaller than that in the gas mixture containing quenching gases, the signal has a zigzag shape corresponding to the long ionization track. This means that, by applying the technique of pulse-shape discrimination (PSD),[6] we can distinguish the signals due to Mössbauer effect from the spurious backgrounds caused by electrons with long ionization tracks. Refined measurements with PSD are also in progress.

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