Magnetic Moment of the 93-keV State of ^{67}Zn by the Nuclear Zeeman Effect*

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Mössbauer measurements of the 93.26-keV transition in ^{67}Zn are reported for sources of ^{67}Ga in ZnO single crystals and ZnO powder as absorber. An external magnetic field of a few hundred oersteds is applied and the value of the magnetic moment of the $(1/2)^-$ first excited state is determined by a quasinull method. We obtain $\mu[(1/2)^-] = +(0.58 \pm 0.03)\mu_N$. The electric field gradient is determined to be positive.

We report measurements of the Mössbauer effect of the 93.26-keV γ ray of ^{67}Zn emitted from a single crystal of ZnO. We have measured the magnetic moment of the $\frac{1}{2}^-$ first excited state by the nuclear Zeeman effect in an external field of a few hundred oersteds. The magnetic moment is obtained by a quasinull method to ± 5% despite a variety of larger uncertainties in the experimental parameters. In addition, we obtain the sign of the quadrupole coupling of the $\frac{5}{2}^-$ ground state and some information on the siting of the ^{67}Ga, whose 78-h decay by electron capture leads to the excited ^{67}Zn. An earlier set of observations reported[1] from this laboratory will be referred to as DP.

The $\frac{1}{2}^-$ first excited state has a mean life of 13.6 μsec. The transition is therefore notable mainly for its narrow linewidth. The minimum observable value, expressed as a Doppler shift,[2] is $2\Gamma_0 = 0.31$ μm/sec. In these units, one nuclear magneton is 0.01013 μm sec^{-1} Oe^{-1}. Thus 100 Oe is adequate for the observation of magnetic splitting.

The drive was the stack of ten quartz crystals mentioned in DP. Typically it was operated at 200 Hz with 370 V_{rms} across each 6-mm-thick X-cut crystal. The absorber was substantially the same as in DP—a compressed and sintered pellet of ZnO, 2.1 g/cm^2 thick, enriched to 89.6% in ^{67}Zn. It had been annealed for 24 h at 700 °C in an oxygen atmosphere and slowly cooled. The sources were made by cyclotron bombardment of single crystals of ZnO of natural isotopic abundance. The crystals were 1-cm disks, 0.5 mm thick, with the hexagonal symmetry axis (c axis) perpendicular to the faces. The magnetic moment measurements were made with the field parallel to the c axis, which was also parallel to the direction of observation of the γ radiation. The bombardments were about 20 μA h of 25-MeV α particles to produce ^{67}Ga directly via ^{64}Zn(α, p) and indirectly as a result of the 19-min decay of ^{67}Ge produced by ^{64}Zn(α, n). The samples after bombardment were deeply colored but became a very pale yellow after being annealed at 700 °C in oxygen[3] for 12 h and then cooled over the course of 6 h. The γ rays were detected by a Ge(Li) detector. The detector's amplified signals passed first through a linear gate (to limit the total counting rate by selecting the spectral region of interest) and then to a single-channel analyzer in the usual way. Initial rates in the window were 3000–6000 counts/sec with a subtractable background of about 20%. The velocity spectrum was recorded in a general-purpose computer in time mode. About 2×10^9 selected counts could be recorded during a run whose typical duration was one week. The source and absorber were maintained at 4.2 °K.

Figure 1 shows a typical velocity spectrum in the absence of an applied magnetic field. The quadrupole splitting observed in DP is present, but the line intensities (1:2:1:3:2:0:0) are appropriate to $E2$ emission along the symmetry axis from a normal Zn site and absorption by a polycrystalline absorber. The velocity range scanned does not extend to the two outermost line positions.[4] The transition with $|\Delta m| = 2$, which should lead to no radiation along the c axis, shows itself as a vestigial dip at $\approx +12$ μm/sec. Its faint presence probably results from radiation damage that could not be annealed out after the bombardment. The observed sequence of intensities shows that the quadrupole coupling is positive. Since the quadrupole

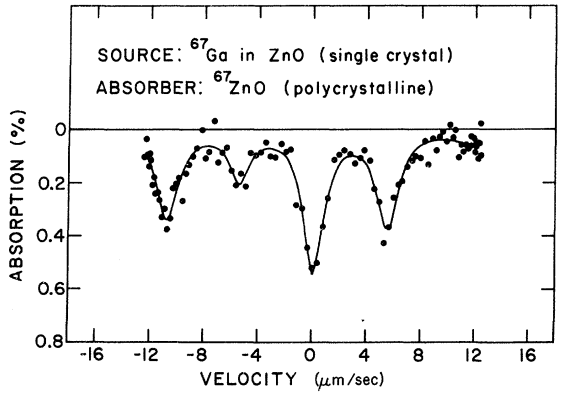

FIG. 1. Typical ^{67}ZnO Mössbauer spectrum in zero magnetic field.

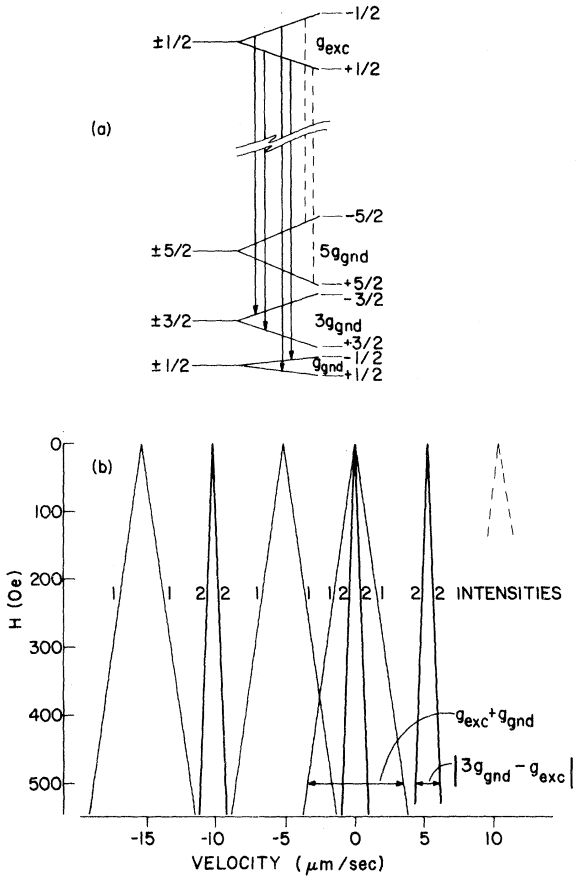

FIG. 2. Effect of an external magnetic field along the c axis of ZnO. (a) Level diagram drawn for $\mu_{exc}=+0.6\mu_N$, $\mu_{gnd}=+0.876\mu_N$, and $e^2qQ>0$ in the ground state. (b) Magnetic field dependence of the expected velocity spectrum. The splitting of the line pairs having intensity 1 is proportional to $g_{gnd}+g_{exc}$ while that of the line pairs having intensity 2 is proportional to $|3g_{gnd}-g_{exc}|$ if $\eta^2 \ll 1$.

moment is also positive (+0.16 b),[5] the field gradient is determined to be positive. This is indeed the sign obtained in DP by a lattice sum. An asymmetry parameter $\eta = 0.23$ was reported in DP and has been corroborated by work at Dubna.[6] We now find, however, that this value is possibly too large. From two runs we obtain $\eta = 0.09 \pm 0.04$. For the quadrupole coupling, we get $e^2qQ = 36.6 \pm 0.3$ μm/sec. This corresponds to 2.75 MHz and is somewhat higher than the 2.47 MHz reported in DP and the 2.32 MHz in the Dubna preprint. All the quoted statistical errors, including those here, must be taken with some caution. In our work, the motion produced by the stack of quartz crystals is always less than 100 Å, and we have at times had evidence of lost motion after the crystals have had their relative positions disturbed. One may note in passing that the entire spectrum displayed in Fig. 1 is about a tenth of the natural width of the 14.4-keV resonance line of ^{57}Fe.

From the corrected area of the central line, we can derive a lower limit for the characteristic temperature Θ_M of the Zn atom in ZnO if the source and absorber are assumed to have the same value. The lower limit applies because we scan only a very small spectral region; and hence almost any source condition that puts the emitting Zn ion in other than the normal charge state and the normal lattice position can be expected to shift the γ-ray energy out of the detected range. Such an event would appear as an apparent loss in recoil-free fraction and hence would lead to a lower value of Θ_M for the source. The value we calculate for Θ_M also depends somewhat on how much of the observed linewidth is to be assigned to the absorber as an intrinsic width Γ_a. The highest possible value, $\Theta_M = 368\,^\circ$K, is associated with the assumption $\Gamma_a = \Gamma_0$. More reasonable assumptions give values between 308 °K (for $\Gamma_a = \Gamma_{obs} - \Gamma_0$) and 315 °K (for $\Gamma_a = \frac{1}{2}\Gamma_{obs}$), where Γ_{obs} is the observed width (1.8 μm/sec in Fig. 1). The quantity Θ_M is calculated from the recoil-free fraction as if the thermal motions were those of a Debye solid with $\Theta_D = \Theta_M$. It can be compared with Θ_D determined in other ways, after correcting the Θ_D value, so that it applies to the zinc atom alone. This was done in DP to give $\Theta_D \approx 290\,^\circ$K from crystallographic data.[7] Acoustic data,[8] similarly corrected, gave $\Theta_D \approx 325\,^\circ$K. The observed recoil-free fraction appears to be too large to allow any substantial deviation from the assumption that the emitting zinc ions are in the normal charge state and in lattice sites with the normal near neighbors. In all likelihood the ^{67}Ga ions therefore are at Zn sites, but it should be noted that some appreciable fraction of the 13.6-μsec mean life of the excited nuclear state is available for the return to normal conditions after the disturbance due to the electron-capture decay in ^{67}Ga.

For the magnetic runs, fields between 131 and 545 Oe were obtained from a small cylindrical Alnico magnet in contact with a soft-iron pole piece. The source was held below the face and just above two thin sheets of soft magnetic shielding material which continued the magnetic circuit. The absorber was contained in a magnetic shield. The field at the source was determined to be uniform within about 1% by traversals with a Hall-effect probe, whose spatial resolution could be determined by traversing the gap between two closely spaced poles

TABLE I. Characteristics of the ^{67}Zn transition.

E_γ (keV)	τ (μsec)	$2\Gamma_0$ (μm/sec)	μ_{gnd} (μ_N)	Q_{gnd} (b)	$I^\pi_{exc} \rightarrow I^\pi_{gnd}$
93.26	13.6	0.31	0.87552	0.16	$\frac{1}{2}^- \rightarrow \frac{1}{2}^-$

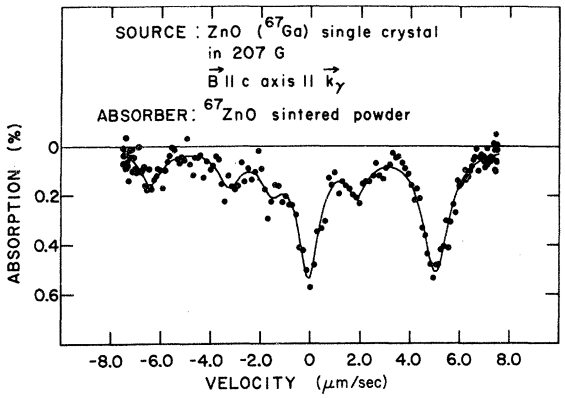

FIG. 3. Mössbauer spectrum of ^{67}ZnO in an external magnetic field of 207 Oe.

of a laboratory electromagnet. By removing the Alnico magnet and changing its remanent magnetization, the field could be varied. The field was measured at room temperature by indirect reference (via the probe) to more absolute instruments, and a correction was determined for liquid-helium temperature. We estimate the over-all accuracy of the field determination to be within 3%.

When the asymmetry parameter is small, the addition of a magnetic field along the symmetry axis has the effect of splitting the three degenerate quadrupole doublets of the ground-state multiplet as if each were a separate nuclear species with its magnetic moment proportional to $|m|$. This is seen in Fig. 2(a), which is plotted for an excited-state magnetic moment equal to $+0.6\mu_N$ and for $e^2qQ>0$ in the ground state. The diagram shows that as a result of the selection rule $\Delta m=\pm 1$, which is appropriate when, in addition, the γ ray is observed along the symmetry axis, the transitions to $m_{\rm gnd}=\pm\frac{1}{2}$ separate more rapidly in energy as the field is increased than do those to $m_{\rm gnd}=\pm\frac{3}{2}$.

In Fig. 2(b), the expected spectrum corresponding to Fig. 2(a) is plotted as a function of the magnetic field. The pairs of lines in this spectrum are of two types—one in which the separation is proportional to $g_{\rm gnd}+g_{\rm exc}$, the sum of the ground-state and excited-state g values, and one in which it is proportional to $|3g_{\rm gnd}-g_{\rm exc}|$. Each member of the latter has twice the intensity of each of the former.

If it should transpire that $3g_{\rm gnd}-g_{\rm exc}=0$ (i.e., if $\mu_{\rm exc}=\frac{3}{5}\mu_{\rm gnd}$), the intense pairs would be unsplit; the observation of this could be considered a null comparison of $g_{\rm exc}$ and $g_{\rm gnd}$; and the result would be independent of most sources of inaccuracy. This turns out to be approximately the case. Figure 3 shows a spectrum in an external field of 207 Oe. At 0 and 5 μm/sec one sees the unsplit pairs, while the four weaker lines of Fig. 2(b) are plainly visible. A negative sign for the excited-state moment is immediately ruled out. At other values of the magnetic field, we have observed the expected crossover at about -2.5 μm/sec and also a broadening of the intense pair. From perturbation theory, one finds that the effect of asymmetry is to decrease the splitting of the $\pm\frac{3}{2}$ doublet by the amount $2\eta^2A^2B/(A^2-B^2)$, where $A=3e^2qQ/40$ and $B=\frac{2}{5}\mu_{\rm gnd}H$. For $H=545$ Oe—our strongest field—and $\eta=0.09$, this correction is 0.058 μm/sec, while if η is as large as 0.23 it is 0.42 μm/sec.[9] If we accept the smaller value of η, the two higher field runs (339 and 545 Oe) give $|\mu_{\rm exc}-\frac{3}{5}\mu_{\rm gnd}|=0.057\mu_N$. In all of the five runs used in this investigation, the separation of the weak lines is consistent only with $\mu_{\rm exc}>\frac{3}{5}\mu_{\rm gnd}$. The absolute-value bars can therefore be removed, and from the known value $\mu_{\rm gnd}=+0.876\mu_N$ we get $\mu_{\rm exc}=+(0.58\pm0.03)\mu_N$, where the error is taken as half the correction.

The nucleus ^{67}Zn seems best represented by the pairing model with Fermi energy lying between the single-neutron $f_{5/2}$ and $p_{1/2}$ levels. Evidence for this is the trend of spectroscopic factors measured for the Zn isotopes[10] and the fact that the transition we have studied is interesting as a Mössbauer nucleus primarily because it is retarded ~ 10 times below the single-particle $E2$ estimate.[11] On this basis, the $\frac{5}{2}^-$ ground state and $\frac{1}{2}^-$ first excited state are to be considered single-quasiparticle states. The theoretical magnetic moment of such a state in an odd-mass nucleus is that of the corresponding particle state[12]; hence the Schmidt value is as good an expectation for one as the other. The moment measured is indeed not far from the Schmidt value $\mu(\text{Schmidt})=+0.64\mu_N$ for a $p_{1/2}$ neutron.

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Electron-Spin Resonance of N_4^- Defects in Irradiated RbN_3†

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An N_4^- molecular ion is observed by ESR at 92 K in single-crystal rubidium azide (RbN_3) following uv or γ irradiation at 77 K and a 35-min anneal at 227 K. The ESR spectra are characteristic of an unpaired electron interacting equally with four equivalent nitrogen nuclei. The spin-Hamiltonian parameters are similar to those of the planar N_4^- defect in KN_3; however, the growth and annealing behaviors of this defect differ in these two crystals. For both materials, trapped nitrogen atoms found following irradiation anneal at about 150 K. In both, N_4^- ions are formed from thermal annealing at approximately 200 K; however, the N_2^- intermediate reported in KN_3 is not identified in RbN_3. Slow thermal decay of N_4^- defects in RbN_3 occurs at temperatures as low as 227 K. From measurements of the rate of decay at several temperatures an annealing activation energy of 0.47 ± 0.04 eV is determined, which is approximately one-half that found for N_4^- ions in KN_3.

I. INTRODUCTION

The alkali azides (NaN_3, KN_3, RbN_3, and CsN_3) are known to be especially sensitive to decomposition by ultraviolet light and ionizing radiation. Numerous investigations have been made by ESR and by optical absorption of radiation-induced defects stabilized in these materials. These include ESR studies of the F center,[1] trapped nitrogen atoms,[2] and N_2^- molecular ions[3,4] in trigonal-structured NaN_3. For tetragonal KN_3, trapped nitrogen atoms,[5] N_2^- ions,[5,6] and N_4^- ions[6,7] have been identified by spin resonance. RbN_3 and CsN_3, which have crystal structures as does KN_3, have not been studied as extensively. Only the trapped nitrogen atom has previously been investigated in x-irradiated RbN_3 (Ref. 8); and in CsN_3, only the study of an electron trapped at a calcium impurity cation following uv irradiation at 77 K has been published.[9] Some work has been done to correlate ESR spectra to optical-absorption bands. This includes optical studies on the F center in NaN_3.[10] Also, in a recent investigation by Bogan *et al.*[11] on uv-irradiated KN_3, the thermal conversion of the 565-nm band to the 580-, 700-, and 780-nm bands is correlated with ESR observations of the conversion of N_2^- to N_4^- defects. They interpret their results using a planar N_4^- ion occupying a single azide-ion vacancy. A planar model, in contrast to the originally suggested linear model,[7] has been proposed by several investigators to explain the observed equal hyperfine coupling to four nitrogen nuclei.[6,11,12] Since KN_3, RbN_3, and CsN_3 are alike structurally, they might be expected to exhibit the same radiation-induced species. The present work was designed to further investigate irradiated RbN_3; the N_4^- molecular ion has been detected and its character in RbN_3 is described.

Several review articles have discussed the crystal structures and properties of azides.[13–15] Rubidium azide has a body-centered tetragonal structure with the unit cell shown in Fig. 1. The linear azide ion resides in two sites which are equivalent for a 90° rotation about the c axis. The symmetry axis of the azide ion for one site is directed along the [110] direction, and for the other along [$\bar{1}$10]. Lattice dimensions for alkali azides having this structure increase as the cation radius increases; these dimensions are given for KN_3, RbN_3, and CsN_3 in the caption to Fig. 1. In each of these crystals the site size for the azide ion is approximately the same.

II. EXPERIMENTAL

Rubidium-azide single crystals were grown by slow evaporation from saturated aqueous solution. These crystals grow as clear square platelets with the edges corresponding to the [110] and [$\bar{1}$10]