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E. Hermon, D. Simkin, R. Haddad, W. Muir. MAGNETIC PROPERTIES OF  $\text{SnCo}_2\text{O}_4$  SPINEL II. Journal de Physique Colloques, 1977, 38 (C1), pp.C1-131-C1-133. 10.1051/jphyscol:1977125 . jpa-00216984

**HAL Id: jpa-00216984**

**<https://hal.science/jpa-00216984v1>**

Submitted on 4 Feb 2008

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## MAGNETIC PROPERTIES OF $\text{SnCo}_2\text{O}_4$ SPINEL II

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**Résumé.** — Le composé  $\text{SnCo}_2\text{O}_4$  est un spinel inverse IV-II dont les ions Co sont également distribués dans les sites octaédriques et tétraédriques. Les ions Sn occupent les restants des sites octaédriques. On pensait d'abord que ce composé se classait comme un ferrimagnétique de Néel de type p, avec une aimantation résiduelle de  $10^{-2} \mu_B$  par ion  $\text{Co}^{2+}$ . Des champs coercitifs dépassant 8 kOe avaient été annoncés à 20 K ; des mesures d'effet Mössbauer indiquaient un champ interne d'environ 80 kOe.

Le présent travail étend les mesures magnétiques à des champs plus élevés et à des températures plus basses. L'aimantation n'a pas de valeur résiduelle comme publié auparavant, mais tombe à zéro à 12 K environ, indiquant un antiferromagnétisme aux températures les plus basses. A 16 K l'aimantation est  $2,2 \times 10^{-3} \mu_B$  par ion  $\text{Co}^{2+}$  ; le champ coercitif dépasse 50 kOe. En vue d'obtenir de plus amples informations sur l'état ordonné, on a effectué un calcul de la résultante des champs dipolaires des deux sous-réseaux  $\text{Co}^{2+}$  agissant sur les sites Sn. On a trouvé que ce champ dipolaire était d'environ 8 kOe, c'est-à-dire d'un ordre de grandeur inférieur à la valeur mesurée par effet Mössbauer. Ceci indique une contribution directe des ions Sn au superéchange.

**Abstract.** — The compound  $\text{SnCo}_2\text{O}_4$  is an inverted IV-II spinel with the Co ions equally distributed among the octahedral and tetrahedral sites. The Sn ions occupy the remaining octahedral sites. This compound was previously thought to order as a Neel p-type ferrimagnet with a residual magnetization of  $1 \times 10^{-2} \mu_B$  per  $\text{Co}^{2+}$  ion. Coercive forces in excess of 8 kOe at 20 K were reported and the Mössbauer effect on the tin nucleus indicated an internal field of about 80 kOe.

The present paper extends the magnetic measurements to higher fields and lower temperatures. The magnetization does not have a residual value as previously reported but drops to zero at about 12 K indicating antiferromagnetism at the lowest temperatures. At 16 K the magnetization is  $2.2 \times 10^{-3} \mu_B$  per  $\text{Co}^{2+}$  ion and the coercive force is in excess of 50 kOe. In order to obtain further information about the ordered state a calculation of the resultant of the dipolar fields from the two  $\text{Co}^{2+}$  sublattices at the Sn sites was made. This dipolar field was found to be about 8 kOe or an order of magnitude smaller than the value measured by Mössbauer effect. This indicates direct participation of the Sn ions in the superexchange.

**1. Introduction.** — The original interest in this compound was as one end member in a proposed study of the solid solution series  $\text{ZnFe}_2\text{O}_4$ - $\text{SnCo}_2\text{O}_4$ . In our previous paper [2] we showed this material to be ferrimagnetic with an apparent residual magnetization of about  $0.02 \mu_B$  per formula unit at temperatures less than 20 K. The coercive force at this temperature was found to be greater than 8 kOe. The present paper extends the magnetization measurements to lower temperatures and higher fields.

**2. Method.** — The material was prepared using standard ceramic techniques as outlined in reference [2].

Magnetic measurements were made in fields up to 55 kOe using a laboratory made vibrating sample magnetometer operating in a superconducting solenoid. The arrangement has been described by Cochrane [3]. Measurements were made by sweeping the field at

constant temperature. Those measurements for which the temperature varied by more than 1 % from start to finish of the field sweep were rejected. The data obtained are shown in figure 1.

**3. Discussion.** — As we have previously shown [2], the magnetic susceptibility,  $\chi$ , above the ferrimagnetic Neel temperature,  $T_{FN}$  is typical of a two sublattice ferrimagnet [4] and takes the form

$$1/\chi = T/C + 1/\chi_0 - \sigma/(T - \theta') \quad (1)$$

where  $C = 4.3 \pm 0.2$  emu/mole,  $1/\chi_0 = 35 \pm 1$  (emu/mole) $^{-1}$ ,  $\theta' = 41 \pm 2$  K,  $\sigma = 160 \pm 10$  (emu/mole) $^{-1}$  and  $T_{FN} = 44 \pm 2$  K. The effective magneton number of the  $\text{Co}^{2+}$  ions derived from the Curie constant is  $5.0 \pm 0.2$  in agreement with the usually measured value of 4.8 [5]. The values of the molecular field

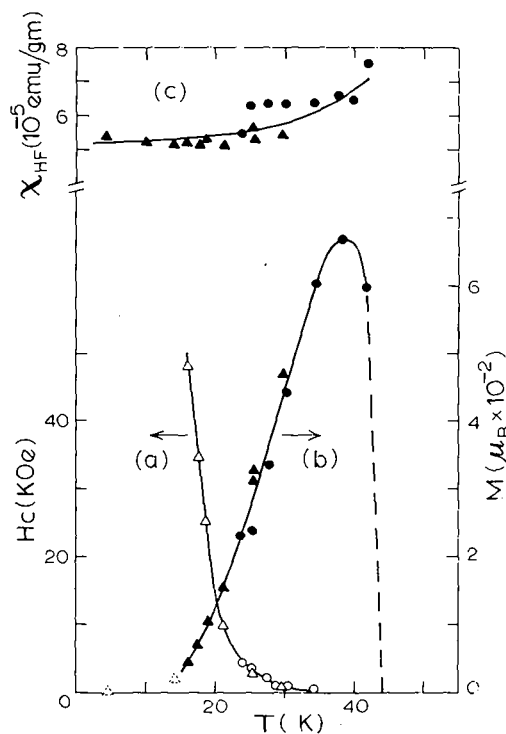


FIG. 1. — Data from ref. [2] is indicated by ● or ○ while data presented for the first time is shown as ▲ or △: a) Coercive force as a function of temperature. b) Magnetization per  $\text{Co}^{2+}$  ion as a function of temperature. Dotted symbols indicate doubtful or non closure of the hysteresis loop. c) High field susceptibility  $\chi_{\text{HF}} = \partial M / \partial H$   $H \rightarrow \infty$  as a function of temperature.

constants derived from the above parameter are  $N_{\text{AA}} = 38$  mole/emu,  $N_{\text{BB}} = 15$  mole/emu and  $N_{\text{AB}} = -45$  mole/emu. The signs of the molecular field constants indicate ferromagnetic ordering within each sublattice and antiferromagnetic ordering between the sublattices. The magnetization data shown in figure 1b suggests that the material has essentially zero magnetization at  $T = 0$ . Our previous measurements at higher temperatures, which are shown as dots in the figure, are in good agreement with the present results. However, taken by themselves they suggested a leveling of the magnetization at about  $0.01 \mu_{\text{B}}$  per cobalt ion at 25 K. This has proved not to be the case and the magnetization decreases steadily towards zero as the temperature is decreased. Unfortunately at temperatures below 15 K we were unable to close hysteresis loop with the 55 kOe field available. However the magnetization dropped by a factor of 5 to about  $0.002 \mu_{\text{B}}$  per cobalt ion when the temperature was lowered from 25 to 15 K. This suggests either a compensation point near 12 K or antiferromagnetic ordering at zero temperature. Measurements at 4 K and below failed to show any sign of spontaneous magnetization thus favoring antiferromagnetic ordering at zero temperature. The behaviour of the

low temperature high field susceptibility ( $\chi_{\text{HF}} = \partial M / \partial H$   $H \rightarrow \infty$ ) shown in figure 1c is also suggestive of antiferromagnetism.

The antiferromagnetic nature of the magnetization results, at  $T = 0$ , considered in the light of the molecular field constants suggests that we have two equally magnetized sublattices which are antiferromagnetically coupled. If, as we expect, the  $\text{Co}^{2+}$  ions are equally distributed among the A and B sites [1] then we must conclude that the  $\text{Co}^{2+}$  ions have the same moment on each site. This is somewhat surprising since the B site octahedral coordination gives the  $\text{Co}^{2+}$  ion a  ${}^4\text{T}_{1\text{g}}$  ground state which allows an orbital contribution to the magnetic moment while the A site tetrahedral coordination gives the  $\text{Co}^{2+}$  ion a  ${}^4\text{A}_2$  ground state which allows no orbital contribution [6] and results the spin only moment of  $3 \mu_{\text{B}}$  per  $\text{Co}^{2+}$  ion.

The coercive force is shown in figure 1a and is in excess of 50 kOe at 15 K. Due to field limitations we were not able to measure the coercive force below 15 K. No signs of saturation were seen down to 15 K. The large coercive force is probably a result of the known large magnetocrystalline anisotropy of materials containing  $\text{Co}^{2+}$  ions.

In our previous paper [2] we reported Mössbauer measurement on the  ${}^{119}\text{Sn}$  nucleus for the material in the ordered state. A hyperfine splitting was observed which corresponded to an internal field of 80 kOe or an ordering temperature of 24 K if we assume a moment of  $3 \mu_{\text{B}}$  per  $\text{Co}^{2+}$  ion. This is in reasonable agreement with the measured value of  $44 \pm 2$  K. In an effort to determine the nature of the internal field we have calculated the field at the Sn sites due to the resultant of the dipolar fields from the two  $\text{Co}^{2+}$  sublattices. This calculation is based on a modified form of a calculation presented previously by one of the present authors [7]. The value of the resultant of the dipolar fields from the two  $\text{Co}^{2+}$  sublattices at the Sn sites was found to be about 8 kOe. This value is an order of magnitude smaller than the measured value of the internal field and suggests that the Sn ions are participating directly in the superexchange.

**4. Conclusions.** — The ferrimagnetic spinel,  $\text{SnCo}_2\text{O}_4$  appears to have two equally populated sublattices colinearly aligned and antiferromagnetically coupled. The magnetization of the sublattices at zero temperature is identical with experimental error and results in an antiferromagnetic material at the lowest temperatures. At 15 K the coercive force is in excess of 50 kOe and shows no sign of saturation.

This resultant of the dipolar fields from the two  $\text{Co}^{2+}$  sublattices gives an internal field of the Sn sites of about 8 kOe. This is an order of magnitude less than the internal field measured by the Mössbauer effect and indicates that the Sn ions are participating directly in the superexchange interaction.

## References

- [1] POIX, P., *Ann. Chim.* **9** (1964) 274.
- [2] HERMON, E., SIMKIN, D. J., HADDAD, R. J. and MUIR, W. B. Proc. 21st Conf. on Magnetism and Magnetic Materials (1975).
- [3] COCHRANE, R. W., PLISCHKE, M., STÖM-OLSEN, J. O., *Phys. Rev.* **B 9** (1974) 3013.
- [4] NÉEL, L. *Anns. de Phys.* **3** (1948) 137.
- [5] MORRISH, A. H., *The Physical Principles of Magnetism* (John Wiley and Sons N. Y.) 1965 p. 67.
- [6] FIGGIS, B. N. *Introduction to Ligand Fields* (Interscience Publishers) 1966.
- [7] SIMKIN, D. J., *Phys. Rev.* **177** (1969) 1008.