INVESTIGATION OF MAGNETIC STRUCTURES AND PHASE TRANSITIONS IN NiS_2 BY ^{61}Ni -MÖSSBAUER SPECTROSCOPY

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Résumé. — Les études des interactions hyperfines magnétiques dipolaires et électriques quadrupolaires aux noyaux ^{61}Ni dans $\text{NiS}_{1,93}$ de la structure cubique de pyrite dans la région de températures $4,2 \text{ K} \leq T \leq 50 \text{ K}$ ont mené aux résultats suivants. Entre $30,9 \text{ K}$ et $T_N = 44,5 \text{ K}$ les moments magnétiques des ions nickel sont alignés parallèles aux axes locaux de symétrie trigonale. Au-dessous de $30,9 \text{ K}$ nous trouvons deux sites de nickel distingués par des angles différents entre la direction du moment magnétique et l'axe local de symétrie. Pour à peu près 50 % des ions nickel la direction du moment commence à changer à $(30,9 \pm 0,1) \text{ K}$, pour les autres à $(30,2 \pm 0,1) \text{ K}$. D'une analyse des champs hyperfins magnétiques au sens des interactions dipôle-dipôle anisotropes et des rapports des constantes de couplage quadrupolaire nous dérivons des angles de 77° et de 39° entre les moments magnétiques et les axes de symétrie pour les deux sites. Qualitativement les mêmes résultats sont obtenus pour $\text{NiS}_{1,96}$ et $\text{NiS}_{2,00}$ dans la région de basses températures avec des petits changements de températures critiques et des paramètres d'interactions hyperfines. Il paraît, pourtant, que T_N croît rapidement avec la teneur de soufre. Une distribution statique des moments magnétiques ou des effets de relaxation mène à un élargissement significatif des raies d'absorption entre 50 K et T_N .

Abstract. — Measurements of the magnetic dipole and electric quadrupole interactions at ^{61}Ni in $\text{NiS}_{1,93}$ with cubic pyrite structure in the temperature region $4.2 \text{ K} \leq T \leq 50 \text{ K}$ have yielded the following results. Between 30.9 K and $T_N = 44.5 \text{ K}$ the magnetic moments on Ni ions are aligned parallel to the local trigonal symmetry axis. Below 30.9 K we find two nickel sites distinguished by different angles between the direction of the magnetic moment and the local symmetry axis. For about 50 % of the nickel ions the moment direction begins to change at $(30.9 \pm 0.1) \text{ K}$, for the other ones at $(30.2 \pm 0.1) \text{ K}$. From an analysis of the magnetic hyperfine fields in terms of anisotropic dipole-dipole interactions and from the ratios of the effective quadrupole constants we derive values of 77° and 39° for the angles between magnetic moments and symmetry axes at the two sites. Qualitatively the same results are obtained for $\text{NiS}_{1,96}$ and $\text{NiS}_{2,00}$ in the low-temperature region with small changes of critical temperatures and hyperfine-interaction parameters. However, T_N appears to increase rapidly with increasing sulfur content. Either a static distribution of magnetic moments or relaxation effects lead to a significant broadening of the absorption lines in the temperature region between 50 K and T_N .

Recent studies of NiS_2 with cubic pyrite structure by neutron diffraction [1] and by measurements of magnetic susceptibility and electrical resistivity [2, 3] have established the occurrence of two magnetic phase transitions in this compound for compositions slightly deficient in sulfur content. Near the composition $\text{NiS}_{1,9}$ antiferromagnetic order is found below $T_N \sim 40\text{--}50 \text{ K}$, and the material becomes weakly ferromagnetic below $T_c \sim 30\text{--}31 \text{ K}$. For both phases, the magnetic moment arrangements have not yet been determined.

We have now investigated the temperature dependence of hyperfine interactions at ^{61}Ni nuclei in a sample with composition $\text{NiS}_{1,93}$ in the temperature range $4.2 \text{ K} \leq T \leq 50 \text{ K}$ by Mössbauer spectroscopy.

The experimental results are summarized in figure 1. Some preliminary results have also been obtained with samples of $\text{NiS}_{1,96}$ and $\text{NiS}_{2,00}$, prepared by high-pressure synthesis with nickel enriched to 75 % ^{61}Ni . X-ray diffraction and susceptibility measurements of all samples gave results in agreement with those reported previously [2, 3]. The apparatus, experimental techniques, and data analysis procedures were the same as described in [4].

For $T \geq 45 \text{ K}$ (paramagnetic phase) we find a slightly broadened single line. By comparison with the unsplit absorption spectrum of a NiV (14 %) absorber, taken with the same source immediately after the spectrum of $\text{NiS}_{1,93}$, we deduce a quadrupole coupling constant $|v_Q| = |e^2 qQ/h| = (8 \pm 3) \text{ MHz}$.

FIG. 1. — Temperature dependence of hyperfine interaction parameters in $\text{NiS}_{1.93}$. ● antiferromagnetic phase, x α -sites, ○ β -sites. (a) Magnetic hyperfine field, (b) effective quadrupole coupling constant, (c) fraction of ^{61}Ni -nuclei occupying β -sites.

For $31 \text{ K} \leq T \leq 44 \text{ K}$ (antiferromagnetic phase) the ^{61}Ni nuclei experience a magnetic hyperfine field H_{hf} whose temperature dependence is quite well described by the molecular-field approximation with $T_N = 44.5 \text{ K}$ and $|H_{hf}(T = 0)| = 47 \text{ kG}$. The effective quadrupole coupling constant, $v_Q^{eff} = \frac{1}{2}(3 \cos^2 \theta - 1) \cdot e^2 qQ/h$, where θ is the angle between the direction of $\mathbf{H}_{hf}$ and the principal axis of the field-gradient tensor, is given by $v_Q^{eff} = (-5.8 \pm 0.2) \text{ MHz}$, independent of temperature.

From the fact that we find the same magnetic hyperfine field and the same value of v_Q^{eff} for all ^{61}Ni nuclei in conjunction with the results of neutron diffraction [1] we conclude that the magnetic moment on any nickel ion is parallel to that (111)-direction which is the local trigonal symmetry axis. That is, $\theta = 0$, and the experimental value of v_Q^{eff} is equal to $v_Q = e^2 qQ/h$.

At $(30.9 \pm 0.1) \text{ K}$ a discontinuity of the slope of the H_{hf} -vs.- T -curve is observed for about 50 % of the ^{61}Ni nuclei (β -sites), whereas the field on the other nuclei (α -sites) remains practically constant down to $(30.2 \pm 0.1) \text{ K}$. For temperatures below 30.2 K the field on all ^{61}Ni nuclei deviates from the curve extrapolated from the antiferromagnetic phase (Fig. 1a). However, in the entire temperature region below

30.9 K, we find two nickel sites with different values of H_{hf} (Fig. 1a) and of v_Q^{eff} (Fig. 1b). The effective quadrupole coupling constants change gradually between 30.9 K and 29 K. Below 29 K we find the values $v_{Q,\alpha}^{eff} = (-2.8 \pm 0.1) \text{ MHz}$, $v_{Q,\beta}^{eff} = (2.4 \pm 0.2) \text{ MHz}$, independent of temperature. Between about 29 K and 25 K the fraction of ^{61}Ni nuclei in β -sites decreases gradually from about 50 % to about 25 % (Fig. 1c).

The changes of H_{hf} near 30 K could be caused by similar changes of the values of the nickel moments. However, this would lead to corresponding changes of the intensities of magnetic powder diffraction lines which have not been reported in the literature. Therefore it seems more likely that the observed effects are caused by rotations of the magnetic moments in conjunction with anisotropic hyperfine interactions.

The Hamiltonian for the magnetic hyperfine interaction in a coordinate system with the z-axis parallel to the direction of the magnetic moment can be written in the form :

$$H_{\text{magn}} = \mu_{\text{nuc}} [A_0 + \frac{1}{2} A_D (3 \cos^2 \theta - 1)] S_z \cdot I_z - \frac{3}{4} \mu_{\text{nuc}} A_D \sin \theta \cos \theta \cdot S_z \cdot (I_+ + I_-) \quad (1)$$

with the usual notation for the nuclear spin operators I_x, I_y, I_z , $I_+ = I_x + iI_y$, $I_- = I_x - iI_y$ and the electronic spin operator S_z . The angle θ is again that between the moment direction and the symmetry axis. The quantity A_0 is determined by the isotropic part of the hyperfine interaction : the contact term and the interaction with the orbital moment. The anisotropic part, A_D , originates from the dipole-dipole interaction between electronic and nuclear spins. The orbital term may also contribute to the anisotropy if the electronic g-tensor is anisotropic [5]. As EPR measurements on nickel ions in $\text{Fe}_{1-x}\text{Ni}_x\text{S}_2$ with the same structure have shown that in this case g_x is very nearly the same as g_z [6], we assume that the anisotropy in NiS_2 can be ascribed entirely to the dipole-dipole interaction.

Treating the anisotropic part of the Hamiltonian, eq. (1), as a perturbation to second order, we can express the magnetic hyperfine interaction in terms of an effective magnetic hyperfine field, given by

$$H_{hf}^{eff} = -A_0 \cdot \langle S_z \rangle \cdot [1 + \frac{1}{2}(3 \cos^2 \theta - 1) \cdot (A_D/A_0) + (9/8) \cdot \cos^2 \theta \cdot (1 - \cos^2 \theta) \cdot (A_D/A_0)^2] \quad (2)$$

As no significant structural changes have been observed in the critical temperature region, we analyze our results assuming changes only of the moment directions, that is of the angle θ , not of the intrinsic hyperfine interaction parameters A_0 , A_D and v_Q . From a comparison of the experimental values of the hyperfine fields $H_{hf,\alpha}^{eff}$ and $H_{hf,\beta}^{eff}$ at 4.2 K with the value extrapolated from the antiferromagnetic phase, which we set equal to $H_{hf}^{eff}(\theta = 0) = -A_0 \cdot \langle S_z \rangle \cdot [1 + A_D/A_0]$ and using the ratio

$$v_{Q,\alpha}^{eff}/v_{Q,\beta}^{eff} = (3 \cdot \cos^2 \theta_\alpha - 1)/(3 \cdot \cos^2 \theta_\beta - 1) = -1.16$$

we obtain the values $\theta_\alpha = 39^\circ$, $\theta_\beta = 77^\circ$, both with an uncertainty of about 10 %. The same values for these angles are obtained from a comparison of $\nu_{Q,\alpha}^{\text{eff}}$ and $\nu_{Q,\beta}^{\text{eff}}$ with the value of ν_Q measured in the antiferromagnetic phase. This agreement lends support to the assumptions involved in the derivation.

For the hyperfine interaction parameters we derive the values :

$$|A_0 \langle S_z \rangle| = 87 \text{ kG}, \quad |A_D \langle S_z \rangle| = 40 \text{ kG},$$

with $A_D/A_0 < 0$. The dipole-dipole term A_D is closely related to the contribution of the valence electrons to the electric-field gradient, both quantities being proportional to $\langle (3 \cos^2 \theta - 1)/r^3 \rangle$ [5]. Using $\langle S_z \rangle = 1.2 \mu_B$ as given by Hastings and Corliss [1], we derive : $|\langle (3 \cos^2 \theta - 1)/r^3 \rangle_{\text{mag}}| = 3.6 \times 10^{24} \text{ cm}^{-3}$.

For the quadrupole coupling constant we have to account for the screening factor $(1 - R)$. As no calculation of the value of R for Ni^{2+} is known to us, we estimate it from a comparison with iron to be about 0.3. Then we obtain

$$\langle (3 \cos^2 \theta - 1)/r^3 \rangle_{\text{quadrup}} = -1.5 \times 10^{24} \text{ cm}^{-3}.$$

The discrepancy between these two results may have

several causes : (a) an anisotropic contribution of the electronic orbital moment, (b) a larger value of the nickel moment than that given by Hastings and Corliss, (c) a positive lattice contribution to the electric field gradient, partially compensating the gradient due to the valence electrons, and (d) a different radial distribution of spin and charge densities.

In the samples of composition $\text{NiS}_{1.96}$ and $\text{NiS}_{2.00}$ we find essentially the same phenomena as in $\text{NiS}_{1.93}$ in the temperature region below 45 K. With increasing sulfur content, the critical temperature for the moment rotation increases slightly to about 34 K for $\text{NiS}_{2.00}$. The magnetic hyperfine fields at 4.2 K decrease only by a few percent. As the bulk magnetization decreases very rapidly with increasing sulfur content in this concentration region, the directions of the magnetic moments must change to an antiferromagnetic arrangement.

The Néel temperature increases rapidly with the sulfur content. In $\text{NiS}_{2.00}$ we found so far a magnetic splitting up to 70 K. At the same time, the absorption lines are broadened strongly for $T \geq 50$ K. This can be due either to a static distribution of magnetic moments or to relaxation effects.

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