Paramagnetic Resonance Spectrum of Cobalt in Cerium Magnesium Nitrate at 4°K*

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Paramagnetic resonance spectra of cobalt in crystals containing cerium and bismuth magnesium nitrate have been studied at 4°K for various cerium-bismuth ratios. It is found that the cobalt hyperfine spectrum, well resolved in pure bismuth magnesium nitrate, is strongly attenuated by the addition of small percentages of cerium. For ionic cerium concentrations higher than 20% of the cerium-bismuth total, the cobalt hyperfine components cannot be resolved at all, except for the particular case of a 50% mixture. We attribute the attenuation of the cobalt spectrum to magnetic dipole interactions with the cerium ion, and suggest that this may also account for the fact that the observed degree of Gorter-Rose orientation of Co⁶⁰ in cerium magnesium nitrate disagrees with the results of calculations that do not include the effect of dipole-dipole interactions.

THE paramagnetic resonance spectra of dilute cobalt in bismuth magnesium nitrate have been measured by Trenam[1] at 20°K. His work has shown that there exist two nonequivalent ions per unit cell, each having the same axis of symmetry for their respective spectra but quite different values for their spectroscopic splitting factors and hyperfine interaction coefficients (see Table I). An isomorphous salt, cerium magnesium nitrate containing cobalt concentrations of $\frac{1}{2}\%$ to 1% has been used for some time in nuclear orientation experiments.[2,3] For a quantitative calculation of orientation effects, it is necessary to know the electronic g-factors and hyperfine component separations of the cobalt ion in the salt employed. We have attempted to determine these parameters in cerium magnesium nitrate at 4°K, and have found two distinct broad electronic resonances yielding cobalt g factors in good agreement with those in bismuth magnesium nitrate[1] at 20°K. However, the cobalt hyperfine spectrum is completely suppressed, so that no precise determination of the hyperfine separations could be made. The measurements were repeated using mixed crystals containing both cerium and bismuth in several different proportions, in order to determine whether the attenuation of the cobalt hyperfine structure is due to the cerium ion. The results establish that it is, and show that comparatively modest concentrations of cerium are sufficient to supress the cobalt hyperfine spectrum to the point of vanishing in the noise background.

A Zeeman modulation spectrometer for three-centimeter wavelengths was employed in making the measurements; it made use of a reflection cavity in one arm of a balanced hybrid-tee microwave bridge. A barrel-type electromagnet with a gap of $2\frac{1}{4}$ in. and a tapered pole with a face diameter of $5\frac{1}{2}$ in. was employed. The homogeneity at the center of the gap was one part in five thousand. The field current was controlled by means of a series stabilizing circuit which permitted the field to be varied from 0 to 4000 gauss, and at the same time effectively eliminated both ripple and drift. The field was calibrated by use of a proton resonance magnetometer. Microwave power was supplied by a Varian X-13 klystron which provided up to 100 mw incident upon the cavity.

The samples were single crystals grown in weak solutions of nitric acid. The cobalt ionic concentration in all samples was about one-half percent that of magnesium. The samples were mounted on a Teflon bucket, and we replaced in a region of maximum r-f magnetic field in the cavity. The bucket was attached to a gear train outside the cavity which permitted rotation of the sample from a position at the top of the cryostat. No attempt was made to keep the liquid helium from entering the resonant cavity, but aside from lowering the resonant frequency of the cavity due to the dielectric constant of liquid helium, no adverse effects were detected as a result of its presence.

The cobalt spectra examined show symmetry about an axis perpendicular to the flat face of the crystal; thus the spectra may be described in terms of components of g parallel and perpendicular to this axis. The hyperfine interaction coefficients A and B belong to parallel and perpendicular orientations respectively. The spectra obtained can be explained by the spin-

[1] R. S. Trenam, Proc. Phys. Soc. (London) A66, 118 (1953).

[2] Ambler, Grace, Halban, Kurti, Durand, Johnson, and Lemmer, Phil. Mag. 44, 216 (1953).

[3] Jastram, Sapp, and Daunt, Phys. Rev. 101, 1381 (1956).

TABLE I. $Bi_2Mg_3(NO_3)_{12}\cdot24H_2O$ (1% cobalt). 20°K (Trenam).

	$g_{\parallel}$	$g_{\perp}$	$A\times10^4$, cm⁻¹	$B\times10^4$, cm⁻¹
X ion	4.108±0.003	4.385±0.003	85±1	103±1
Y ion	7.29 ±0.01	2.338±0.004	283±1	≤1

TABLE II. X ion. $(Bi+Ce)_2Mg_3(NO_3)_{12} \cdot 24H_2O$ ($\frac{1}{2}\%$ cobalt). 4°K.

% Ce	g_{11}	$g_\perp$	$A \times 10^4$, cm^{-1}	$B \times 10^4$, cm^{-1}
0	4.145±0.002	4.415±0.002	95±3	103±3
10	4.12 ±0.01	4.45 ±0.01	82±9	114±9
20	4.22 ±0.01	4.22 ±0.01	90±9	90±9
50	4.30 ±0.01	4.31 ±0.01	89.7±9	107±9
80	4.02 ±0.01	4.45 ±0.01	...	...
100	4.14 ±0.01	...	...	...

TABLE III. Y ion. $(Bi+Ce)_2Mg_3(NO_3)_{12} \cdot 24H_2O$ ($\frac{1}{2}\%$ cobalt). 4°K.

% Ce	g_{11}	$g_\perp$	$A \times 10^4$, cm^{-1}	$B \times 10^4$, cm^{-1}
0	7.20±0.01	2.39±0.002	302±6	<1
10	...	2.37±0.01	...	...
20	7.41	2.36±0.01	...	...
50	10.55	...	...	...
80	7.33	2.36±0.01	...	...
100	7.3	...	...	...

resonance Hamiltonian[4-6]:

$$\mathcal{3C} = g_{11}\beta H_z S_z + g_\perp\beta(H_x S_x + H_y S_y)$$
$$+ A(S_z I_z) + B(S_x I_x + S_y I_y). \quad (1)$$

Our accuracy limited us to using only the first-order perturbation terms in this Hamiltonian, since the second-order terms were of the same order of magnitude as our uncertainty. Cobalt in this salt has an effective electron spin $S = \frac{1}{2}$ and a nuclear spin $I = \frac{7}{2}$, so that the hyperfine structure consists of eight equally spaced components. It is necessary to cool the salt to about 20°K or below in order to detect the electronic transition. The object of the present experiment was to determine the hyperfine separations at 4°K, and to investigate the effect of cerium ion concentration on the width of the cobalt hyperfine components.

RESULTS

The results obtained from our experiments are given in Tables II and III, and the spectra obtained are shown in Figs. 1–4. Our results for pure bismuth magnesium nitrate (zero percent cerium) agree quite well with Trenam's[1] results at higher temperatures, and the spectra show the hyperfine structure quite well resolved. The two nonequivalent ions per unit cell that Trenam observed have also been observed by us, and we follow Trenam's nomenclature in labeling them the X and Y ions. It will be noted in the spectra for the perpendicular orientation of the Y ion in the zero-percent cerium case (Fig. 4) that the pattern is quite complicated. A calculation based on second-order terms only gives a spectrum consistent with what is observed: four unequally spaced lines, each possibly split by a comparatively small first-order contribution. The experimental accuracy for the 0% cerium case was the best for all of the spectra, since the presence of cerium in the sample reduced the signal to just above noise level (see Figs. 1–4), making determination of the position of the lines more uncertain.

The resolution of the hyperfine structure decreased greatly for ten percent cerium concentration, but the lines were still quite detectable for the X ions. The Y ions show no resolution of hyperfine structure at all;

[4] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

[5] B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics* (The Physical Society, London, 1953), Vol. 16, p. 109.

[6] B. Bleaney, Phil. Mag. **42**, 441 (1951).

in fact we were unable to detect the resonance in the parallel orientation. The perpendicular orientation for the Y ion does show traces of structure. These continue to be visible all the way up to eighty percent cerium (Fig. 4).

The 20% concentration of cerium still permits resolution of the hyperfine structure resulting from the X ions, but one will note that here the g values depart from their zero-percent values by amounts that are greater than the experimental error. Misorientation of the crystal was checked as a possible source of this discrepancy, but was ruled out. The trace for the parallel orientation of the Y ion (Fig. 3) shows a curious one-sided derivative curve with no structure. This asymmetry makes it difficult to assign a g value for this resonance; we have taken the point where we think the trace has started as the place from which to compute g. This procedure at least gives g values in accord with that obtained at 0% cerium.

The results on 50% cerium are similar in nature to those for twenty percent. The hyperfine structure of the X-ion resonances is still resolvable although it is very weak, but the g values have departed even further from the 0% cerium case. An unexplained result at this concentration is the disappearance of the Y-ion resonance for the perpendicular orientation; this resonance is otherwise quite strong and occurs at the same place for each concentration.

With 80% cerium, we can no longer resolve the hyperfine structure resulting from either of the ions, although the trace for the Y ion perpendicular does indicate that there is some residual effect present. The g values for the X-ion resonances are again close to what they were for 0% cerium. The result is similar for the 100% cerium case.

It will be noted that the values of A and B for the hyperfine interaction (Table II) remain constant within experimental error for the X ions as the percentage of cerium is increased, despite the variations that appear in the g values: The cerium interaction broadens and shifts the electron resonance, but has little effect on the cobalt hyperfine structure. The measured hyperfine-coefficient values are in good agreement with those determined by Trenam at 20°K.

The power level incident upon the resonant cavity was varied, with the result that in every case it was possible to saturate or partially saturate the resonances
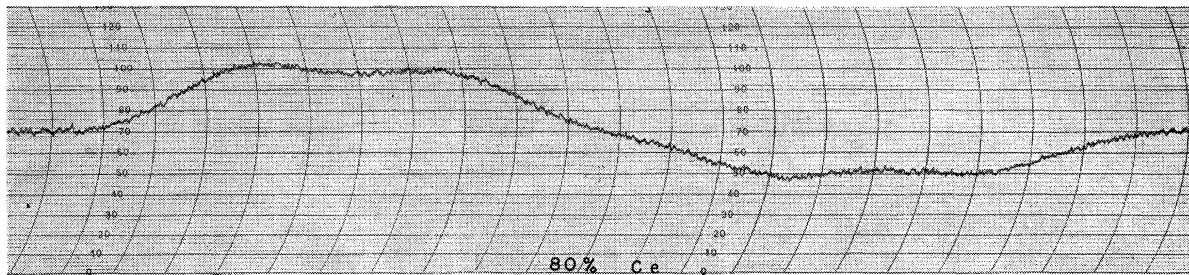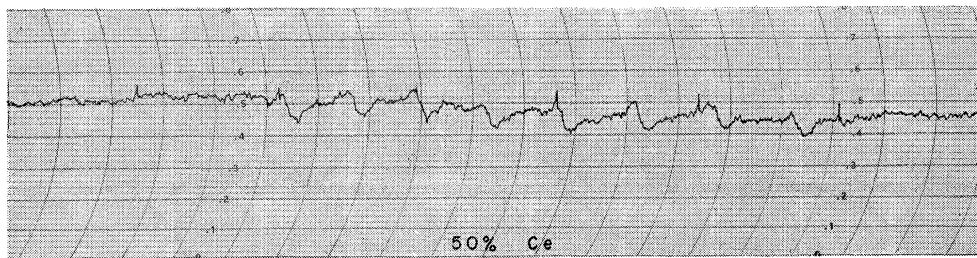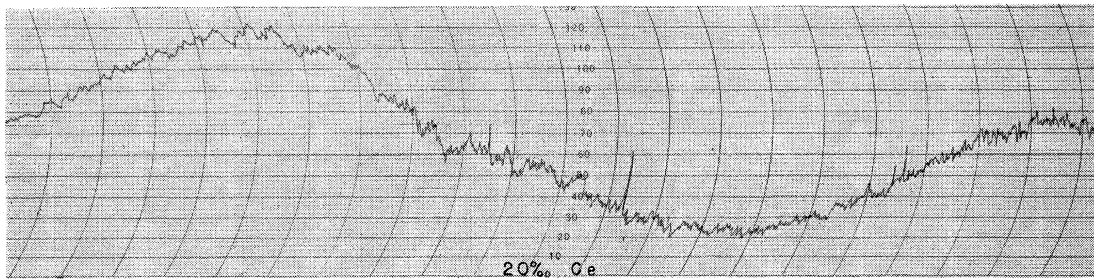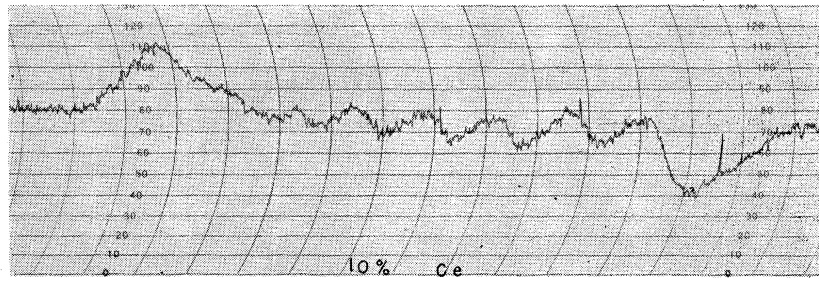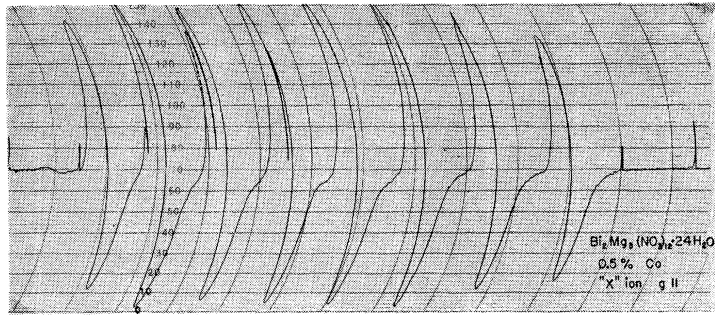
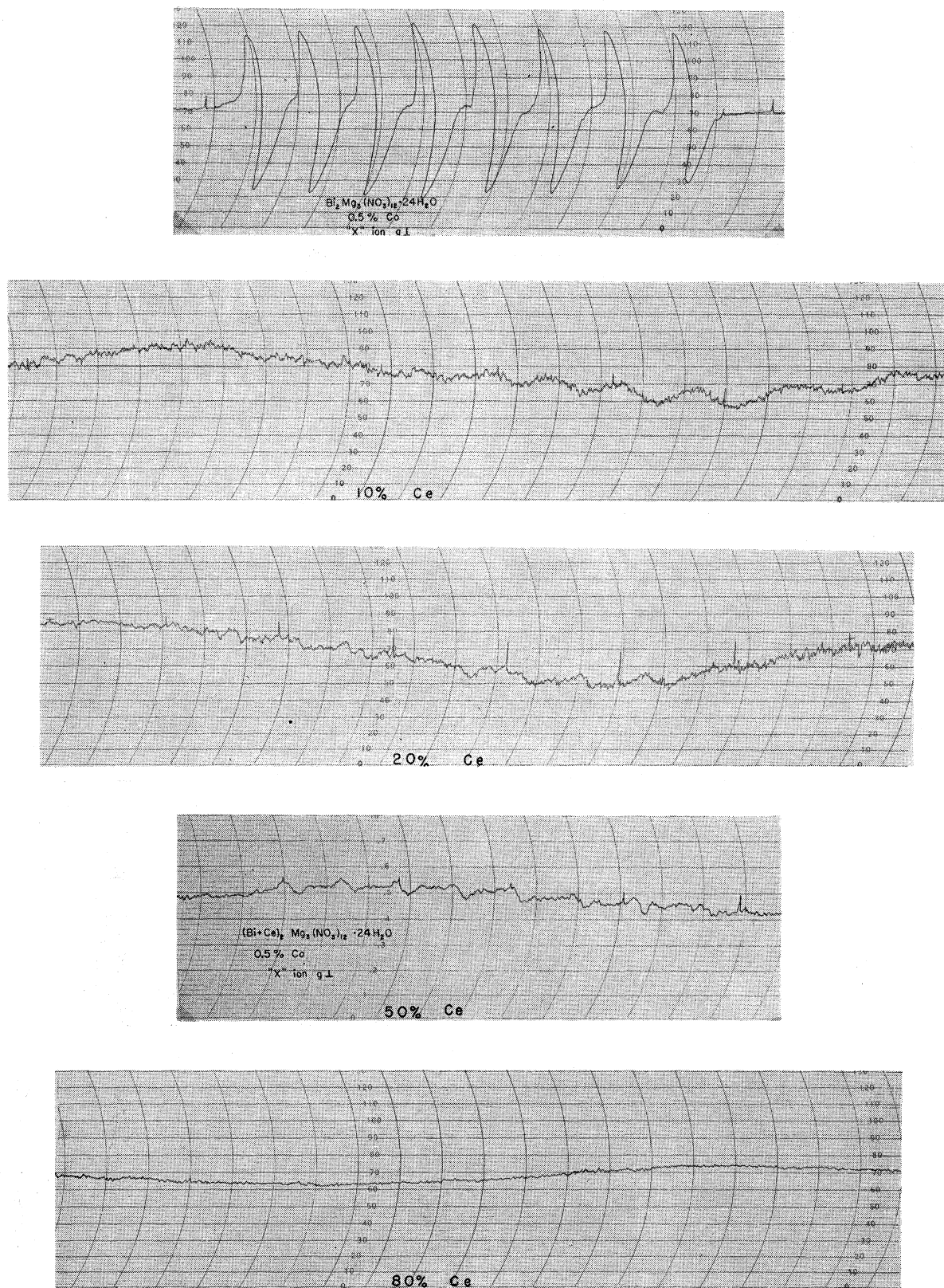FIG. 1. X-ion resonances. Parallel orientation.

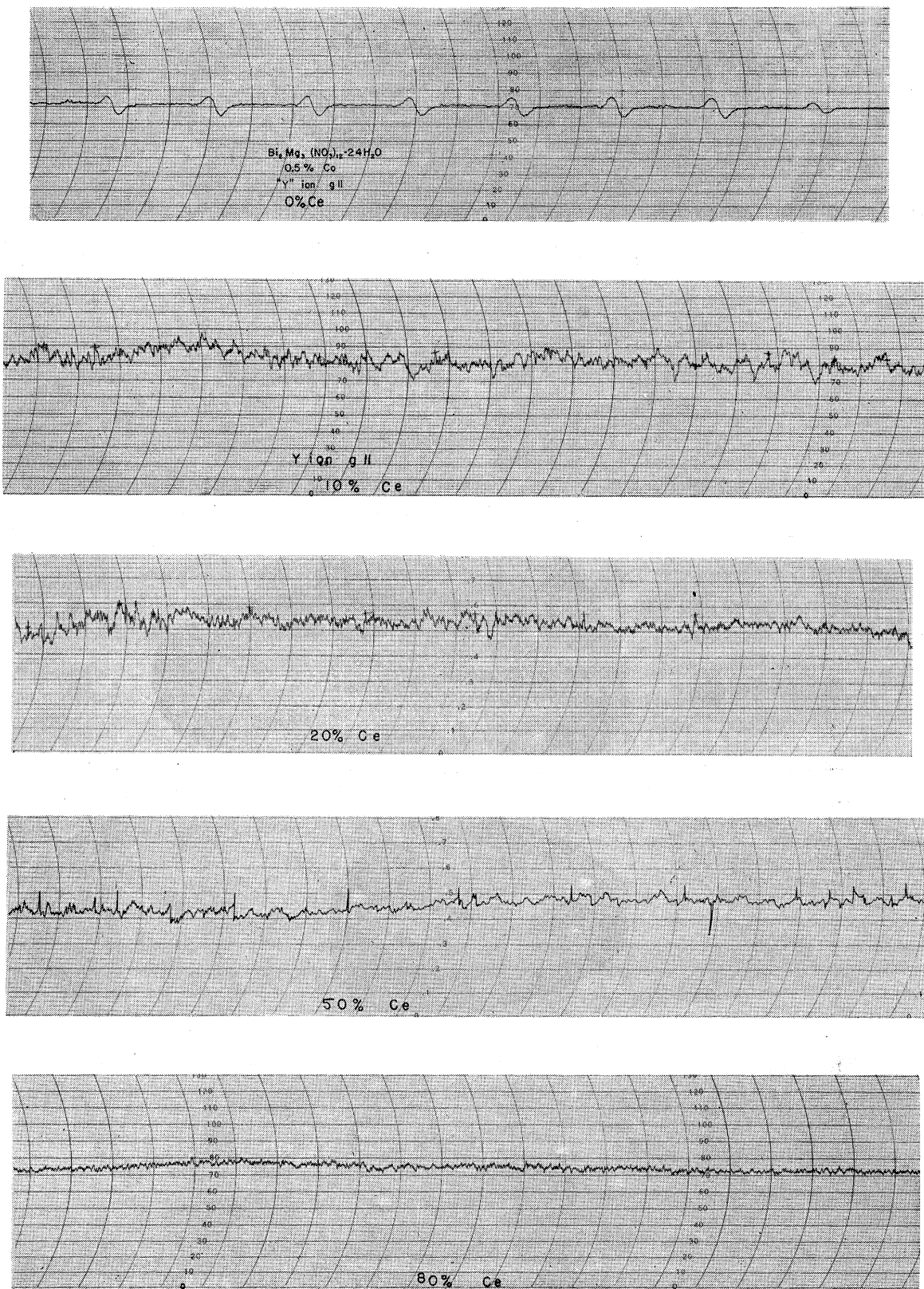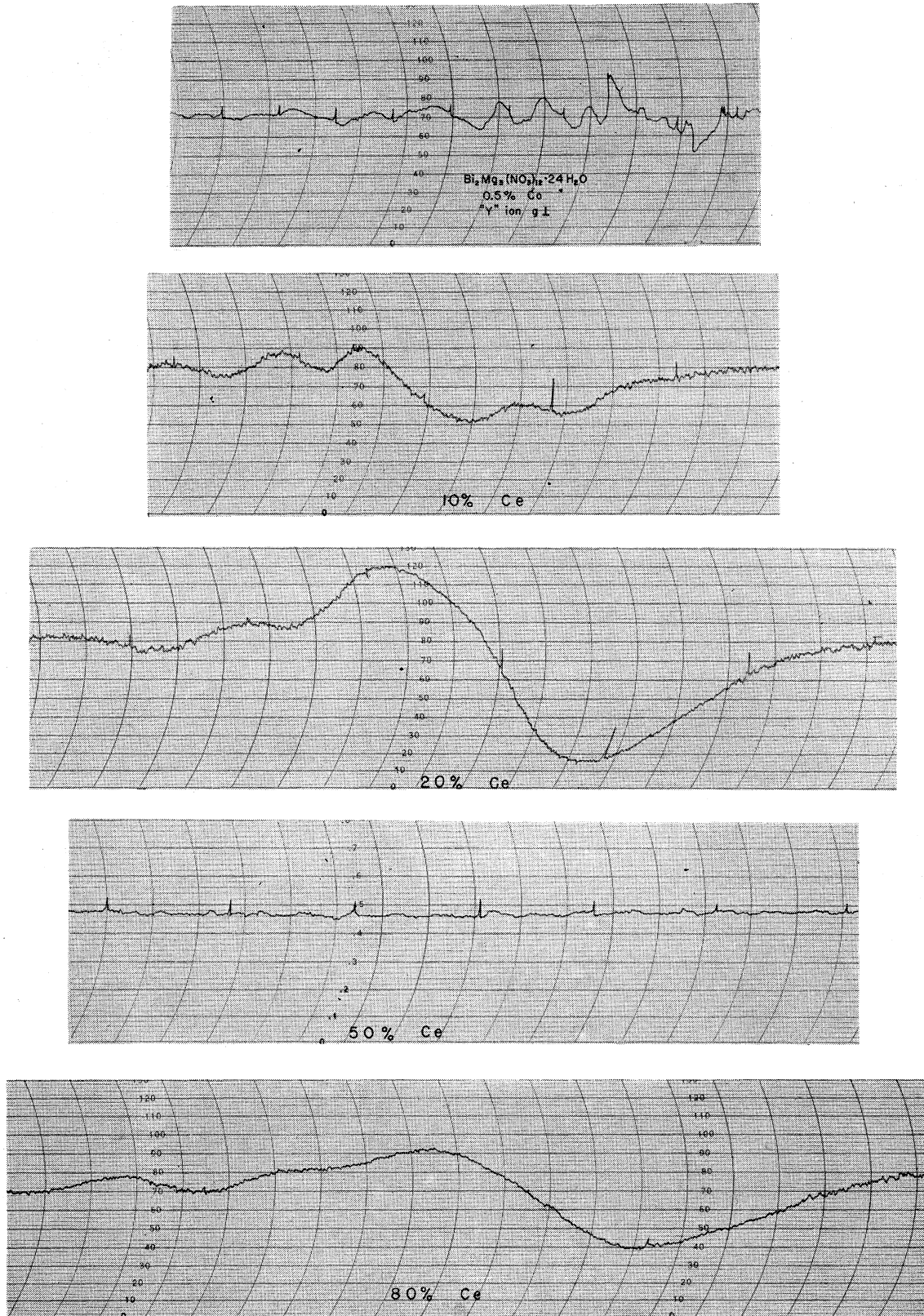FIG. 2. X-ion resonances. Perpendicular orientation.

FIG. 3. Y-ion resonances. Parallel orientation.

FIG. 4. *Y*-ion resonances. Perpendicular orientation.

involved. We found that a range of powers could always be found which afforded sensitive detection without saturation. By operating always within this range, we could insure that an observed absence of a resolved hyperfine resonance signal is due to the presence of the cerium and not to a broadening produced by saturation of the transitions involved. The effects that result from temperature are connected with the saturation question, since, as the temperature is lowered, the relaxation time for the electron spin system increases, thus causing saturation to occur at lower microwave power; however, the observed spectra indicate that we are not yet at a temperature low enough to seriously hinder our observations.

Since the attenuation of the hyperfine spectrum is not caused by the power saturation effect, we feel that the most probable cause is the magnetic dipole interaction between the cerium and cobalt ions. If one examines the traces for the X ions for the concentrations of 0, 10, and 20%, it will be noticed that while the hyperfine splitting remains unchanged, the breadth of the lines increases, and that the total width of the pattern progressively increases. It is not probable that this is due to a marked decrease in the relaxation time, since it was found that saturation effects occurred for approximately the same power in the 80% cerium concentrations as for the zero-percent cerium concentrations. We conclude therefore that the broadening is of the spin-spin type rather than spin-lattice.

The resonance of the free radical diphenyl-picrylhydrazyl was observed for each run, and we were not able to detect any variation from its reported resonance at $g=2.00$ at 4°K. We have also observed the resonance due to cerium in its perpendicular orientation, and we confirm the value of Cooke et al.[7] of $g_{\perp}=1.84$. This gives us confidence that the results obtained are not in serious error as a result of some unknown cumulative effect.

An experiment was also performed on $\frac{1}{2}\%$ cobalt in lanthanum magnesium nitrate at 4°K to see how this

[7] Cooke, Duffus, and Wolfe, Phil. Mag. 44, 623 (1953).

TABLE IV. $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ ($\frac{1}{2}\%$ cobalt). 4°K.

	$g_{||}$	$g_{\perp}$	$A \times 10^4$, cm^{-1}	$B \times 10^4$, cm^{-1}
X ion	4.05±0.002	4.43±0.002	80.7±3	103.3±3
Y ion	7.23±0.01	2.31±0.002	278.8±6	≤1

spectrum compared with the one of bismuth magnesium nitrate. We found only a very slight difference; the values are given in Table IV.

NUCLEAR ORIENTATION

It has been known for some time that the observed degree of Gorter-Rose nuclear orientation of cobalt ions in cerium magnesium nitrate substantially differs from the results of calculations based on a hyperfine interaction that does not include dipole-dipole terms.[8] Such terms may reasonably be expected to diminish the degree of orientation; however, not enough is yet known about the crystal structure of cerium magnesium nitrate to permit a reliable calculation of their effect. The present resonance experiments confirm the presence of strong dipole-dipole coupling between the cerium and cobalt ions; together with orientation experiments carried out with 50% lanthanum-cerium (magnesium nitrate) crystals,[8] which yield degrees of orientation in better agreement with the computed values, they indicate that the observed attenuation in the Gorter-Rose orientation is very probably due to dipole-dipole interactions.

ACKNOWLEDGMENTS

[8] C. S. Schroeder, thesis, The Ohio State University, 1956 (unpublished).

FIG. 1. *X*-ion resonances. Parallel orientation.

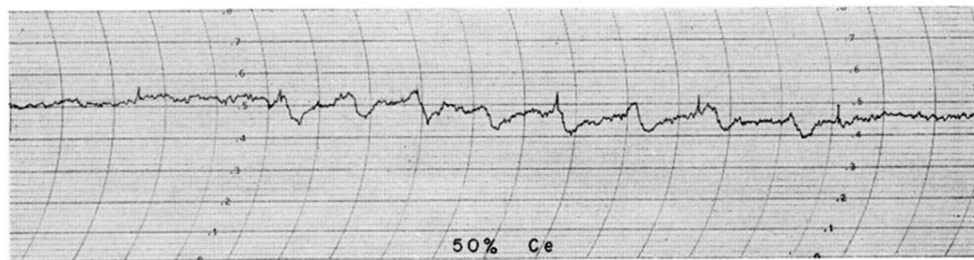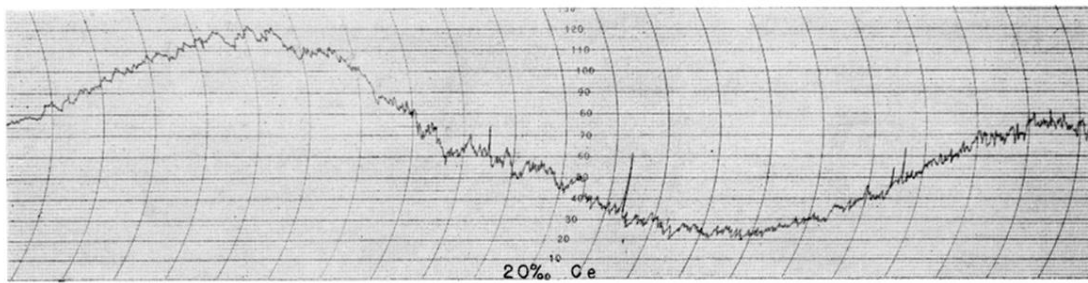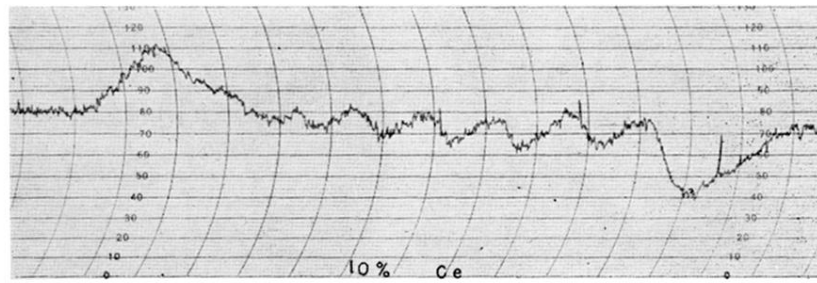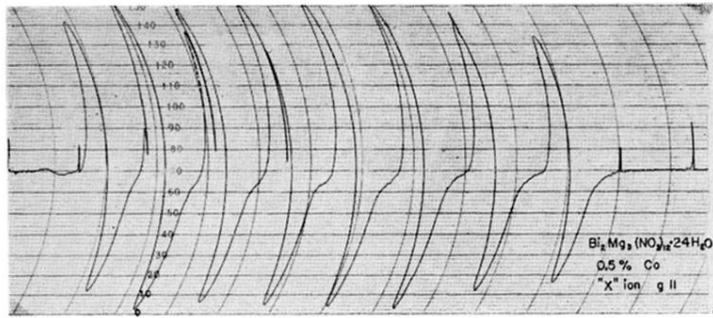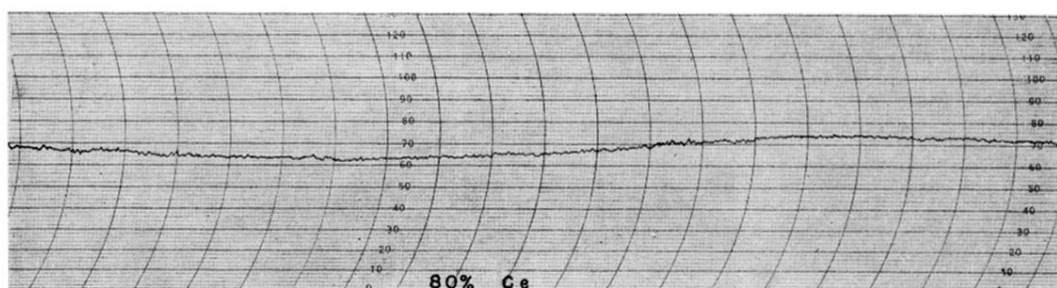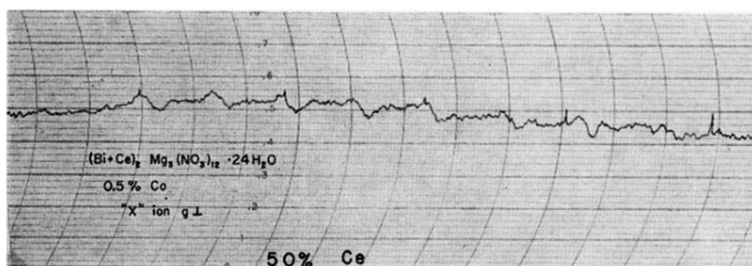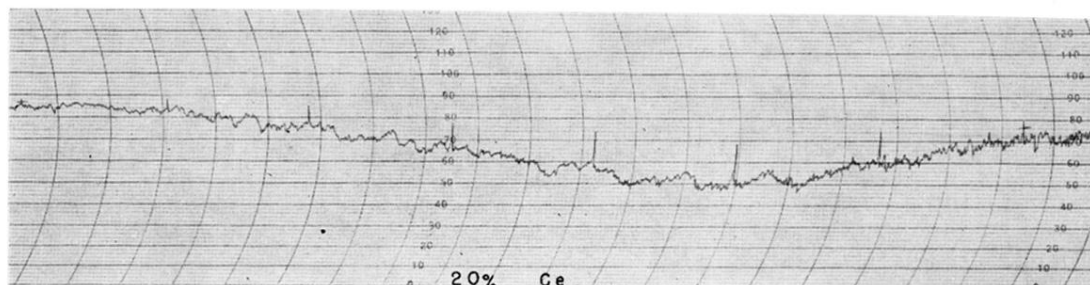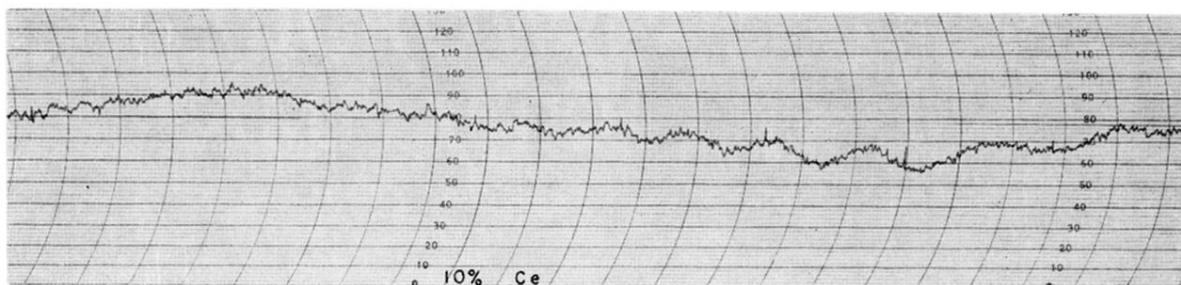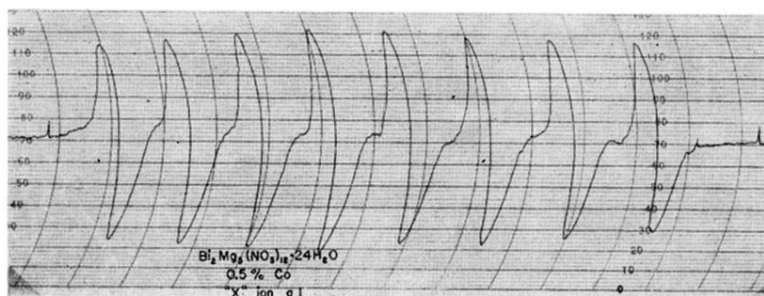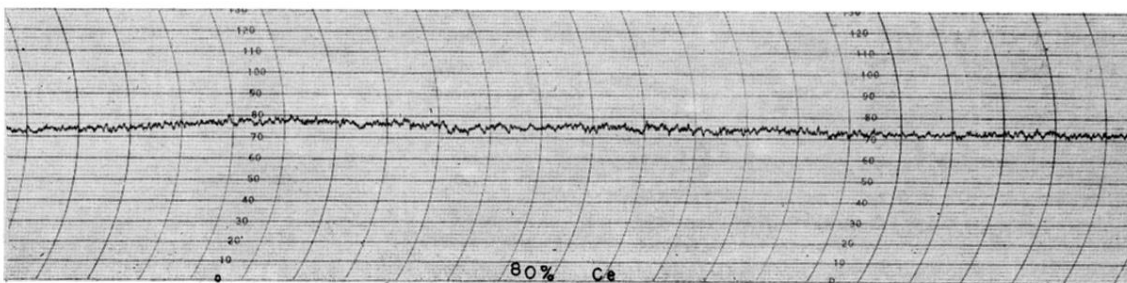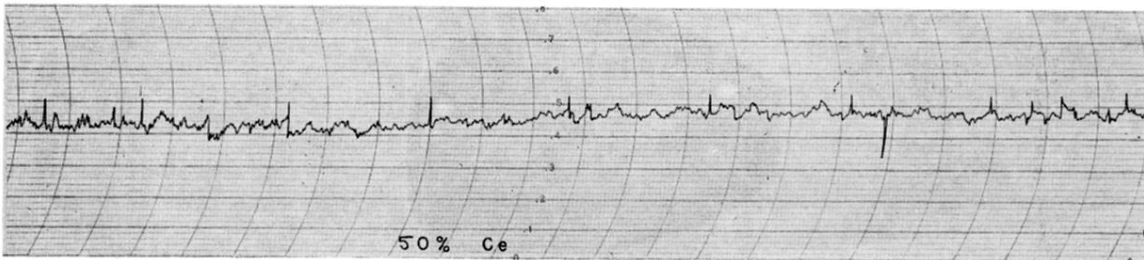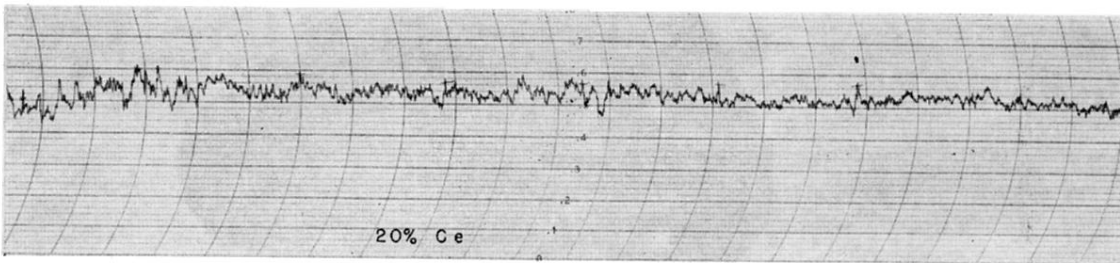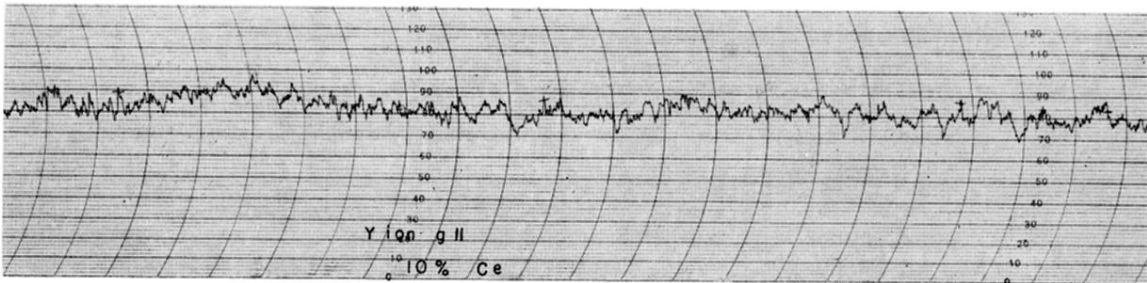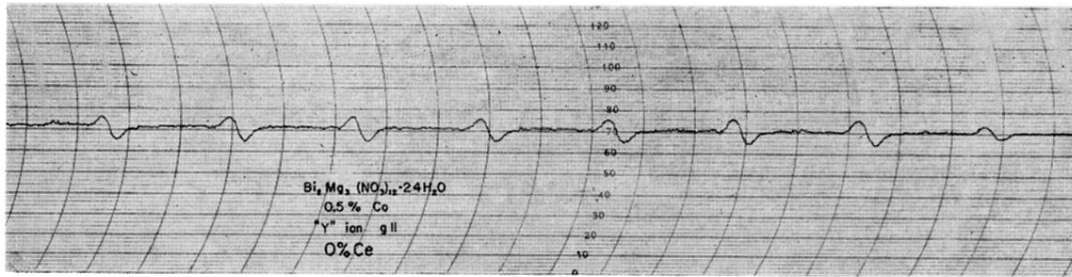FIG. 2. *X*-ion resonances. Perpendicular orientation.
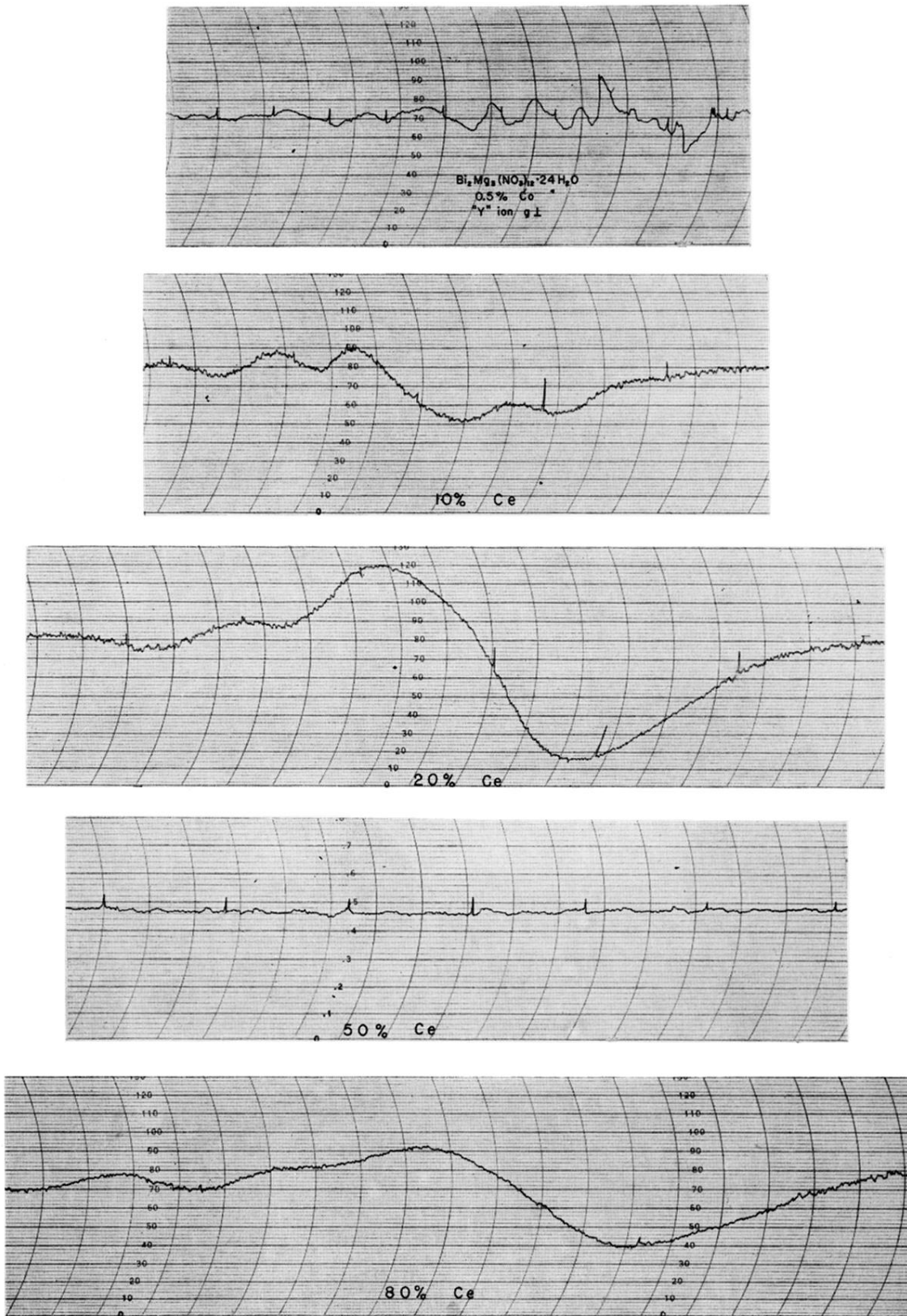
FIG. 3. Y-ion resonances. Parallel orientation.

FIG. 4. *Y*-ion resonances. Perpendicular orientation.