08.5—7   MAGNETIC ORDERING IN THE NATURAL ORTHOPYROXENE $Fe_{0.87}Mg_{0.13}SiO_3$. By A. Wiedenmann[a], J.R. Regnard[a] and S.S. Hafner[b].
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In the crystal structure of orthopyroxene $Fe_xMg_{1-x}SiO_3$ two nonequivalent positions M_1 and M_2 of oxygen octahedra are occupied by Fe^{2+} and Mg^{2+} with a preference of Fe^{2+} for the more distorted M_2 site. In the unit cell edge sharing octahedra build up four ribbons of infinite length along the c axis well separated from each other ($d = 4.9$ Å). Each ribbon consists of two linear chains of M_2 which enclose a zigzag chain of M_1 (Virgo and Hafner, Amer. Mineral. (1970) 55, 201). Investigations of the magnetic properties of the natural pyroxene $Fe_{0.87}Mg_{0.13}SiO_3$ were performed on a polycrystalline sample of 100 mg. The powder susceptibility follows a Curie-Weiss law with $\Theta_p = 34$ K and $\mu_{eff} = 5.24$ μ_B, indicating large orbital contributions. χ exhibits an inflection point at $T_N = 26$ K reflecting an antiferromagnetic ordering. The onset of long range magnetic order at T_N was confirmed by neutron diffraction. The propagation vector is $\vec{k} = [000]$ indicative for a collinear magnetic structure. From an intensity refinement the coupling between the 16 sublattices was obtained: all the moments within a ribbon are aligned ferromagnetically along the b axis with an antiferromagnetic coupling between neighbouring ribbons. The ferromagnetic exchange interaction between the nearest neighbours within the ribbons ($d \cong 3.1$ Å) is certainly much stronger than the antiferromagnetic coupling of the moments between neighbouring ribbons, giving rise to a special type of 1D magnetic behaviour. Mössbauer experiments in the paramagnetic region revealed two distinct quadrupole interactions of Fe^{2+} of 3.0 and 1.99 mm/s for the sites M_1 and M_2, respectively. Below the transition temperature the hyperfine spectra (with large linewidth of about 0.8 mm/s) are well described by a distribution of distinct electric field gradients and magnetic hyperfine fields due to the different Mg^{2+}, Fe^{2+} configurations surrounding M_1 and M_2 as nearest neighbours.

08.6—1   ESR AND MÖSSBAUER STUDIES OF Cu- AND Fe-CONTAINING SULFOSALTS. By K.Bente, V.Kupcik, Min.-Krist.Institut Univ. Göttingen, G.Amthauer, Institut f.Miner. und Krist. Univ. Marburg, D.Siebert, Phys.Chem. Institut Univ. Freiburg

ESR and Mössbauer studies were carried out on the Cu- and Fe-containing sulfosalts kobellite $((Cu,Fe)Pb_6Sb_2Bi_4S_{16})$, $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$, covellite (CuS), idaite (Cu_5FeS_6), and $Cu_4Bi_4S_9$, which contain lacks of positive charge basing on Cu^+, Pb^{++}, Sb^{+++}, Bi^{+++}, Fe^{++}, S^{2-} and S_2^{2-} (if covellite fragments are present). The phases were synthesized under condensed conditions using the elements (99.999%) as starting materials. For the synthesis of the phases containing Fe in minor amounts, Fe enriched in ^{57}Fe was used. The ESR and Mössbauer studies were performed from room temperature to the temperature of liquid nitrogen (LN_2).
The ESR studies gave no Cu^{++} signals for covellite over the whole temperature range and Cu^{++} signals for $Cu_4Bi_4S_9$ at $T \leqslant 173K$ (g=1.91) and for idaite at $T \leqslant 96K$ (g=1.87). Because of the charge balance of these phases, mixed valence state of Cu ($\sim 1.5+$) has to be suggested at temperatures without an ESR signal. This suggestion is verified in the case of idaite showing mixed valence state for Fe ($\sim 2.5+$) by Mössbauer studies with an isomer shift of $\delta = 0.35$ for tetrahedrally coordinated Fe. ESR studies on the phases kobellite and $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$ show paramagnetic signals for Cu^{++} over the whole temperature range with g=2.01 and 2.019 respectively.
Mössbauer studies lead to Fe^{++} in both cases. An empirical term for the mixed valence state and/or the valence of 2+ for Cu in positive charge deficient sulfosalts is proposed.