PHYSICAL REVIEW VOLUME 186, NUMBER 2 10 OCTOBER 1969

Polarized-Neutron-Diffraction Study of Magnetic Moments in Yttrium-Cobalt Alloys

E. KRÉN,* J. SCHWEIZER, AND F. TASSET
Centre d'Etudes Nucléaires, Grenoble, France

(Received 12 September 1969; revised manuscript received 1 April 1969)

The magnetic moments in the ordered YCo_5, Y_2Co_7, and YCo_3 intermetallic compounds with closely related crystal structures have been investigated on single crystals using the polarized-neutron-diffraction technique. By assuming that only the cobalt atoms have magnetic moments and using Moon's experimental cobalt form factor extrapolated smoothly to unity, a discrepancy was found between the measured and calculated magnetic-structure factors. This can be explained by the existence of either a magnetic moment at the yttrium sites coupled antiparallel to the cobalt moments, or a diffuse negative-spin polarization. In the present study, it is not possible to decide between the two models. The ferromagnetically aligned magnetic moments on the cobalt atoms are influenced by the yttrium neighbors; they are the smallest in YCo_3, which is the richest in yttrium, and in all cases are the smallest at the sites having the most yttrium neighbors.

1. INTRODUCTION

SEVERAL intermetallic compounds, each existing only in a very narrow concentration range, occur in the Co-rich side of the rare-earth–cobalt systems. In these alloys a negative coupling was observed between the spins of the rare-earth and Co atoms.[1] It seemed of interest to investigate the magnetic structure of the Y-Co alloys, which have similar crystal-structure types as given, e.g., in the phase diagram of Strnat *et al.*[2] A preliminary powder-neutron-diffraction study[3] with a poor experimental accuracy showed a ferromagnetic structure for YCo_3. In the present measurements the magnetic structure of the YCo_3, Y_2Co_7, and YCo_5 single crystals has been investigated by polarized neutrons.

2. CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES

The YCo_5, Y_2Co_7, YCo_3, and YCo_2 phase have closely related crystal structures. The basic unit is the hexagonal YCo_5 with the space group *P6/mmm*,[4] its unit cell containing two different Co sites and one Y site (Fig. 1). The unit cell of Y_2Co_7 [Fig. 2(a)] can be derived from three superposed cells of YCo_5 by substituting a Y atom for one of the Co-I atoms and by submitting this new threefold unit to a rhombohedral translation. The Y atoms in the plane of the substitution are displaced in the direction of the *c* axis to increase the distance between them. There are five Co and two Y sites, which are determined by five independent position parameters in space group $R\bar{3}m$.[5] The structure of YCo_3 [Fig. 2(b)] can be derived similarly from two superposed unit cells of YCo_5, getting again the space group $R\bar{3}m$.[5] The three Co and two Y sites

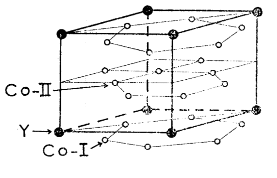
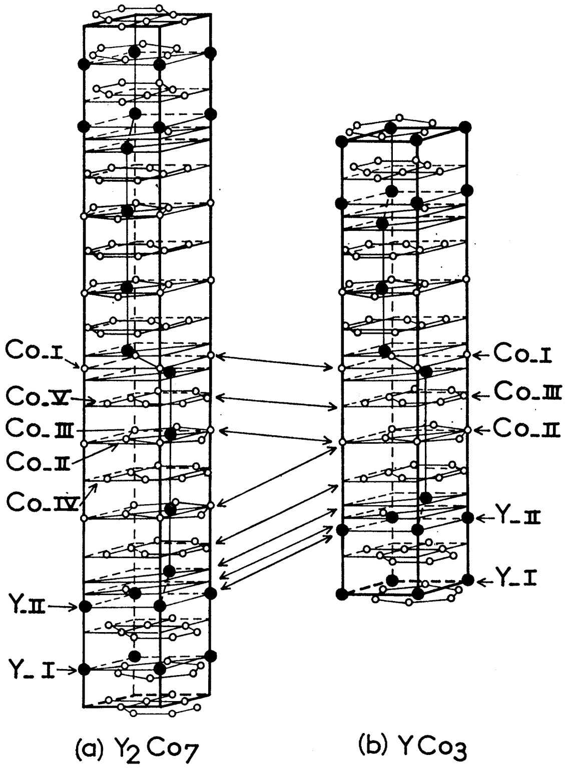


FIG. 1. Crystal structure of YCo_5. The Y and Co atoms are represented by full and open circles, respectively.



(a) Y_2Co_7 (b) YCo_3

FIG. 2. Crystal structure of (a) Y_2Co_7 and (b) YCo_3. The Y and Co atoms are represented by full and open circles, respectively. The crystallographic sites which are identical in the two structures are shown by arrows.

---

* On leave from the Central Research Institute for Physics, Budapest, Hungary. Now returned.

[1] R. Lemaire, Cobalt **32**, 132 (1966); **33**, 201 (1966).

[2] K. J. Strnat, W. Ostertag, N. J. Adams, and J. C. Olson, Fifth Rare-Earth Research Conference 1965 (unpublished).

[3] R. Lemaire, R. Pauthenet, J. Schweizer, and I. Silvera, J. Phys. Chem. Solids **28**, 2471 (1967).

[4] J. H. Wernick and S. Geller, Acta Cryst. **12**, 662 (1959).

[5] E. F. Bertaut, R. Lemaire, and J. Schweizer, Bull. Soc. Franc. Mineral. Crist. **88**, 580 (1965).

TABLE I. Values of the lattice parameters a and c at room temperature, the Curie temperature T_C, and the extrapolated saturation magnetization σ_0 of a unit cell for YCo_5, Y_2Co_7, and YCo_3 intermetallic compounds.

	YCo_5	Y_2Co_7	YCo_3
a (Å)	4.945	5.002	5.016
c (Å)	3.983	36.21	24.35
T_C (°K)	977	639	301
σ_0 (μ_B)	7.5	7.4	1.4

are described by two independent position parameters. In this paper, the hexagonal description of these rhombohedral structures will be applied. The unit cell of YCo_2 is obtained by substituting a Y atom for one Co-I atom in every unit cell; the space group is $Fd3m$.[6] In the two-phase fields of the phase diagram these phases can be crystallized together, having common axes a and c, because of the large similarities in the crystal structures.

The magnetization-versus-temperature curves obtained with polycrystalline specimens[1] exhibit ferromagnetic behavior for YCo_5 and Y_2Co_7 and ferrimagnetic behavior for YCo_3, while YCo_2 is paramagnetic. The values of the Curie temperature T_C and the saturation magnetization σ_0 extrapolated to 0°K are given in Table I. A strong uniaxial magnetocrystalline anisotropy was observed, the c axis being the direction of the easy magnetization in all cases.

3. EXPERIMENTAL

The alloys were prepared by melting Y of 99.9% and Co of 99.99% purity in an alumina crucible under a purified helium atmosphere. The single crystals were grown in an alumina crucible cooled at its lower pointed end and placed inside a graphite cylinder around which a heating coil was lifted with a velocity of 15 mm/h. Although the products obtained were not entirely single crystals for Y_2Co_7 and YCo_3, single-crystal pieces of appropriate dimension could be selected after crushing.

According to the x-ray investigations by the rotating crystal method, the YCo_5 crystal contains a single phase, the YCo_3 crystal has small amount of the YCo_2 phase, while the Y_2Co_7 crystal is contaminated by the YCo_3 phase. These impurity phases have common a and c axes with the parent phases. The values of the lattice parameters a and c determined by the Debye-Scherrer method are given in Table I. The atomic position parameters for YCo_3 and Y_2Co_7 were assumed to be the same as in $HoCo_3$ and Gd_2Co_7, respectively.[5] The composition of the YCo_3 and Y_2Co_7 crystals is certainly stoichiometric due to the extremely narrow stability range of these phases. The composition of the YCo_5 crystal was checked by x-ray fluorescence analysis and by a study of the lattice parameters, and it was found to be also stoichiometric.

The magnetic moments were measured by the polarized-neutron-diffraction technique, which is a relative method comparing the scattered intensities obtained with positive and negative neutron polarization. Consequently, the measurements can be performed even in the presence of an impurity phase, provided that the investigated reflections belong to one phase only. The present study was thus limited to the characteristic super-reflections of each phase, which occur in addition to the common basic reflections. The single-crystal specimen was mounted in a liquid-helium cryostat with its c axis parallel to the external magnetic field of 14 kOe, determining the direction of the polarization vector of the neutron beam. In the usual experimental arrangement with a counter moving in the horizontal plane, only the reflections of the zone ($hk0$) can be measured, since any other setting of the crystal results in a large depolarization of the beam due to the incomplete saturation of the sample having strong uniaxial anisotropy. To collect reflections in other zones, the measurements were performed by an apparatus

TABLE II. Observed and calculated values of the magnetic-structure factor F_M at 4.2°K in Y_2Co_7. The calculated values were obtained by least-squares refinements: (A) assuming $\mu_{Y\text{-I}}=\mu_{Y\text{-II}}=0$ and using all reflections, (B) assuming $\mu_{Y\text{-I}}=\mu_{Y\text{-II}}=0$, but using only the six last reflections, (C) assuming $\mu_{Y\text{-I}}\neq0$, $\mu_{Y\text{-II}}\neq0$, and (D) assuming $\mu_{Y\text{-I}}=\mu_{Y\text{-II}}=0$ and using a scaled-up free-atom $3d$ form factor for Co.

						$F_{M,\text{calc}}$ (10^{-12} cm)			
h	k	l	$\sin\theta/\lambda$	γ	$F_{M,\text{obs}}$ (10^{-12} cm)	A	B	C	D
1	0	1	0.116	−1.97	−2.11±0.09	−1.87	−1.80	−2.10	−2.02
0	1	2	0.119	−2.90	−0.78±0.12	−0.71	−0.70	−0.83	−0.78
1	0	4	0.128	−0.64	0.40±0.06	0.38	0.35	0.41	0.41
0	1	8	0.160	−0.36	0.29±0.06	0.27	0.25	0.27	0.25
1	0	10	0.180	−0.06	0.18±0.03	0.23	0.21	0.18	0.21
0	1	11	0.191	0.08	−0.20±0.05	−0.15	−0.14	−0.17	−0.16
0	2	1	0.231	0.30	1.08±0.04	1.11	1.09	1.09	1.10
2	0	2	0.233	0.55	0.89±0.04	0.92	0.88	0.89	0.90
0	2	4	0.238	0.19	−0.29±0.02	−0.29	−0.29	−0.29	−0.29
2	0	5	0.241	0.55	−0.62±0.10	−0.63	−0.59	−0.62	−0.61
0	2	7	0.250	0.84	1.23±0.08	1.21	1.19	1.15	1.18
2	0	8	0.256	1.35	2.32±0.25	2.63	2.54	2.52	2.54

---

[6] J. H. Wernick and S. Geller, Trans. AIME **218**, 867 (1960).

TABLE III. Observed and calculated values of the magnetic-structure factor F_M at 4.2°K in YCo_3. The calculated values were obtained by least-squares refinements: (A) assuming $\mu_{Y\text{-I}}=2\mu_{Y\text{-II}}\neq 0$, and (B) assuming $\mu_Y=0$ and using the scaled-up $3d$ form factor for Co.

h	k	l	$\sin\theta/\lambda$	γ	$F_{M,\text{obs}}$ (10^{-12} cm)	$F_{M,\text{calc}}$ (10^{-12} cm) A	B
1	0	1	0.117	-0.697 ± 0.019	-0.59 ± 0.02	-0.58	-0.58
1	0	7	0.184	-0.054 ± 0.009	-0.12 ± 0.02	-0.14	-0.15
0	1	8	0.200	0.020 ± 0.006	0.04 ± 0.01	0.06	0.05
0	2	1	0.231	0.058 ± 0.001	0.15 ± 0.01	0.15	0.15
2	0	2	0.234	0.170 ± 0.007	0.22 ± 0.01	0.20	0.20
2	0	5	0.252	0.437 ± 0.012	-0.63 ± 0.02	-0.64	-0.64

TABLE IV. Observed and calculated values of the magnetic-structure factor F_M at 4.2°K in YCo_5. The calculated values were obtained by least-squares refinements: (A) assuming $\mu_Y\neq 0$, and (B) assuming $\mu_Y=0$ and using the scaled-up $3d$ form factor for Co.

h	k	l	$\sin\theta/\lambda$	γ	$F_{M,\text{obs}}$ (10^{-12} cm)	$F_{M,\text{calc}}$ (10^{-12} cm) A	B
1	0	0	0.117	-3.124	-0.91 ± 0.04	-0.91	-0.95
1	1	0	0.200	0.382	0.40 ± 0.02	0.38	0.39
2	0	0	0.235	0.552	0.71 ± 0.03	0.68	0.68
1	1	1	0.240	0.646	0.99 ± 0.05	1.00	1.00
2	0	1	0.288	5.107	-1.07 ± 0.10	-1.21	-1.21
2	1	0	0.311	-1.871	-0.54 ± 0.12	-0.52	-0.52
3	0	0	0.352	0.208	0.22 ± 0.01	0.22	0.22
2	2	0	0.406	0.413	0.84 ± 0.02	0.84	0.83

allowing the counter to lift from the horizontal plane in an angular interval of 28°. The accuracy of this method was calculated earlier.[7]

Single-crystal specimens of irregular shape were used with the approximate size of 4×2×3 mm for YCo_3, 6×1×5 mm for Y_2Co_7, and 4×1×4.5 mm for YCo_5, the last numerals giving the dimension in the direction of the c axis. The reflections were measured in the three symmetrical positions around the threefold c axis, and the equivalence of these reflections gave evidence that the crystals were free from extinction effects. The presence of multiple scattering was tested by rotating the crystals around the scattering vector. Since no change in any of the measured polarization ratios could be detected, the possible contribution to the scattered intensity from multiple scattering was considered to be not significant. The possible depolarization of the beam in the sample was checked by measuring the (111) reflection of a Heusler-alloy (Cu_2MnAl) single crystal stuck successively in front of and behind the sample. A slight depolarization was found in Y_2Co_7 and YCo_5.

4. RESULTS

The polarization ration $R=I_+/I_-$, where I_+ and I_- are the intensities with positive and negative polarization, was measured at 4.2°K for 6, 12, and 8 reflections in YCo_3, Y_2Co_7, and YCo_5, respectively. The measurements on YCo_3 were repeated at 90 and 215°K, as well. The observed values of R were corrected for the incomplete polarization of the incident beam (0.980) and for the incomplete polarization reversal (0.995) to obtain the ratio $\gamma=F_M/F_N$, where F_M and F_N are the magnetic- and nuclear-structure factors, respectively. Calculating F_N from the nuclear scattering amplitudes $b_Y=0.79$ and $b_{Co}=0.25$, the values of F_M were obtained. The results are given in Tables II–V.

The magnetic moments associated with the different sites in the unit cell were computed from the observed values of F_M by least-squares refinements. The calculations were performed first for Y_2Co_7, which has the largest unit cell and thus the most reflections measurable at the low-angle region.

In Y_2Co_7, the Co-II atoms have identical environments. Consequently, their magnetic moments were taken to be identical. In the first refinement, the magnetic moments for the Co sites were calculated by assuming that the Y atoms have no magnetic moment and by using the experimental form factor of Co measured by Moon[8] extrapolated smoothly towards unity at $(\sin\theta)/\lambda=0$. The calculated values of F_M and the magnetic moments are given in column A of Tables II and VI, respectively. As can be seen, the agreement between the measured and calculated values of F_M is very poor for the reflections at low angles. This can be explained by supposing the existence of magnetic moments on the Y atoms. Assuming that similar to the other $4d$ elements, Y has a form factor falling more rapidly with the reflection angle than that of Co, its

TABLE V. Observed and calculated values of the magnetic-structure factor F_M at 90 and 215°K in YCo_3. The calculated values were obtained by least-squares refinements using the form factor of Y derived for Y_2Co_7.

h	k	l	90°K γ	$F_{M,\text{obs}}$	$F_{M,\text{calc}}$	215°K γ	$F_{M,\text{obs}}$	$F_{M,\text{calc}}$
1	0	1	-0.639 ± 0.023	-0.54 ± 0.02	-0.54	-0.264 ± 0.003	-0.22 ± 0.01	-0.22
1	0	7	-0.044 ± 0.008	-0.10 ± 0.01	-0.12	-0.014 ± 0.006	-0.03 ± 0.01	-0.05
0	1	8	0.014 ± 0.010	0.03 ± 0.02	0.05	0.002 ± 0.006	0.00 ± 0.01	0.01
0	2	1	0.058 ± 0.001	0.15 ± 0.01	0.15	0.029 ± 0.001	0.08 ± 0.01	0.08
2	0	2	0.152 ± 0.004	0.20 ± 0.01	0.18	0.073 ± 0.005	0.09 ± 0.01	0.08
2	0	5	0.409 ± 0.016	-0.59 ± 0.02	-0.60	0.187 ± 0.006	-0.27 ± 0.01	-0.27

---

[7] A. Delapalme, R. Georges, and J. Schweizer, Nucl. Instr. Methods **63**, 283 (1968).

[8] R. M. Moon, Phys. Rev. **136**, A195 (1964).

TABLE VI. Magnetic moments at 4.2°K in Y_2Co_7 obtained by the least-squares refinements explained in Table II. μ_{total} is the magnetic moment of a unit cell. All values are given in μ_B.

	A	B	C	D
$\mu_{\text{Y-I}}$	...	...	−1.02±0.24	...
$\mu_{\text{Y-II}}$	...	...	−0.45±0.22	...
$\mu_{\text{Co-I}}$	1.36±0.10	1.26±0.06	1.31±0.06	1.28±0.06
$\mu_{\text{Co-II}}-\mu_{\text{Co-III}}$	1.52±0.08	1.47±0.06	1.44±0.06	1.45±0.05
$\mu_{\text{Co-IV}}$	1.41±0.05	1.37±0.02	1.34±0.03	1.37±0.03
$\mu_{\text{Co-V}}$	1.14±0.03	1.10±0.02	1.10±0.02	1.11±0.02
μ_{total}	9.25±0.20	8.92±0.14	7.32±0.35	8.92±0.13

TABLE VIII. Magnetic moments at 4.2°K in YCo_5 obtained by the least-squares refinements explained in Table IV. μ_{tot} is the magnetic moment of a unit cell. All values are given in μ_B.

	A	B
μ_{Y}	−0.40±0.30	...
$\mu_{\text{Co-I}}$	1.68±0.04	1.66±0.04
$\mu_{\text{Co-II}}$	1.67±0.04	1.66±0.04
μ_{total}	7.97±0.34	8.30±0.15

contribution to the scattered intensities at higher angles thus being negligible, a new refinement of the magnetic moments of Co was carried out, this time using only the six reflections at higher angles [from (021) to (208)]. The obtained moments and the calculated values of F_M for all the 12 reflections are given in column B of Tables II and VI. The difference ΔF_M between the calculated and observed values of F_M for the first six reflections can be now attributed to the contribution of yttrium. Extrapolating to $(\sin\theta)/\lambda=0$, the values of the form factor can be deduced. The results of a new refinement using the form factor thus determined are given in column C of Tables II and VI. The agreement between the calculated and measured values of F_M is quite good.

As suggested by Moon,[9] the discrepancy between the measured and calculated values of F_M can be also explained by another model in which the Y atoms have no magnetic moment, but the Co moments are separated into a *3d*-like part and a negative constant, similar to the metallic Co. The magnetic moments for the Co sites are calculated with a scaled-up (by a factor of 1.18) free-atom 3d form factor as determined in metallic Co.[8] The results for this model are given in column D of Tables II and VI. A good agreement between the measured and calculated values of F_M can be seen for the first reflections; the values for the Co moments are very similar to those in the previous model, but they now imply both a local *3d* moment and a diffuse negative moment.

The results of the least-squares refinements, assuming that the Y atoms have magnetic moments and using the form factor of Y determined above, are given in column A of Tables III and VII for YCo_3 and in column A of Tables IV and VIII for YCo_5. Since in YCo_3 the values of $\mu_{\text{Y-I}}$ and $\mu_{\text{Y-II}}$ cannot be calculated separately because of the form of the structure factor expressions, $\mu_{\text{Y-I}}=2\mu_{\text{Y-II}}$ was assumed as in Y_2Co_7. The results of the least-square refinement based on the data at 90 and 215°K for YCo_3 are given in Tables V and VII. The results of the calculations for the Co moments at 4.2°K in YCo_3 and YCo_5, assuming that the Y atoms have no magnetic moments and using the same scaled-up form factor for the Co as above for Y_2Co_7, are given in column B of Tables III, IV, VII, and VIII.

TABLE VII. Magnetic moments at 4.2, 90, and 215°K in YCo_3 obtained by the least-squares refinements explained in Tables III and V. μ_{tot} is the magnetic moment of a unit cell. All values are given in μ_B.

	4.2°K A	4.2°K B	90°K	215°K
$\mu_{\text{Y-I}}=2\mu_{\text{Y-II}}$	−0.35±0.19	...	−0.30±0.22	−0.07±0.10
$\mu_{\text{Co-I}}$	0.55±0.04	0.55±0.03	0.49±0.04	0.18±0.03
$\mu_{\text{Co-II}}$	0.83±0.05	0.79±0.04	0.78±0.06	0.34±0.03
$\mu_{\text{Co-III}}$	0.40±0.02	0.40±0.01	0.37±0.02	0.17±0.01
μ_{total}	1.30±0.27	1.51±0.04	1.22±0.33	0.59±0.16

The polarization ratios for the YCo_3 phase occurring in small quantity in the Y_2Co_7 crystal were also measured at 4.2°K and were found to be identical with those measured in the YCo_3 crystal.

5. DISCUSSION

The magnetic moments measured in the three compounds are summarized in Fig. 3. The results obtained on pure Co metal[8] and on YCo_2 having no magnetic order at all[10] are also included. The moments associated with the sites having identical environments are connected by straight lines in the figure.

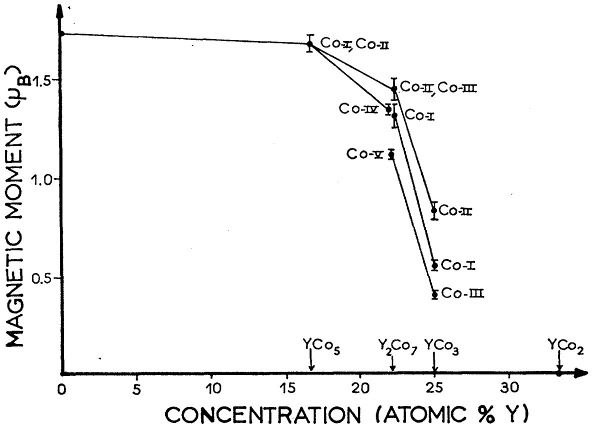


FIG. 3. Magnetic moments associated with the different Co sites in pure Co, YCo_5, Y_2Co_7, YCo_3 (present study), and YCo_2 (Ref. 9).

---

[9] R. M. Moon (private communication).

[10] R. Lemaire and J. Schweizer, Phys. Letters 21, 366 (1966).

As seen in Fig. 3, the magnetic moment of Co decreases with increasing concentration of Y in a strikingly similar way for the different crystallographic sites. The decrease is probably a consequency of the gradual filling up of the 3*d* band of the cobalt, and this is further supported by the fact that the highest magnetic moments of Co in a compound are associated with the crystallographic sites having the least Y nearest neighbor (Co-II sites in both Y_2Co_7 and YCo_3), while the lowest values are associated with those having the most Y neighbors (Co-V in Y_2Co_7 and Co-III in YCo_3).

The Co-I and Co-II sites in YCo_5 have the same value of magnetic moment, while those for the corresponding Co-II, or Co-III and Co-IV sites in Y_2Co_7 are different. As seen in Fig. 3, the magnetic moment of Co, which is strongly dependent on the Y concentration between Y_2Co_7 and YCo_3, is rather insensitive to the composition near YCo_5. Thus, the difference in the local electronic concentrations around the Co-I and Co-II sites of YCo_5 does not produce a noticeable change in the Co moments.

The magnetic moment on the Y atoms, if it exists, is probably induced by the ferromagnetic Co environment. The values of the observed Y moment can be compared with the induced moments on other 4*d*-metal atoms: 1.0 μ_B on Rh and 0.34 μ_B on Pd in FeRh and $FePd_3$, respectively.[11,12] It is higher at Y_I sites which have 18 nearest-neighbor Co atoms than at Y_{II} sites which have only 12. The form factor of Y as evaluated from the Y_2Co_7 data changes sign around $(\sin\theta)/\lambda = 0.17$.

The values of the total magnetic moment μ_{total} of a unit cell are given in Tables VI–VIII and are in good agreement with the results of the magnetization measurements, shown in Table I, for the model in which the Y moment exists. For the other model, the agreement is not so good. This may indicate that the ratio between the 3*d*-like moment and diffuse negative polarization is different from the ratio measured in metallic Co. However, it seems difficult to determine this ratio with the help of the magnetization results obtained with polycrystalline specimens because of the inaccuracy of these measurements due to the very large magnetic anisotropy.

Present measurements do not allow us to decide between the two interpretations of the results. Further measurements are in progress in order to obtain a spin-density map of YCo_5 by Fourier inversion.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Professor E. F. Bertaut for his encouragement and to Dr. R. M. Moon for his suggestions. One of the authors (E. K.) is particularly grateful to the Centre National de la Recherche Scientifique for the financial support enabling him to work in this laboratory.

---

[11] E. F. Bertaut, F. de Bergevin, and G. Roult, Compt. Rend. **256**, 1688 (1963).

[12] G. Shirane, R. Nathans, S. J. Pickart, and H. A. Alperin, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 223.