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SOME LOW TEMPERATURE STUDIES ON GLASS

PART I: ESR of Barium Alumino Borate Glasses  
Containing  $Ce^{3+}$ \*

by

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## ABSTRACT

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#### PART I: ESR of Barium Alumino Borate Glasses Containing $\text{Ce}^{3+}$

The ESR for a series of Barium Alumino Borate glasses containing up to 7.5 mole % Ce, mostly as  $\text{Ce}^{3+}$ , was studied at about liquid Helium temperature. Some samples were also X-irradiated and the resulting changes in their ESR spectra were observed. A broad resonance at  $g_{||} = 3.18$  was attributed to  $\text{Ce}^{3+}$  ions in the glasses studied. This resonance increased in intensity with increasing  $\text{Ce}^{3+}$  in the glass, which was achieved by increasing the total cerium introduced in the glass melted under strongly reducing conditions, or by irradiating the glass originally containing  $\text{Ce}^{4+}$ . This resonance was observed at low temperatures and disappeared at about 200°K. Oxidation-Reduction reactions were induced in these glasses as a result of X-irradiation.

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PART I: ESR of Barium Alumino Borate Glasses Containing Ce<sup>3+</sup>

I - INTRODUCTION

Ce<sup>3+</sup> is a 4f<sup>1</sup> ion whose ground state is <sup>2</sup>F<sub>5/2</sub>.

It is possible to assume that the ground state can be split by a ligand field of axial symmetry, and that this splitting is small compared with the energy of the first excited state <sup>2</sup>F<sub>7/2</sub>, which for Ce<sup>3+</sup> lies at about 2200cm<sup>-1</sup>. If we work entirely within the ground manifold  $J = \frac{5}{2}$ , and neglect admixtures of  $J = \frac{7}{2}$  and of higher excited states, the sixfold  $J = \frac{5}{2}$  manifold splits into three doublets whose wave-functions are:

$$|J_z = \pm \frac{1}{2}\rangle, \quad |J_z = \pm \frac{3}{2}\rangle, \quad |J_z = \pm \frac{5}{2}\rangle$$

For the ground state  $J = \frac{5}{2}$ , the principal g-values are:

$$|\pm \frac{1}{2}\rangle \quad g_{||} = \frac{6}{7} = 0.86 \quad ; \quad g_{\perp} = \frac{18}{7} = 2.57;$$

$$|\pm \frac{3}{2}\rangle \quad g_{||} = \frac{18}{7} = 2.57 \quad ; \quad g_{\perp} = 0 \quad ;$$

$$|\pm \frac{5}{2}\rangle \quad g_{||} = \frac{30}{7} = 4.29 \quad ; \quad g_{\perp} = 0 \quad .$$

A number of corrections have been suggested for the above

values; one of which is to include higher order Zeeman effects and to take into account contributions from the state  $J = \frac{7}{2}$ , which will result in a finite value for  $g_{\parallel}$  rather than zero in the case of a pure  $J_z = \pm \frac{5}{2}$  doublet. The above calculations were made on the basis of a crystal field of  $C_{3h}$  symmetry as in the case of Cerium ethylsulphate and anhydrous Cerium chloride. More complicated states are found in the case of  $C_{3v}$  symmetry  $[(Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O)]$ . The experimental results obtained for these salts are shown below in the Table 1.

Although there have been a number of ESR publications for  $Ce^{3+}$  in crystals<sup>1-8</sup>, to the best of our knowledge, no such studies in glass are available in the open literature. This is probably due to the necessity of using very low temperatures for observing the very broad resonance characteristic of  $Ce^{3+}$ . Most of the work reported in this paper was conducted in the vicinity of liquid Helium temperature (5-10°K).

## II - EXPERIMENTAL

All glasses were of the molar composition 20%  $Al_2O_3$ , 30% BaO, 50%  $B_2O_3$ . Analytical reagent-grade Aluminum hydroxide and Barium Carbonate were used to introduce  $Al_2O_3$  and BaO in all samples. A.R. Ammonium pentaborate was used to introduce  $B_2O_3$  in the reduced samples, while Boric acid was used for the oxidized samples. Cerium was introduced as

Salt	Symmetry	Diluent	T(°K)	$g_{  }$	$g_{\perp}$	
$Ce(C_2H_5SO_4) \cdot 9H_2O$	$C_{3h}$	La	4.2	0.955	2.185	ground state <sup>1</sup>
				3.72	0.20	excited doublet
$CeCl_3$	$C_{3h}$	La	4.2	4.0366	0.17	Hutchison <sup>2</sup> and Wong (1958)
$Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$	$C_{3v}$	La	4.2	0.25	1.84	Bowers <sup>3</sup> and Owen (1955)
				0.032	1.8264	Ruby, Benoit <sup>4</sup> and Jeffries (1962)

T A B L E 1

Cerous oxalate in all samples.

Melting was conducted in 100m $\pm$  platinum-10% Rhodium crucibles for about  $4\frac{1}{2}$  hours in a controlled atmosphere Silicon carbide heated furnace at a temperature of about 1250 $^{\circ}$ C. To ensure reduction of Cerium, nitrogen atmosphere was maintained continuously during melting. Furthermore, increasing amounts of ammonium oxalate were added to the batch and/or placed in the furnace as the Cerium content was increased.

Samples were annealed at a temperature of about 450 $^{\circ}$ C and cut to about 0.6 x 0.3 x 0.3 cm for ESR and irradiation studies.

ESR measurements were carried out using a homodyne, reflection type spectrometer which operates in the X band (at  $\sim$ 9GH). Low temperatures were obtained by passing liquid Helium continuously through a sample holder Dewars inserted in a multi-purpose V-4531 Varian Cavity.

X-irradiation was conducted with a Phillips type 1008/65 X-Rays unit, using a tungsten target and a 35KV and 35mA beam.

### III - RESULTS AND DISCUSSION

Figure 1 shows the effect of temperature of measurement on the intrinsic ESR spectrum of a reduced glass C<sub>2</sub> containing 0.5 mole % Ce. Room temperature measurements showed no resonance for the range 0-18kG. On the other hand,

at about 5.0°K, a weak line is observed at  $g \approx 4.3$  and attributed to  $\text{Fe}^{3+}$  impurity in the glass.<sup>9-11</sup> In addition, a strong very broad resonance extends from about 1.6kG to 18kG. The complete signal (expected to be axially symmetric) could not be recorded since the available magnet does not give fields higher than about 18kG.  $g_{||}$  measured for this sample and other samples in this study was calculated to be about  $3.18 \pm 0.08$ .  $g_{\perp}$  would be expected to have a value less than 0.3. These results are better compared with those obtained for Cerium salts of  $C_{3h}$  symmetry (Table 1), which suggests that most of the  $\text{Ce}^{3+}$  in the glasses studied may have a distorted  $C_{3h}$  symmetry with respect to the oxygen ligands in the glass.

Figure 2 shows the effect of increasing  $\text{Ce}^{3+}$  concentration on the ESR spectrum. Increasing Ce content in the strongly reduced glasses from 0.1 mole % ( $C_1$ ) to 1.0 mole % ( $C_3$ ) and 7.5 mole % ( $C_{12}$ ) is accompanied by a corresponding increase in the intensity of the broad resonance, thus confirming that it is due to  $\text{Ce}^{3+}$ . The resonance due to  $\text{Fe}^{3+}$  at  $g \approx 4.3$  was difficult to detect as the Cerium content was increased to 7.5 mole %. This may be attributed to the stronger reducing conditions used for melting the higher Cerium glasses.

Figure 3 shows a plot of the intensity of the broad Cerium band (taken as the distance between the minimum at  $\sim 2.1\text{kG}$  and the maximum at  $\sim 6.5\text{kG}$ ) versus the total amount of Cerium introduced in the batch. The decrease in the slope

of the curve at higher Cerium contents may be partly attributed to the presence of some  $Ce^{4+}$  ions in the high Cerium glass since visual inspection showed that it is more and more difficult to get complete reduction as the total Cerium content is increased. This could be supported by magnetic susceptibility measurements for the same samples (to be reported later). Furthermore, the possibility of a change in the structural role of  $Ce^{3+}$  at high concentrations merits consideration.

The effect of the oxidation state of Cerium on the low temperature ESR spectrum is clearly shown in Figure 4. Samples  $B_2$  and  $C_1$  contain the same concentration of Cerium (0.1 mole %). However,  $B_2$  was melted under oxidizing conditions while  $C_1$  was melted under strongly reducing conditions. The intensity of the  $Fe^{3+}$  line at  $g = 4.3$  shows the effect of melting conditions. Two other weak lines at  $g = 6$  and  $g = 2$  are shown by the oxidized sample and are also attributed to  $Fe^{3+}$  impurity<sup>9-11</sup>. These lines are not easily detected in the spectrum for the reduced  $C_1$  sample. The  $Ce^{3+}$  absorption may be slightly indicated in the spectrum for the  $B_2$  sample which suggests a minute concentration of  $Ce^{3+}$  in that glass melted in air.

When glass  $B_2$  (containing 0.1 % Ce and melted in air) was X-irradiated for 16 hours at about  $90^{\circ}K$ , the following observations could be made (Figure 5):

- 1) A strong sharp resonance in the vicinity of  $g = 2$  was clearly induced as a result of irradiation. Other

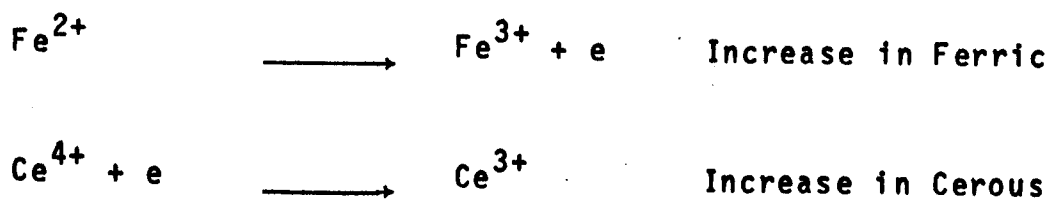


studies to be reported later have shown that this resonance is mainly due to the well known complex borate resonance attributed to hole centers<sup>12,13,14</sup>.

2) The  $\text{Fe}^{3+}$  resonance at  $g \approx 6$ , 4.3 and 2 increase in intensity as a result of X-irradiation.

3) The broad  $\text{Ce}^{3+}$  resonance which was very slightly indicated in the unirradiated sample, has clearly grown as a result of irradiation.

While the first observation is attributed to the trapping of a hole at a Boron-oxygen system, the increase in both  $\text{Fe}^{3+}$  and  $\text{Ce}^{3+}$  as a result of X-irradiation of the glass can be considered as an induced oxidation-reduction reaction:



It should be noted here that while  $\text{Fe}^{3+}$  and  $\text{Ce}^{3+}$  lines were clearly observed to increase as a result of irradiation,  $\text{Ce}^{4+}$  has no ESR and the line due to the minute impurity of  $\text{Fe}^{2+}$  (expected at about  $g \approx 3.3$ ) seems to be overlapped by the strong lines due to  $\text{Fe}^{3+}$  ( $g \approx 4.3$ ) and the broad  $\text{Ce}^{3+}$  line ( $g_{||} \approx 3.18$ ).

Figure 6 shows the effect of X-irradiation (16 hours at about  $90^{\circ}\text{K}$ ) on glass  $\text{C}_1$  (0.1 % Ce, reduced). The

following observations can be made:

1) A strong resonance is induced at about  $g \sim 2$ , partly attributed to the remaining complex borate resonance and partly due to the presence of  $Ce^{3+}$  in the glass (details of this center will be discussed in Part II).

2) The  $g = 4.3$  line due to  $Fe^{3+}$  decreases in intensity as a result of X-irradiation. Since this glass was melted under reducing conditions, other weaker lines attributed to  $Fe^{3+}$  could not be detected. Furthermore, the strong broad  $Ce^{3+}$  line made it impossible to observe the  $Fe^{2+}$  line expected at about  $g = 3.3$ .

3) The broad  $Ce^{3+}$  line ( $g_{||} \approx 3.18$ ) decreased in intensity as a result of irradiation.

Again the last two observations can be attributed to an induced oxidation-reduction reaction:



Optical studies reported earlier<sup>15</sup> showed that Cerium is oxidized or reduced by irradiation depending on its original state in the glass. On the other hand, ESR and optical studies of other types of glasses showed similar changes in the state of oxidation of iron as a result of irradiation<sup>16,17</sup>.

#### IV - CONCLUSIONS

A broad resonance at  $g_{||} = 3.18$  was observed in glasses containing Cerium and melted under strongly reducing conditions. This resonance increased in intensity with increasing  $Ce^{3+}$  in the glass, which was achieved by increasing the total Cerium introduced in the glass melted under strongly reducing conditions, or by irradiating the glass originally containing  $Ce^{4+}$ . This resonance was observed at low temperatures and disappeared at about  $200^{\circ}K$  (Figure 7). Oxidation-reduction reactions were induced in these glasses as a result of X-irradiation.

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FIGURE CAPTIONS

Fig. 1: Effect of temperature of measurement on intrinsic ESR spectrum of reduced glass containing 0.5 mole % Ce, before irradiation. Intensity scale 0.5 V/cm.

1. Room temperature
2. 5K.

Fig. 2: Effect of increasing  $Ce^{3+}$  concentration on intrinsic ESR spectrum at low temperature.

1. Glass  $C_1$ , 0.1 mole % Ce
2. Glass  $C_3$ , 1.0 mole % Ce
3. Glass  $C_{12}$ , 7.5 mole % Ce

(While attenuation for most measurements was taken at  $db = 22$ , low temperature measurements of  $C_{12}$  were taken at lower power ( $db = 28$ ) due to saturation effects).

Fig. 3: Effect of increasing Cerium concentration on the intensity of the  $Ce^{3+}$  line at  $g_{||} = 3.18$ .

Fig. 4: Effect of oxidation state of Cerium on intrinsic ESR spectrum at low temperature ( $T = 5K$ ). Mole % Ce = 0.1.

Intensity scale 0.33 V/cm/gr.

1. Glass  $C_1$  (reduced)
2. Glass  $B_2$  (oxidized)

Fig. 5: Effect of X-irradiation on oxidation state of Cerium and Iron in a glass melted under oxidizing conditions.  $T = 5K$ .  
Mole % Ce = 0.1. Intensity scale 0.33 V/cm.  
1. Before irradiation.  
2. After irradiation.

Fig. 6: Effect of X-irradiation on oxidation state of Cerium and Iron in a glass melted under strongly reducing conditions.  $T = 5K$ . Mole % Ce = 0.1. Intensity scale 0.33 V/cm.  
1. Before irradiation  
2. After irradiation

Fig. 7: Effect of increasing temperature of measurement on the intensity of the  $Ce^{3+}$  resonance ( $g_{||} = 3.18$ ).

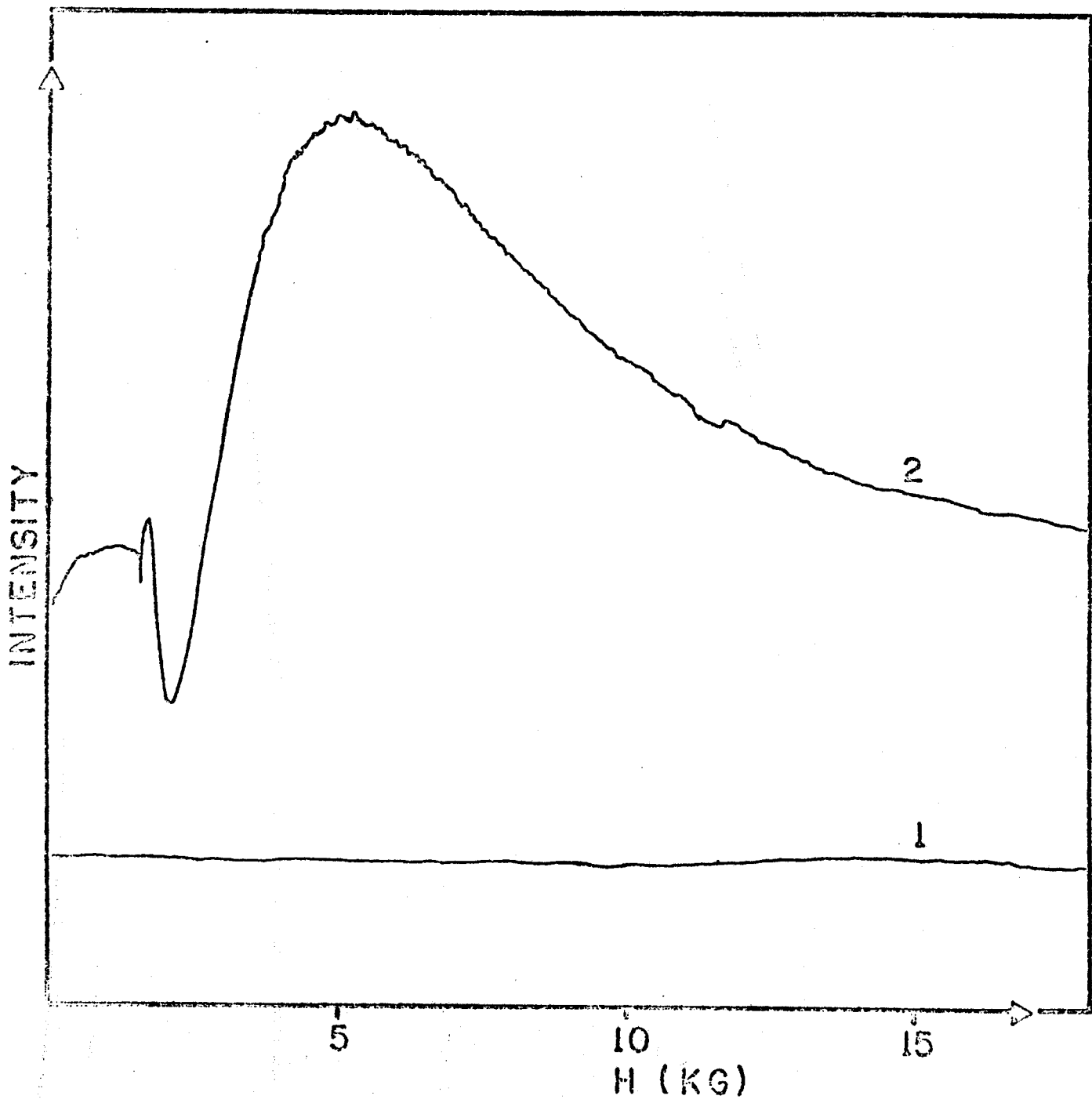


Fig. 1



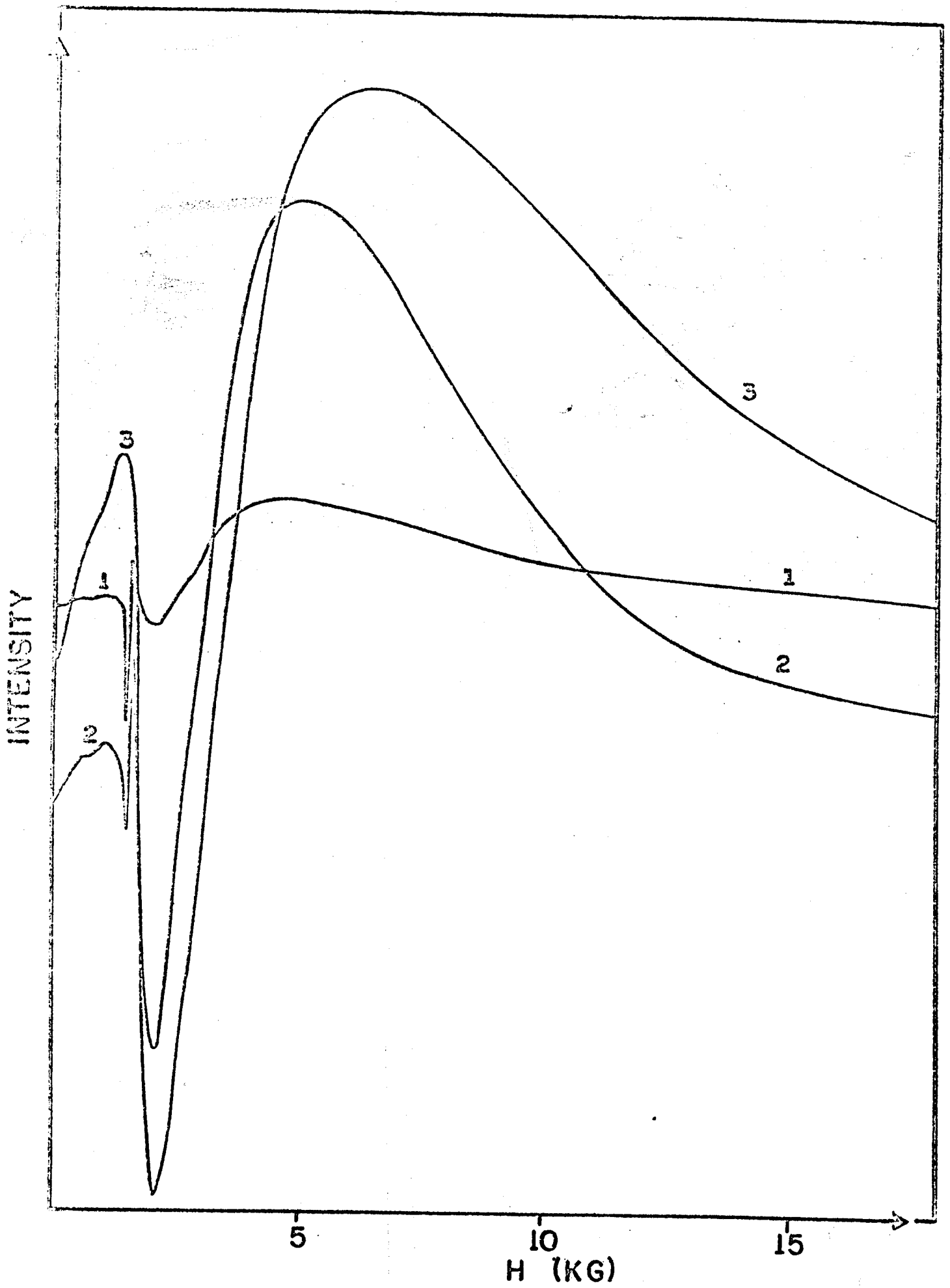


Fig. 2

INTENSITY AT  $g_{11} = 3.18$

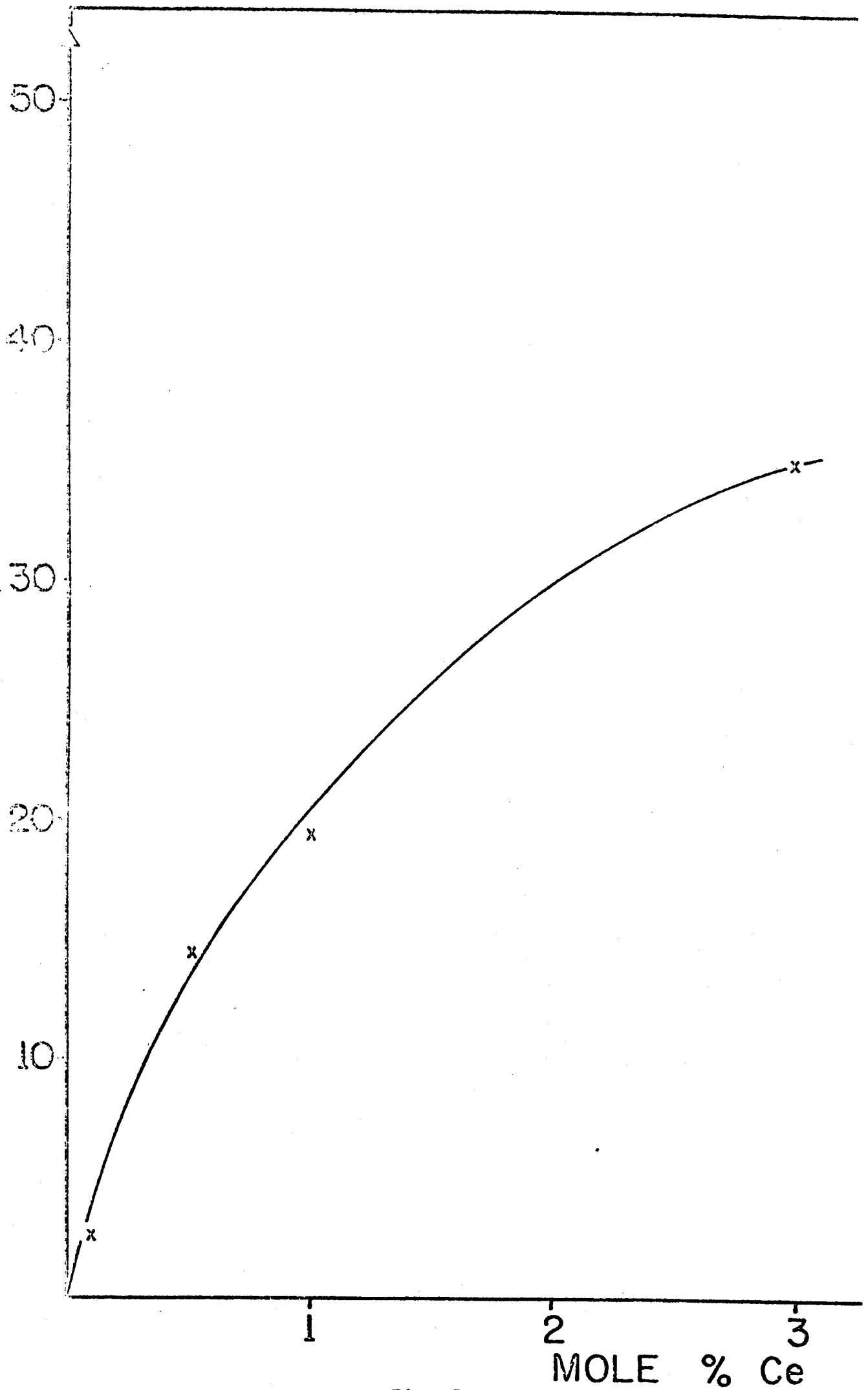


Fig. 3

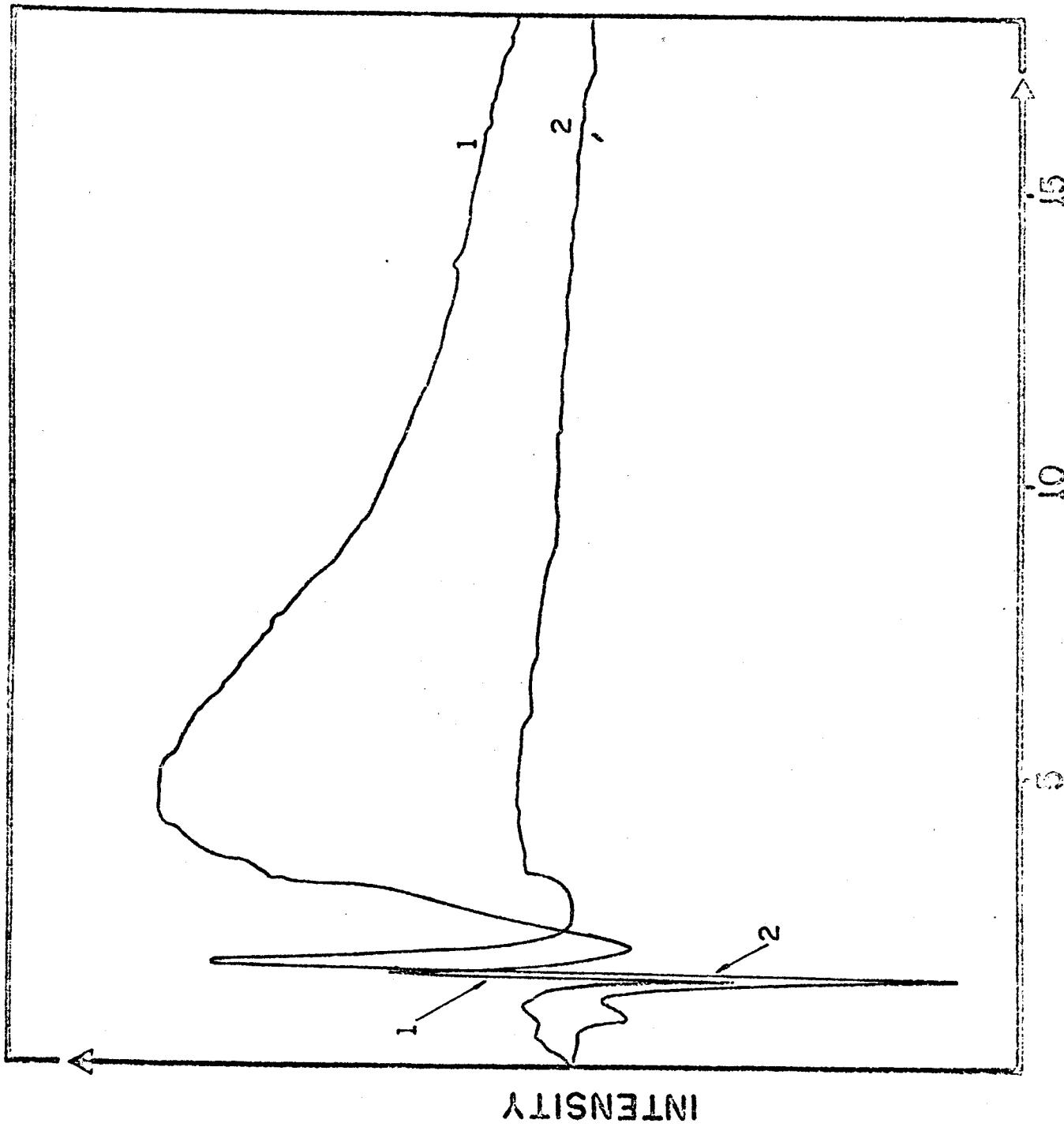


Fig. 4  $H(KG)$

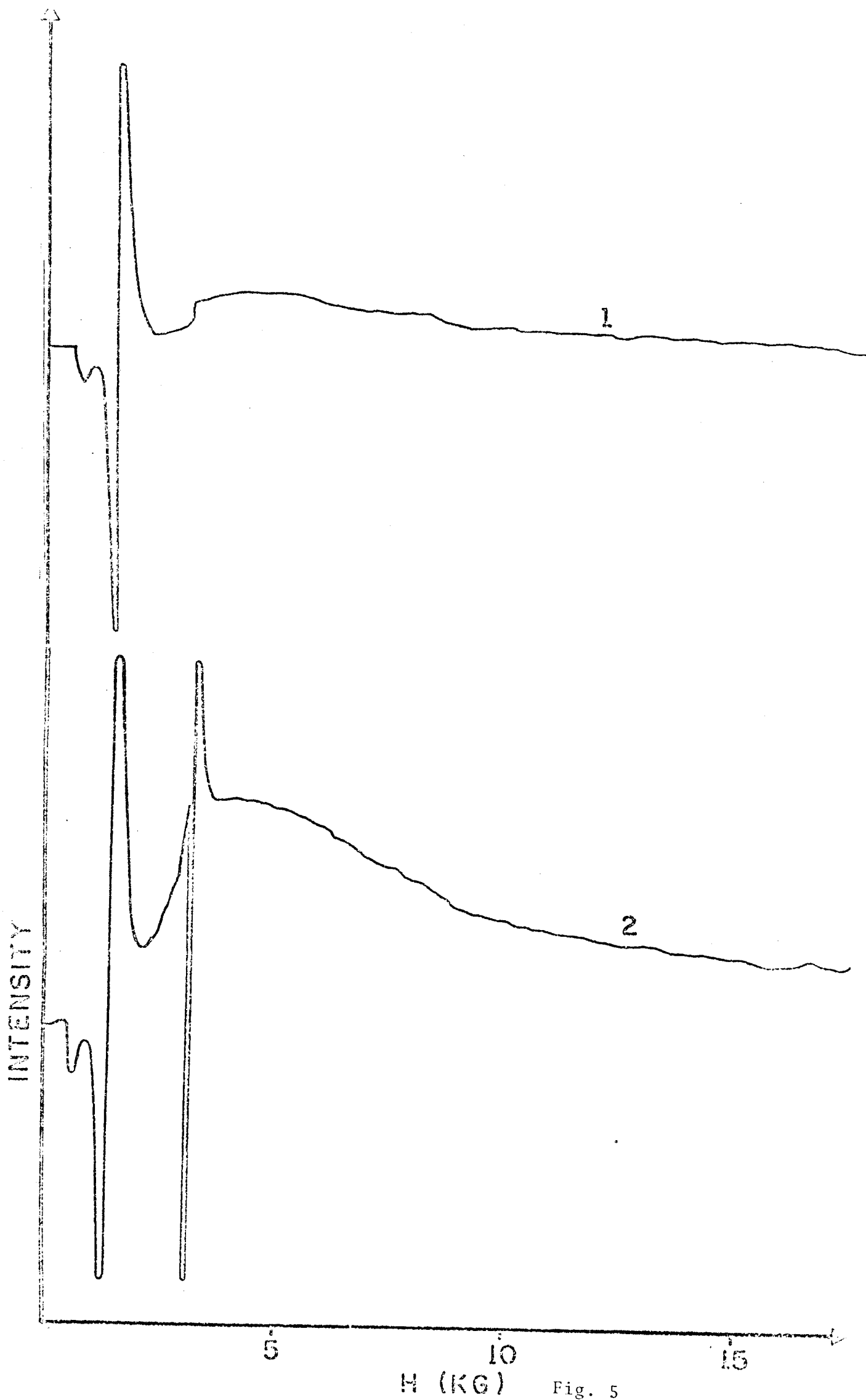


Fig. 5

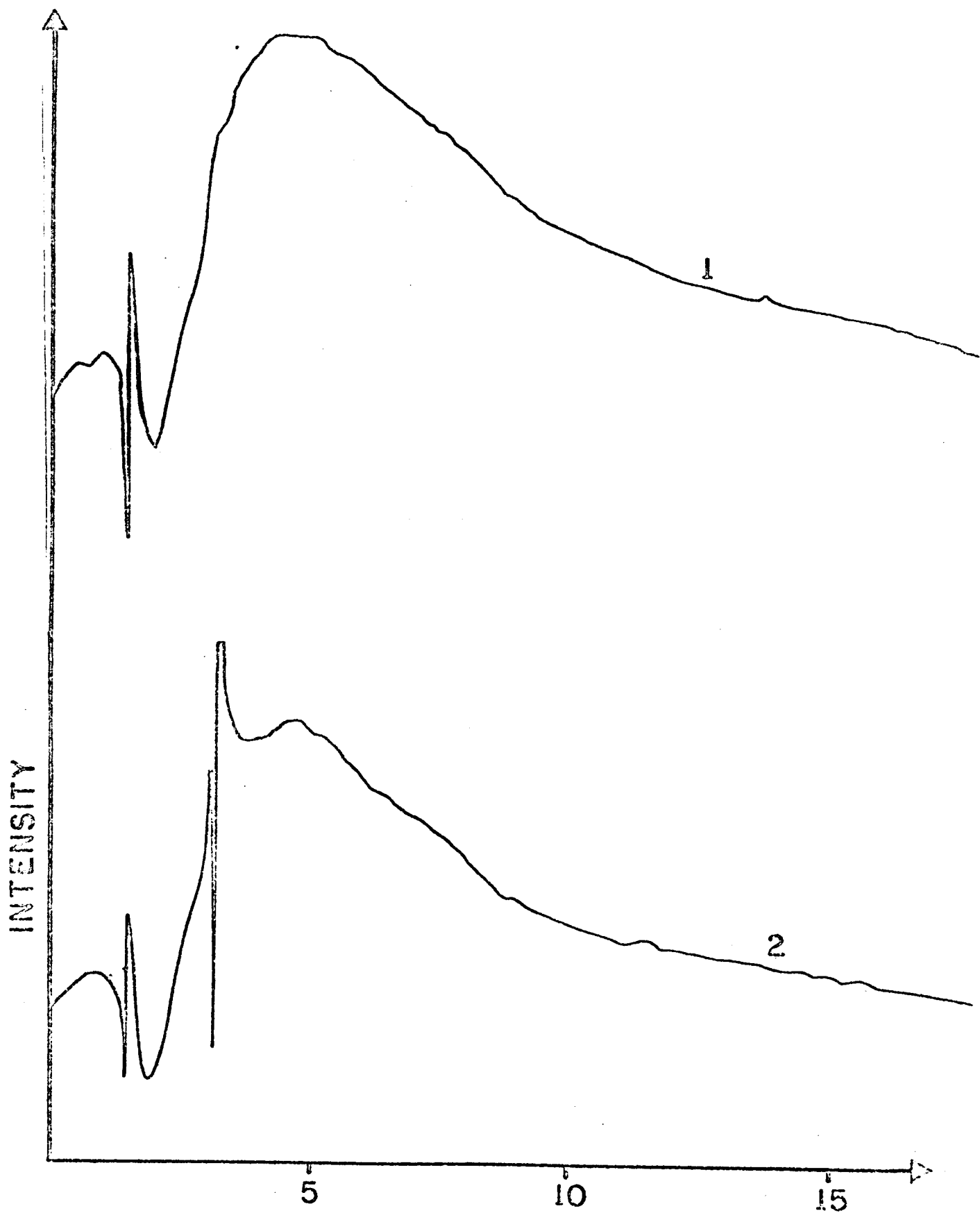


Fig. 6 H (KG)

Fig. 7

