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INVESTIGATION OF THE METAL-TO-SEMIMETAL TRANSITION IN NiS BY $^{61}$Ni-MÖSSBAUER SPECTROSCOPY

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Abstract. — Mössbauer spectroscopy with $^{61}$Ni has been employed to investigate vibrational, magnetic and electronic properties of hexagonal NiS in the semimetallic antiferromagnetic and in the metallic, Pauli-paramagnetic phase. Upon transition to the metallic state the recoilless fraction decreases significantly, corresponding to a change of the Debye-temperature by about 20 %. There is at most a small change of isomer shift at the transition. The relative decrease of the magnetic hyperfine field with temperature is proportional to $T^2$, as expected for single-electron excitations in itinerant antiferromagnets. A decrease of the electric field gradient both with temperature and with increasing content of Ni-vacancies in the antiferromagnetic phase indicates changes of the electronic structure which may promote the transition to the metallic state.

The stoichiometric compound NiS with the hexagonal NiAs-structure exhibits a metal-semimetal transition at $T_1 = 265$ K. The low-temperature phase is an antiferromagnetic semimetal and the high temperature phase a Pauli-paramagnetic metal [1]. The transition temperature depends strongly on the composition as shown in figure 1 and it is suppressed completely by less than 4 % Ni vacancies. Results of Mössbauer effect measurements on NiS samples doped with $^{57}$Fe have been published by Coey et al. [2] and Gosselin et al. [3]. Here we report results of Mössbauer spectroscopy with $^{61}$Ni in NiS samples as a function of stoichiometry and temperature.

Samples of NiS were produced in the usual way by heating Ni and S in a quartz tube as reported by Trahan et al. [4]. The spectra have been taken with a conventional Mössbauer spectrometer as described by F. E. Obenshain [5]. The velocity was calibrated by measuring simultaneously the hyperfine interaction of $^{57}$Fe in iron. The source was a $^{57}$FeNi (14 %) alloy. It was irradiated by a 20 MeV proton beam in the Karlsruhe cyclotron giving $^{61}$Ni* by the reaction $^{64}$Ni(p, $\alpha$) $^{61}$Co$^{1}$Ni. $^{61}$Ni*. With one irradiation 1 or 2 spectra could be taken within 4 h. During all measurements the source was kept at 4.2 K. The

FIG. 1. — Concentration dependence of the transition temperature $T_1$, the magnetic moment per nickel ion $\mu_{Ni}$, the magnetic hyperfine field $H_{hf}$, and the quadrupole coupling constant $v_Q$ in NiS. The figure displays relative values, normalized to 1 for $y = 1$. Absolute values for $y = 1$ are $T_1 = 265$ K, $\mu_{Ni} = 1.4 \mu_B$, $|H_{hf}| = 112$ kG, $v_Q = 1.6$ MHz.
The Mössbauer spectra of $^{63}$Ni in compounds Ni$_2$S

with $y \geq 0.971$ in the antiferromagnetic phase consist of 12 lines, corresponding to a magnetic dipole and an electric quadrupole interaction, without an indication of an unsplit component as found for $^{57}$Fe in NiS [2, 3]. Upon transition to the metallic phase the spectrum abruptly changes to a single line. The presence of an electric quadrupole interaction of about the same strength as in the antiferromagnetic phase cannot be excluded.

We find a strong decrease of the recoilless fraction $f$ at the transition from the antiferromagnetic to the metallic state as shown in figure 2. A least-squares fit of the temperature dependence of the magnetic hyperfine field cannot be explained by magnon excitations. The decrease of the magnetic hyperfine field at $T = 160$ K is several percent, whereas the spin wave model results in a decrease of $10^{-5}$ at this temperature. The observed change of the magnetic hyperfine field with temperature can be accounted for by single-particle excitations of an itinerant antiferromagnet. Theories using the Hartree-Fock-approximation of Stoner [9], extended to antiferromagnetism by Lidiard [10], or that of Brandt and Gross [11] for collective-electron magnetism with partially split d-bands give a $T^2$-dependence for the sublattice magnetisation at low temperature. With these theories and our $\alpha$ values fictitious Néel temperatures $T_N = 670$ K for Ni$_{0.995}$S and $T_N = 500$ K for Ni$_{0.971}$S can be extrapolated. The concentration dependence of the magnetic hyperfine field at 4.2 K is shown in figure 1. A linear extrapolation of our data yields a magnetic hyperfine field $|H| = 112$ kOe for stoichiometric NiS.

The magnetic hyperfine field is decreasing more slowly with increasing content of cation vacancies than the magnetic moment per Ni-ion, as determined by neutron diffraction [12].

A point-charge calculation of the lattice contribution to the electric field gradient gives a value which is about an order of magnitude larger than the measured values. The difference can be due to shielding of the ionic potentials by conduction electrons or to a compensating contribution by covalent admixture of sulfur 2p-electrons to the nickel valence states. Whichever of these mechanisms is dominant, it would also tend to reduce the intra-atomic exchange interaction at the absorber temperature could be varied between 4.2 K and 160 K. All spectra were analyzed by a least-squares fit to the full Mössbauer transmission integral with a computer program by J. Burton [6].
nickel ions which is assumed to cause the magnetic order. The observed decrease of the quadrupole interaction with increasing deviation from stoichiometry as shown in figure 1 indicates a strengthening of this mechanism in agreement with the observed decrease of the transition temperature. The observation of a similar decrease of the quadrupole interaction with increasing temperature supports this point of view.

References