

PROTON MAGNETIC RESONANCE IN SYNTHETIC ZINC SULPHIDES

A.M.Bondar**, **S.V.Kozerenko****, **A.I.Rebrov****

*Baikov Institute of metallurgy and material science, Russian Academy of Science

** Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Science

This study was supported by the Russian Fundamental Research Foundation (Project No. 00-05-65372)

Herald DGGGMS RAS № 5 (15)'2000 v.2

URL: http://www.scgis.ru/russian/cp1251/h_dgggms/5-2000/hydroterm5.eng

Sulfide compounds which comprise a number of mineral species are known to have a numerous set of useful properties: from valuable electrophysical, optical, semiconductive (thermoelectric driving forces, photo - and X-ray luminescent etc.) up to important for mineralogy and geochemistry typomorphic criteria used in prospering and estimates of rare metal ore deposits. The traditional X-ray diffraction and crystallochemical studies cannot give a direct answer on the question: why the sulfides are characterized with such variable physical, chemical and electrophysical properties? We used direct radiospectrometric methods such as nuclear magnetic resonance (NMR) and specifically the proton magnetic resonance (PMR) of broad bands. This allowed to prove the existence of hydrogen-bearing groups in the crystalline structure of minerals in question and in their artificial analogs. Besides the possibility of heterovalent isomorphous substitution in their anion sublattice was demonstrated. It means that S^{2-} atoms could be partly substituted for hydroxyl and (or) hydrosulfide groups, so that the possibility of compositional and property variations of these compounds are markedly enlarged (Bokij, Bondar', 1978; Kalinichenko et al., 1981; Kozerenko et al., 1995) [1-3].

It should be pointed out that the differential discrimination of proton-bearing groups forming different chemical bond types in sulfides was attained only by use of special high resolution PMR technique. This method allows the averaging of strong dipole-dipole interaction and separation of different types of chemically nonequivalent protons in the composition studied samples.

High-resolution PMR spectra of synthetic sphalerites (ZnS) obtained at different temperature in process of hydro-thermal synthesis were recorded. Several types of hydrogen-bearing groups were revealed. PMR spectra were registered at room temperature on Bruker MSL-300 Spectrometer on a frequency of 300,130 MHz by use of special CRAMPS (Combination Rotation And Multiple Pulse Sequence) techniques. This techniques allowed to use MREV-8 pulse sequence for elimination of 1H homonuclear dipole-dipole interaction along with sample rotation at magic angle ($54,7^\circ$) in order to average the chemical shift tensor anisotropy as well as to average more weak heteronuclear magnetic dipole-dipole interaction. Sample rotation velocity was 2.5-3 kHz, 90° pulse duration was 1.5 μ s, $\square\square$ -

chemical shifts in PMR spectra were measured in relation to tetramethylsilane.

Up to five different types of chemically nonequivalent proton-bearing groups are distinctly revealed on PMR spectra, the former being determined both as hydroxyl and hydrosulfide groups. The comparison of PMR data on synthetic ZnS obtained for low synthesis temperature ($25^\circ C$) showed that the protons probably are related to oxygen atoms in hydroxyl groups and/or water of hydration and having the chemical shift within $\delta = 4.3 - 4.8$ ppm comprise the significant fraction of total proton content. PMR spectra of ZnS obtained as a result of higher synthesis temperature (50, 100, 150, 200, $250^\circ C$) are characterized by the total proton content increase along with synthesis temperature increase mainly at the expense of broad component $\delta = 4.3 - 0.27$ ppm the signal components with chemical shifts of different chemically nonequivalent protons belonging to oxygen- and sulfur-bearing groups are distinctly observed. Along with synthesis temperature increase from $25^\circ C$ up to $150^\circ C$ (see fig.1) the abrupt decrease of broad component of $\delta \sim 4.3$ ppm line is accompanied by the increase of narrow component ($\delta = 3.1, 1.74, 0.75, 0.27$ ppm) line relative intensity which is probably caused by isolated and located protons.

Thus the variation of chemical shift and spectra component broadness along with the synthesis temperature increase is considered as the indication on the existence of chemically nonequivalent hydrogen atoms (up to five types of those) taking part in different hydrogen bonds at the expense of heterovalent isomorphism in the anion sublattice. The proton existence in the crystalline lattice of sulfides evidently has a substantial influence on the electrophysical (semiconductive) and optical (luminescent) properties of synthetic zinc sulfides.

1. Bokij G.B., Bondar' A.M. On the role of hydrogen in sulfide crystal structure// Dokl. ANSSR.1979. Vol.248. N 4. P.956.
2. Kalinichenko A.M., Matjash I.V., Galiy S.A. et al. Proton magnetic resonance in pyrites of different origin // Geokhimiya. 1982. N5. P.765.
3. Kozerenko S.V., Khramov D.A., Fadeev V.V. et al. A study of pyrite formation mechanism in aqueous solutions at low temperatures and pressures // Geokhimiya. 1995. N9. P.1352.

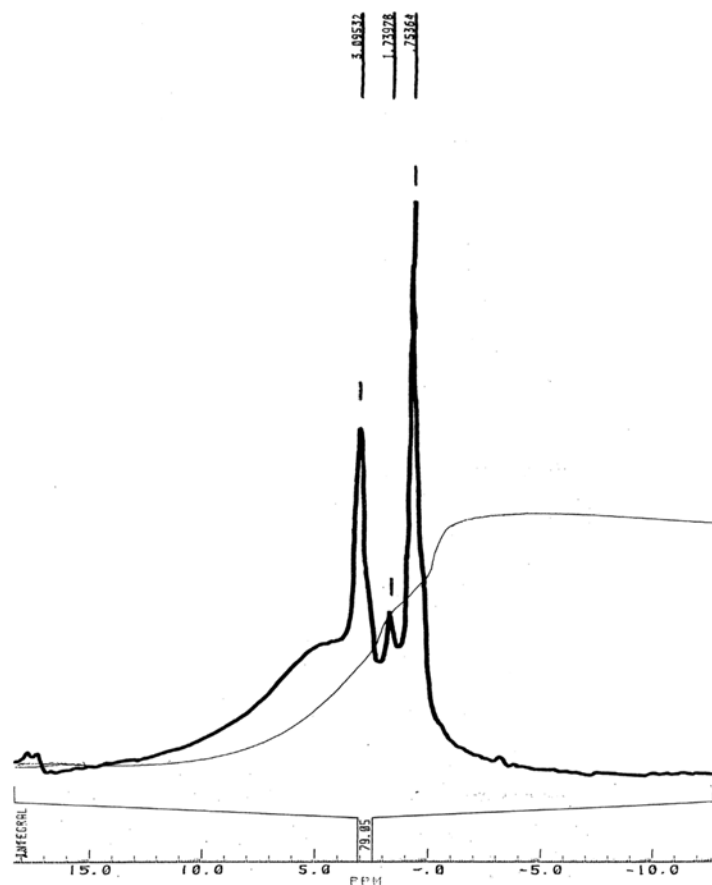


Fig. 1. The high-resolution solid-state proton magnetic resonance spectrum recorded at room temperature on Bruker MSL-300 Spectrometer on a frequency of 300,130 MHz by use CRAMPS techniques from the powdered sample of zinc sulfide synthesized at the temperature 150°C