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**APPLICATION OF A METHOD
OF FREQUENCY MODULATION MÖSSBAUER SPECTROSCOPY
IN ^{67}Zn TO THE PRECISE DETERMINATION
OF THE ELECTRIC QUADRUPOLE INTERACTION OF ^{67}ZnO (*)**

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Résumé. — Un cristal d'oxyde de zinc dopé de ^{67}Ga , oscille sous l'action de fréquences variables appliquées sur un cristal de quartz. Les modes de vibration des bandes résultant de la modulation de fréquence de la raie γ (énergie 93,26 keV) sont analysés par absorption à travers de l'oxyde de zinc. Les fréquences de séparation de l'état fondamental triplet ont été mesurées : $\nu_1 = 361,2 \pm 1,0$ kHz et $\nu_2 = 723 \pm 4$ kHz. Le couplage quadripolaire est $e^2 qQ = 2,408 \pm 0,006$ MHz, et le paramètre d'asymétrie est $\eta = 0,00 \left\{ \begin{array}{l} + 0,065 \\ - 0 \end{array} \right\}$. Nos mesures ont été effectuées à une température de 4,2 K.

Abstract. — A source containing ^{67}Ga in a ZnO single crystal was mechanically oscillated with varying frequency by a quartz crystal. The resulting f-m sidebands of the 93.26 keV γ -ray were thereby swept across the absorption lines of a ZnO absorber. The frequency separations of the ground state triplet are measured to be $\nu_1 = 361.2 \pm 1.0$ kHz and $\nu_2 = 723 \pm 4$ kHz. The quadrupole coupling is $e^2 qQ = 2.408 \pm 0.006$ MHz, and the asymmetry parameter is

$$\eta = 0.00 \left\{ \begin{array}{l} + 0.065 \\ - 0 \end{array} \right\}.$$

All measurements were made at 4.2 K.

In the following we shall describe a system of spectrometry for the Mössbauer effect which for certain special purposes surpasses the conventional doppler shift method. We have applied the method to a determination of the frequency separation of the hyperfine components in ZnO.

Ruby and Bolef [1] were the first to demonstrate frequency modulation of Mössbauer radiation by examining the velocity spectrum of a source (^{57}Co in stainless steel) while it was being mechanically moved at 20 MHz by a quartz crystal. They observed sidebands spaced apart by the velocity equivalent of 20 MHz, as expected; but the intensities were not in agreement with simple theory. The effect has been observed often since and has been used as a calibration method for velocity spectra; mainly for ^{57}Fe [2], but also by Beskrovny [3] and collaborators, for ^{67}Zn . The essential novelty in the present work is that we do not, except incidentally, do conventional Doppler spectroscopy, but we sweep the frequency instead of

the velocity. The sideband frequencies are thereby altered in a programmed manner and when a sideband coincides with an absorption line, there is a transmission dip, as in conventional spectroscopy.

If the frequency of the gamma ray is $\omega_0 = E_\gamma/h$ and the motional frequency of the source is ω_m , the radiation field amplitude has time dependence

$$\Phi(t) = e^{-\Gamma t/2} e^{i(\omega_0 t + a \sin \omega_m t)} \quad (1)$$

The intensity spectrum consists of a series of Lorentzian lines (*sidebands*) of width Γ centered at $\omega_0 \pm n\omega_m$, $n = 0, 1, 2, \dots$. The intensity of the n th sideband at the line center is

$$I_n = I_{-n} = J_n^2(a), \quad (2)$$

where J_n is the Bessel function of order n .

The quantity a , the modulation index, is the maximum deviation of the instantaneous phase of the radiation field from what it would be if the frequency were not modulated. It may also be defined by $a = \omega_d/\omega_m$, where ω_d is the maximum deviation in instantaneous frequency from ω_0 . Figure 1 is a plot of eq. (2) for the first few sidebands. We note that by choice of a one can fairly strongly emphasize a given sideband.

By sweeping the frequency over the range $\Delta\omega_m$, the transmission through an absorber can be investigated

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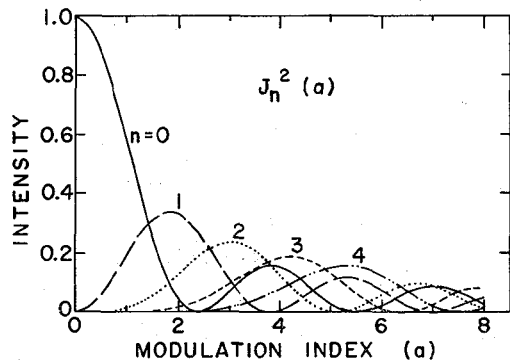


Fig. 1. — Plot of $J_n(a)$ for $n = 0, 1, 2, 3, 4$.

over a range $n(\Delta\omega_m)$. If the modulation is obtained by the Doppler effect with a vibrating driver, we have

$$a = kx_{\max} \quad (3)$$

where k is the magnitude of the gamma ray wave vector and x_{\max} is the amplitude of the motion. The magnitudes of a used in our experiments are less than a few radians, and $\omega_m > \Gamma$. In a conventional Mössbauer velocity experiment with sinusoidal drive, we have typically $\omega_m \ll \Gamma$ and $a \sim 10^8$. For the latter one invariably uses a time description, equivalent to eq. (1), while the frequency domain is more appropriate for our case.

We have used ZnO both as absorber and as source host. There is no detectable relative isomer shift. In such a case, the unshifted component, of amplitude $J_0(a)$, can simulate an absorption resonance, if a varies with frequency. If there were some isomer shift, the variation would result only in distortion of the line shape—generally a lesser evil. If the driver is a piezoelectric crystal with constant voltage amplitude V , piezoelectric coefficient D , and one side is fixed to a rigid backing,

$$a = kDV \quad (4)$$

and is independent of frequency as long as D is. The condition on D is not only non-trivial, it certainly does not hold in the neighborhood of mechanical resonance of the crystal. The spectral density of such resonances is $C(\omega) \sim U\omega^2/v^3$ where U is the crystal volume and v the sound velocity. Although it is not literally applicable to the region of sparse resonances at the bottom of the frequency range, the equation is nevertheless instructive. The ω^2 dependence guarantees that at a frequency only modestly above the lowest mechanical resonance, one will have difficulty finding an interval of adequate size that is free of them. In most experimental arrangements it is likely that one will appreciably excite a large fraction of the available resonances. Thus it is not only the thickness but all dimensions that enter into $C(\omega)$. Also, of course, U is not restricted to the driver volume, but includes appropriately weighted contributions from any tightly coupled supports or backing material, as well as from the source itself.

In the experiment of Cranshaw and Reivari [2] it was found that the sideband intensities were not consistent with a unique modulation index, but could be described by a distribution having a form first suggested by Abragam [4]. With their sample size and frequency (16 MHz), they operated in a region of many high order normal modes, the effect of which made different parts of their vibrating absorber essentially incoherent in phase. The situation is different here. The frequencies actually used are two orders of magnitude lower and we operate below the first detectable mechanical resonance. We have good evidence that only a single modulation index is needed for a good description of our radiation.

The transition in ^{67}Zn is $(1/2^-)_{\text{exc}} \rightarrow (5/2^-)_{\text{gnd}}$, one of a small class of retarded E2 transitions. The Zn^{++} ion is at the center of a slightly distorted tetrahedron of O^{--} ions, and in the absence of magnetic fields the ground state is split into a triplet as described by the quadrupole Hamiltonian:

$$\mathcal{H}_Q = (e^2 qQ/40) \{ 3m_I^2 - 35/4 + (\eta/2)(I_+^2 + I_-^2) \}.$$

To second order the splittings are:

$$\nu_1 \equiv \{ E(\pm 3/2) - E(\pm 1/2) \}/h = (3/20) e^2 qQ(1 + 59\eta^2/54)$$

$$\nu_2 \equiv \{ E(\pm 5/2) - E(\pm 3/2) \}/h = (6/20) e^2 qQ(1 - 11\eta^2/54)$$

and if $R \equiv \nu_2/2\nu_1$,

$$\eta^2 = (1 - R) \{ 54/(11 + 59R) \}.$$

Three measurements at 4.2 K by Mössbauer spectroscopy have been reported. They are:

$$e^2 qQ = 2.47 \pm 0.03 \text{ MHz}, \quad \eta = 0.23 \pm 0.06 [6];$$

$$e^2 qQ = 2.3 \pm 0.1 \text{ MHz}, \quad \eta = 0.19 \pm 0.04 [3]$$

and

$$e^2 qQ = 2.75 \pm 0.03 \text{ MHz}, \quad \eta = 0.09 \pm 0.04 [7].$$

All are based on a somewhat uncertain value of the piezoelectric constants of quartz at low temperature, and in addition, because they have used a stack of crystals, are subject to lost motion at the crystal-crystal contacts. This point was emphasized in ref. [7]. All difficulties stem from the low velocities needed for ^{67}Zn doppler spectroscopy. The natural line width is $2\Gamma_0 = 0.31 \mu\text{m/s}$ (23 kHz), and the typical interval between lines is $\sim 5 \mu\text{m/s}$ (~ 375 kHz). In order for the technique to advance it was considered necessary to establish the ZnO splittings as calibration standards. In this investigation we have determined ν_1 to ± 1 kHz and have obtained a believable value for the asymmetry parameter.

For problems like this that are amenable to frequency modulation spectroscopy, the method has certain advantages. It gives an absolute determination of energy differences at the expense of a dilution of intensity over unused sidebands. The expense is small however, because the method allows precise frequency off-sets, so that counting is restricted to the desired

portion of the spectrum. The gain in efficiency obtained by not scanning over irrelevant spectral areas can, in most cases, more than compensate for the reduction in usable intensity.

In order to display the present state of conventional spectroscopy of ^{67}Zn at this laboratory, we show figures 2 and 3. The first of these is the spectrum

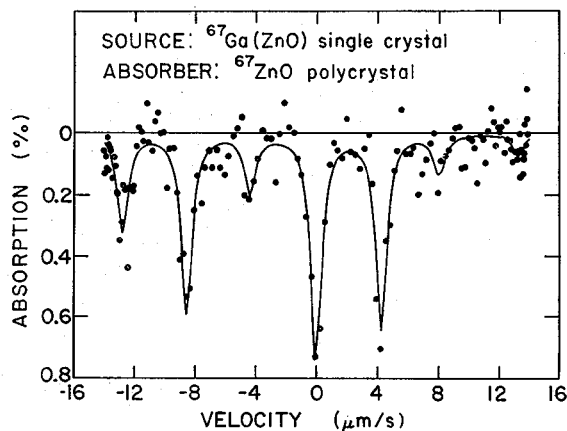


FIG. 2. — Velocity spectrum with single crystal source and polycrystalline absorber. The abscissa scale is appropriate to the precalibration values of piezo-electric constant. It is in error by $\sim 13\%$.

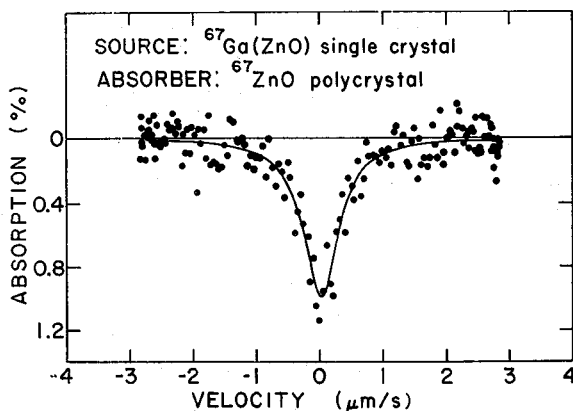


FIG. 3. — Velocity spectrum of the central line at higher dispersion. After correction for the new value of the effective piezo-electric constant, the line width is $0.75 \mu\text{m/s}$.

obtained with the quartz spectrometer described at the 1972 Israel conference [5]. The source is single crystal and the absorber polycrystalline ZnO. The spectrum is similar to, but of higher quality than, figure 6 of ref. [5]. The second of the two figures is a high resolution spectrum of the center line. It has a width of $0.75 \mu\text{m/s}$ (corrected for the altered piezo constants derived from the present study). This is 2.4 times the minimum observable width. The intensity is noteworthy, $\alpha = 1.0\%$ without correction for background. With the latter, including the contribution of an unresolvable neighboring line, we have $\alpha_{\text{corr}} \approx 1.3\%$. We have not found a measurable isomer shift between source and absorber.

Experimental details. — The absorber was 2.1 g/cm^2 of ZnO enriched to 89.6% in ^{67}Zn . It had been sintered and then annealed in oxygen at 700°C for 24 hours and slowly cooled. It was unchanged from its use in earlier investigations [7]. The sources were, as in ref. [7], single crystals of ZnO of normal isotopic abundance containing ^{67}Ga produced *in situ* by cyclotron bombardment. They were disks of various sizes, but generally 4 mm in diameter and 0.35 mm thick, with the c-axis perpendicular to the faces. The radiation was observed along the c-axis. This eliminates the transition to the $m_{\text{gnd}} = \pm 5/2$ level and doubles the intensity of the transition to $m_{\text{gnd}} = \pm 3/2$ compared to an isotropic source. The eliminated transitions can be seen as vestigial remnants in figure 2.

The ^{67}Ga activity can be made by a variety of bombarding particles incident on zinc of natural abundance. One can use ^4He , ^3He , or ^2H . Proton bombardment can also be used, but since it is ^{67}Zn that takes part in the desired reaction, and its natural abundance is only 4.1%, we have not used it. We have established that high current densities on a ZnO target produces sources of poor quality, apparently unimprovable by long annealing. Our best source was produced by bombardment with 12 MeV deuterons at a current density of about $25 \mu\text{A/cm}^2$ for a total of about $20 \mu\text{A-hr}$. It produced a clean 93.26 keV spectrum with an NaI counter, an initial counting rate of 12 000/s, and was used for three half-lives (9 days). All measurements were at 4.2 K.

Despite use of rather small quartz crystals, it was found difficult to avoid mechanical resonances above about 700 kHz. Since it was known that ν_2 would lie in this neighborhood, it was finally necessary to use $n = 3$ for this measurement. Thus the highest frequency in the investigation was less than 400 kHz. The $n = 1$ and earlier $n = 2$ measurements used X-cut quartz cylinders 3 mm thick by 4 mm diameter. The later $n = 2$ and $n = 3$ measurements used a crystal, 5 mm in diameter and 6 mm thick. A small source crystal was cemented to it with silver-loaded silicone grease, which was found to be conductive through thin layers. The ZnO is itself piezoelectric. It was coated completely with silver paint and became one of the electrodes. The quartz was clamped between two disks of dense styrofoam. We did not find any better way to suspend the source assembly and meet the following conditions: 1) The support had to simulate an absence of materials, a structure without mechanical resonance. 2) Nevertheless it had to hold the assembly firmly, in keeping with the need to avoid vibration. With this system the source oscillates with respect to an effective center of mass of the assembly. The position of the center of mass appears to change somewhat with frequency, and hence the modulation index is only roughly calculable from the applied voltage and the crystal constants. However, it could be measured rather well.

Because there is full Mössbauer absorption at $a = 0$, it is possible to get the proportionality between V and a by varying the voltage at constant frequency if the latter does not coincide with a nuclear resonance. We obtained a repetitive saw-tooth voltage from a ramp generator and fed this along with a constant r-f voltage of the desired frequency into a multiplier circuit. The output was a saw-tooth modulated r-f voltage whose amplitude varied linearly with time between about 0.1 and 10 volts. It could be attenuated or amplified as necessary. This was applied across the piezo-crystal and γ -ray counts recorded in successive channels of the multi-scaler device. The latter in our work is a PDP-11 mini-computer with an interface appropriate for time-mode count acquisition. As V and hence a increases, the intensity $J_0^2(a)$ of the unshifted component is traced in accordance with figure 1. A three parameter least-square fit to a function $y = y_0(1 - \alpha J_0^2(bV))$ determines the quantity b that connects modulation index with applied voltage. A sample is shown in figure 4. As one could not always wait for a computer fit, a frequent short-cut was to plot a curve by hand, identify the half-intensity point, and then use the condition $J^2(1.13) = 0.5$. In figure 4,

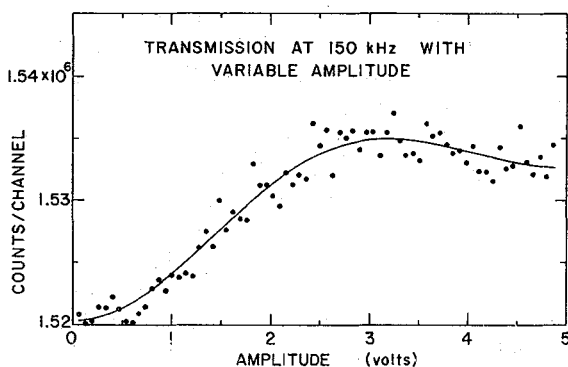


FIG. 4. — Variation of the transmission with the amplitude of a 150 kHz voltage applied to the quartz piezoelectric driver. The curve is the best fitting function of the form

$$f(V) = y_0(1 - \alpha J_0^2(bV))$$

where y_0 , α , and b are adjustable parameters. The values are $y_0 = 1.535 \times 10^6$, $\alpha = 0.96\%$, and $b = 0.75$ radian/volt.

α has the value 0.96. This is about the maximum absorption that we can observe with our line-widths. Cranshaw and Reveiri observed that the unshifted intensity was always more intense than any sideband, a consequence of a broad distribution of modulation indices at fixed ω and V . The contrary holds in our case, and we can assume that the distribution is narrow.

After having determined the quantity b at frequencies neighboring the region of frequency to be scanned, the modulation index was chosen to maximize the effect. The r-f was obtained by a Hewlett-Packard frequency synthesizer, which generates its output from a temperature controlled quartz oscillator. The frequency is chosen by supplying a set of binary-coded

decimal logic voltages to a connector on the synthesizer. These were in turn derived from a counting circuit that advanced by one, two or five, as desired, each time a clock pulse was received. It would count from a lower to an upper three digit number, which had previously been entered on switches, and upon reaching the upper number would emit a reset pulse for the computer and start over. These numbers became the actual frequencies in kHz. The clock pulses were derived by scaling a quartz oscillator. They were also the address advance pulses for the computer. The fractional frequency accuracy of each step was $\sim 10^{-8}$, — much better than needed. A typical run might sweep from 150 to 200 kHz by 1 kHz steps, at a rate of two steps per second. Some of the earlier data were taken with a voltage controllable function generator which could be calibrated by counting it directly into the computer. The overall precision of this system was adequate, about 10^{-4} .

Results. — Figure 5 is a plot showing the ν_1 resonance obtained with the $n = 2$ sideband, and the ν_2 resonance obtained with $n = 3$ all on the same frequency sweep. It was possible to get both because of the variation of b with frequency, aided by tailoring the frequency dependence of the r-f amplitude with an

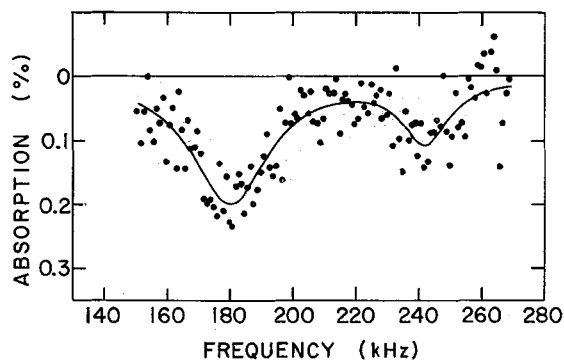


FIG. 5. — Absorption vs. frequency. The instrumental variation of b with frequency was augmented by the amplifier characteristic in order to produce nearly optimum values of the modulation index for the $n = 2$ sideband at the left hand dip and for the $n = 3$ sideband at the right hand dip.

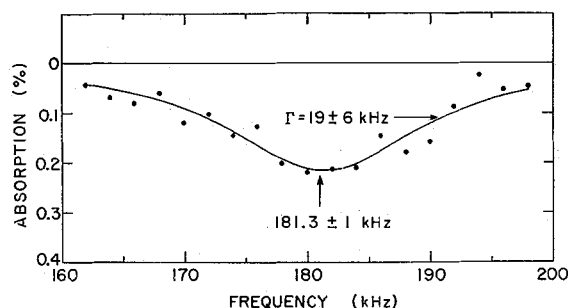


FIG. 6. — Absorption vs. frequency. The hyperfine interval ν_1 is determined in this spectrum taken at a voltage appropriate for maximizing the intensity of the $n = 2$ sideband.

TABLE I

Summary of data

(Tabulated frequencies and widths are in kHz)

Meas. frequency	Meas. width	n	ν_1	Γ
360.6 ± 5	68 ± 22	1	360.6 ± 5	68 ± 22
363.9 ± 3	79 ± 11	1	363.9 ± 3	79 ± 11
183.0 ± 2	23 ± 11	2	365.9 ± 4	46 ± 22
180.3 ± 1.5	24 ± 7	2	360.6 ± 3	48 ± 14
180.0 ± 2	16 ± 5	2	360.0 ± 4	32 ± 10
180.3 ± 1.5	17 ± 5	2	360.6 ± 3	34 ± 10
176.2 ± 2	20 ± 5	2	352.4 ± 4	40 ± 10
180.2 ± 1	30 ± 5	2	360.4 ± 2	60 ± 10
181.3 ± 1	19 ± 6	2	362.6 ± 2	38 ± 12
$\langle \nu_1 \rangle_{\text{av}} = 361.2 \pm 1.0$ kHz				
			ν_2	
241.9 ± 2	19 ± 6	3	725.7 ± 6	57 ± 18
237.7 ± 2	13 ± 5	3	713.1 ± 6	40 ± 14
243.3 ± 2	9 ± 3	3	729.9 ± 6	27 ± 9
$\langle \nu_2 \rangle_{\text{av}} = 723.0 \pm 4$ kHz				

$$R \equiv \nu_2/2 \nu_1 = 1.0008 \pm 0.0062$$

$$e^2 qQ = 2.408 \pm 0.006 \text{ MHz}$$

$$\eta = 0.00 \begin{Bmatrix} +0.065 \\ -0 \end{Bmatrix}$$

amplifier. The latter was of the type used for nuclear pulse amplification, and the adjustments were made with the differentiation and integration controls. Figure 6 shows the $\nu_1, n = 2$ resonance in another run. Table I summarizes the data. The quantity ν_2 was determined in three runs. Its average is 723 ± 4 kHz. The quantity ν_1 was obtained from the average of nine runs. Its value is 361.2 ± 1.0 kHz. The asymmetry parameter is $\eta = 0.00 \begin{Bmatrix} +0.065 \\ -0 \end{Bmatrix}$. We obtain

$$e^2 qQ = 2.408 \pm 0.006 \text{ MHz}.$$

The energy of the gamma ray is known from diffraction spectrometer measurements [8]. It is 93.26 ± 0.04 keV. With this value, the correspondence between frequency and Doppler velocity is $1 \mu\text{m/s} \approx 75.22 \pm 0.03$ kHz. The separations are then $\nu_2 = 4.80 \pm 0.01 \mu\text{m/s}$ and $\nu_1 = 9.61 \pm 0.05 \mu\text{m/s}$.

The uncertainty in our measurement of ν_1 corresponds to the gravitational red-shift in 41 cm.

The effective piezoelectric constant of quartz in our Doppler apparatus is obtained by comparing the data of figure 3 with these results. It is

$$|D_{12}(\text{eff})| = 2.28 \times 10^{-10} \text{ cm/volt at 4.2 K.}$$

However, this is not a proper measurement of the true constant, as no account has been taken of the fringing fields.

Acknowledgment. — We wish to thank Henry Stanton for aid with the computer fitting.

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