

GEOCHEMISTRY

Structural Features and NMR ^{195}Pt Spectroscopy of Cooperite Monocrystals (Natural PtS)

A. V. Ivanov^a, V. I. Palazhchenko^a, V. E. Strikha^a, O. N. Antzutkin^b, and W. Forsling^b

Presented by Academician V.G. Moiseenko, December 12, 2005

Received January 26, 2006

DOI: 10.1134/S1028334X06070312

Cooperite (natural PtS)—a platinum group mineral—is a main platinum source in Cu–Ni sulfide ores. Cooperite commonly crystallizes in two morphological modifications: (i) irregular grains; (ii) less frequent micrometric and submicrometric prismatic crystals associated with Fe–platinum and Os–Ir minerals, which could be formed at high temperatures and, consequently, high chemical activity of sulfur. Xenomorphic segregations of cooperite fill up microcavities and microfractures at margins of mineral grains, indicating the secondary origin of this mineral. This is confirmed by data on chemical modeling of cooperite formation even under relatively moderate-temperature conditions [1, 2]. Cooperite monocrystals are extremely rare. However, they have been found in the Okhotsk platinumiferous province of the Maimakan zone of the Yuna–Dan gold ore cluster in the Russian Far East.

In this work, cooperite monocrystals (natural PtS) are characterized in detail with X-ray diffraction, microprobe, and high-resolution scanning electron microscopy. For the first time, we demonstrate the possibility of the application of static and MAS ^{195}Pt spectroscopy for the study of natural platinum minerals.

The structure of natural PtS samples was determined with the XRD method using a URS-2.0 apparatus (Debye–Scherrer camera, 2.0 ($\text{CuK}\alpha$ radiation, and Ni filter). The monocrystal was rotated around the symmetry axes of the second and fourth orders. Complete indexing was carried out with the powder method. The unit cell parameters were calculated with the least squares method and subsequent iterations taking into consideration the errors based on uncertainties of

experimental data at $\pm 2\theta$ and the deviation of experimental angles from calculated ones.

The results were determined from the ratio of the experimental dispersion 2θ to the mean-square experimental error. The intensity of reflections was determined by the method based on the graphic presentation of the intensity versus reflection angle relationship. The reflection angle was obtained by scanning X-ray patterns and its subsequent preservation as a full-profile 2D description with the measurement of the area under the peak.

The qualitative determination of elements in phases was carried out with a microprobe using a LEO-1420 SEM equipped with a RONTEC energy-dispersive spectrometer. The quantitative analysis was performed using a JSM-35C JEOL SEM equipped with an SDS-35 wave-dispersive spectrometer and ZAF-correction facility. Chemically pure platinum and certified sulfides (PtS, PbS) were used as standards. Morphology and microstructure were studied with high-resolution SEM.

Static and MAS ^{195}Pt NMR spectra were recorded with a CMX-360 pulse spectrometer (Varian/Chemagnetics InfinityPlus, United States) at a working frequency range of 76.909–77.709 MHz with a superconducting magnet ($B_0 = 8.46$ T) and Fourier transformation. The MAS spectra were recorded with the application of initiating 67.5° -pulse (duration 1.5 μs) corresponding to the optimum of excitation band at 125 kHz. The total experimental MAS MNR ^{195}Pt spectrum stretched over ~ 0.8 MHz in the frequency scale. Since the simultaneous excitation of the entire MNR spectrum was impossible, it was recorded in separate fragments with a spacing of 100 kHz, and the fragments were then summed.

To record static and MAS versions of the NMR ^{195}Pt spectra, cooperite samples (~ 310 mg in weight) were placed into rotors made of zirconium dioxide 4.0 mm in diameter. In the first version, the sample was carefully ground because of its high structural ordering. In the second version, natural monocrystals were used for measurements. Rotation of samples under the magic

^aInstitute of Geology and Nature Management, Amur Scientific Center, Far East Division, Russian Academy of Sciences, Relochnyi per. 1, Blagoveshchensk, Amur oblast, 675000 Russia

e-mail: Alexander.v.ivanov@chemist.com

^bDivision of Inorganic Chemistry, Luleå University of Technology, S-971 87, Luleå, Sweden

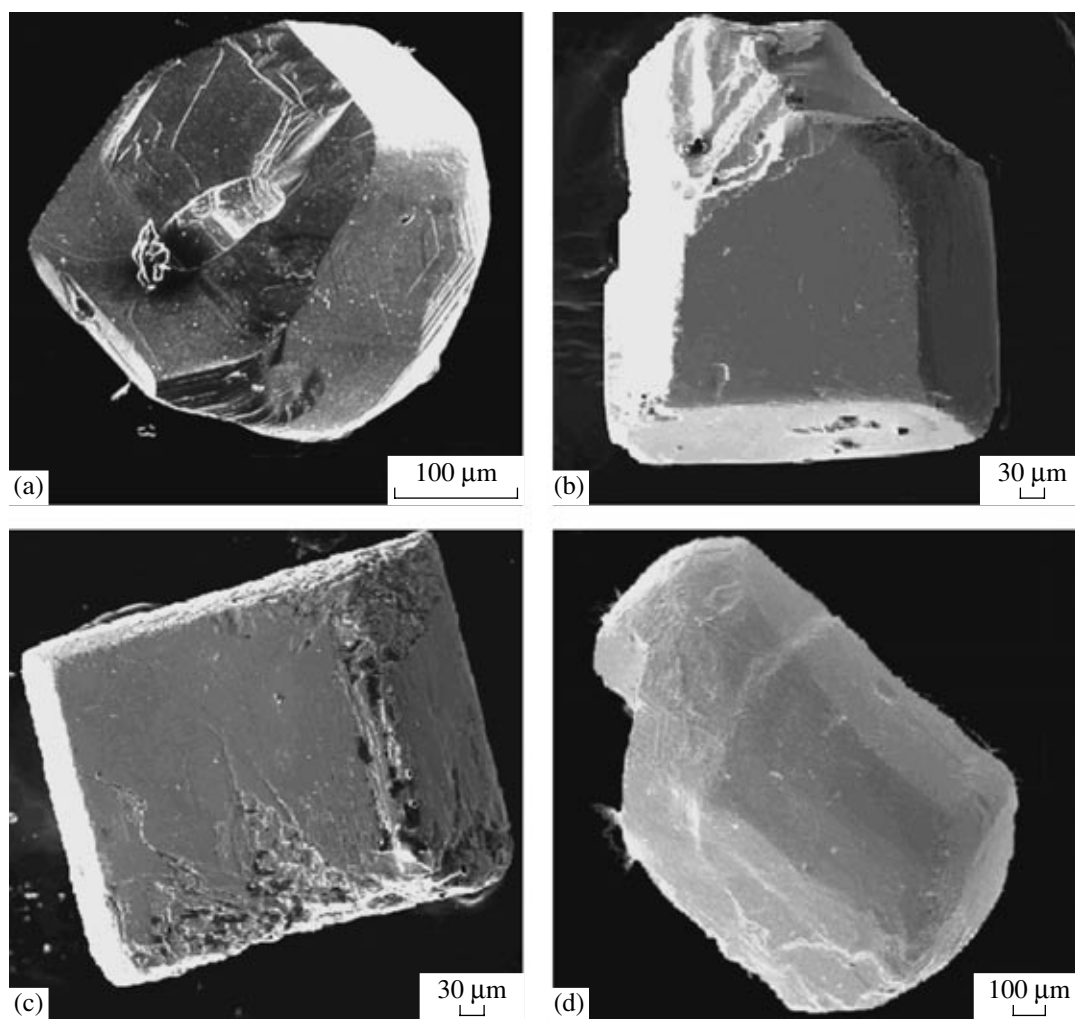


Fig. 1. Cooperite monocrystals.

angle was carried out at a frequency of 8000(1) Hz. The number of data accumulations for each region of the MAS spectrum was equal to 300. The interval between pulses was 4.0 s. The pulse sequence with spin echo ranging from $90^\circ\text{-}\tau$ to $180^\circ\text{-}\tau$] (pulse length 2.0 and 4.8 μs , respectively) and delay $\tau = 160 \mu\text{s}$ was used for the fragment-by-fragment recording of static spectra. The number of data accumulations for each region of the static spectrum was 4512. The interval between initiating pulses was 4.0 s. Because the beginning of MAS spectra interferograms (FID) was distorted by attenuation of the initiating pulse due to the ringdown effect, the distorted region was cut off. Further, in order to avoid phase distortions of the MAS MNR spectrum, the FIDs were shifted by a necessary number of points toward the attenuation region. Since the FIDs included more than 15 rotational echoes, the removal of the initial fragments did not bring about critical distortions of the spectrum. The isotropic chemical shift and principal values of the chemical shift tensor of ^{195}Pt are presented relative to the 0.1 M water solution of $\text{H}_2[\text{PtCl}_6]$ (Merck

Company) set as 0 ppm [3, 4], which corresponds to the ^{195}Pt nuclei resonance frequency of 77.3778 MHz. The homogeneity of the magnetic field was controlled by the width of the reference line of crystalline adamantane equal to 2.4 Hz at the chemical shift $\delta(^{13}\text{C}) = 38.56$ ppm. Parameters of ^{195}Pt MNR were corrected for the drift of magnetic field during experiments. The frequency equivalent of this drift for ^{195}Pt nuclei was 0.044 Hz/h. The magic angle was set at the resonance frequency of the ^{79}Br nuclide (90.189 MHz) according to the standard procedure with the application of KBr. The additional adjustment was carried out to achieve the minimum width of lines in the MAS NMR ^{195}Pt spectrum of cooperite.

SEM and XRD data. The cooperite monocrystals under study have well-developed faces with distinct striation (Fig. 1a). The monocrystals are often broken. Some of them have rounded forms with traces of dissolution (Figs. 1b, 1c). The average size of monocrystals is 200–300 μm . Some crystals are >1 mm in size (Fig. 1d).

The monocrystals are characterized by stoichiometric composition (85.826 wt % Pt and 13.917 wt % S). Figure 2 shows the energy-dispersive spectrum of cooperite that characterizes its elemental composition. The Ni and Pd admixtures pointed out in [5, 6] were not detected by a microprobe equipped with wave-dispersive spectrometer. Most euhedral cooperite crystals did not contain inclusions of the second phase at micrometric and submicrometric levels. Only sporadic sulfide inclusions of the CuS-CuFeS_2 series were noted.

We detected 34 lines in experimental powder XRD patterns. They are consistent with calculations based on the POWDER CELL software [7]. In terms of the set of d/n -spacings, these lines correspond to phase PtS (PDF 26-1302) with 19 lines. However, lines (001), (220), (105), and (222) were not revealed despite the sufficient calculated intensity.

The structure of the studied cooperite samples pertains to space group $P4_2/mmc$ (No. 131) with the following unit cell parameters: $a = 3.4695 \pm 0.0002 \text{ \AA}$, $c = 6.1066 \pm 0.0009 \text{ \AA}$, $c/a = 1.7601 \pm 0.0004$, $V = 73.5080 \text{ \AA}^3$, $Z = 2$, and the calculated density is 10.263 g/cm^3 . The height of the unit cell is equal to the height of two pseudocells formed by tetragonally distorted ($c/2a = 0.88$) simple cubic packing of sulfur atoms. The opposite faces of pseudocells are centered by Pt atoms in such a manner that pseudocells, whose centered faces are parallel to (100) and (010), alternate along [001]. The coordination of Pt and S atoms is formed with the participation of the four nearest neighbors. However, Pt atoms pertain to plane-square chromophores, whereas sulfur occurs in the distorted tetrahedral surrounding of Pt atoms ($d_{\text{Pt-S}_1} = 2.3108 \text{ \AA}$, $d_{\text{Pt-S}_2} = 2.3109 \text{ \AA}$, and $d_{\text{Pt-Pt}} = 3.4695 \text{ \AA}$).

NMR ^{195}Pt spectra. Figure 3a shows the resultant MAS MNR ^{195}Pt spectrum of cooperite monocrystals obtained by the summation of nine separate fragments recorded with a spacing of 100 kHz. The size and shape of the MAS spectrum under discussion indicate that the ^{195}Pt chemical shift tensor is close to the case of axial symmetry. Thereby, the ^{195}Pt chemical shift anisotropy is so great that more than 100 spinning sidebands are present even at a rotation frequency of 8000 (1) Hz. Therefore, we applied the technique of smooth swinging of sample rotation frequency in the MAS experiment to reveal the ^{195}Pt resonance signal in the spectrum's center of gravity (i.e., the centerband), which is characterized by the isotropic chemical shift. In this case, the amplitude of the centerband(s) of gravity of the sample does not change, whereas the sidebands widen catastrophically (Fig. 3b). As follows from the data obtained, the two crystallographically independent Pt sites in the cooperite lattice are structurally equivalent and are characterized by the isotropic chemical shift $\delta(^{195}\text{Pt}) = -1850 \text{ ppm}$ at a resonance signal width of 375 Hz.

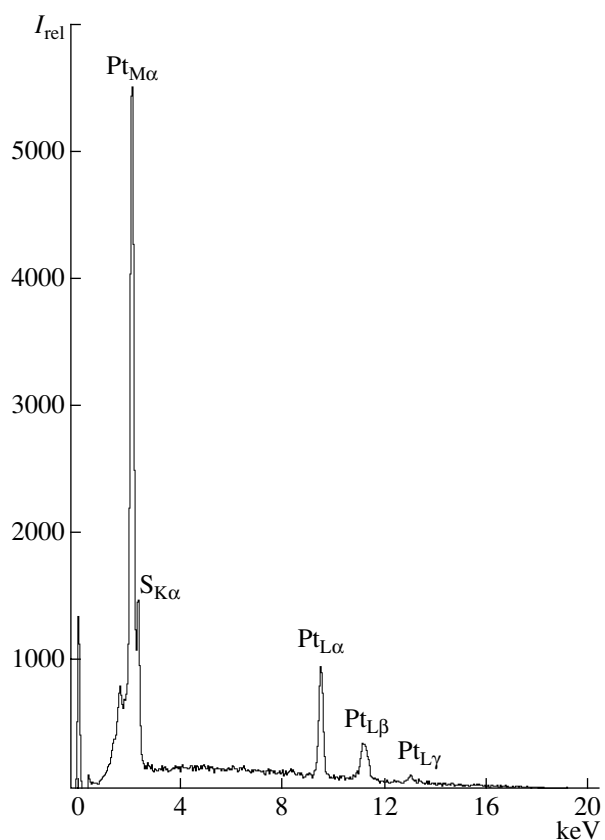


Fig. 2. Energy-dispersive spectrum of cooperite.

To determine principal values of the ^{195}Pt chemical shift tensor, we carried out the fragment-by-fragment recording of the static MNR spectrum of the carefully ground cooperite powder. The profile obtained shows three singularities at $\delta_{xx} = -5920 \pm 20 \text{ ppm}$, $\delta_{yy} = -3734 \pm 5 \text{ ppm}$, and $\delta_{zz} = +4023 \pm 20 \text{ ppm}$. Furthermore, based on the experimental data, we also calculated the ^{195}Pt chemical shift anisotropy $\delta_{\text{aniso}} = 5873 \text{ ppm}$ (specified as $\delta_{\text{aniso}} = \delta_{zz} - \delta_{\text{iso}}$) and asymmetry parameter $\eta = 0.37$ $\{\eta = (\delta_{yy} - \delta_{xx}) / (\delta_{zz} - \delta_{\text{iso}})\}$. It should be noted that $\eta = 0$ corresponds to the case of the axisymmetric chemical shift tensor, whereas the increase in η from 0 to 1 reflects an enhanced contribution of rhombicity. Thus, the η value obtained for cooperite indicates a 37% contribution of this constituent.

One can assume with a high degree of probability that the least shielded direction of the platinum nucleus (z axis of the chemical shift tensor) coincides with the four-fold axis of square-planed chromophore $[\text{PtS}_4]$. The other two directions cannot coincide with molecular axes x and y , because the very small difference (0.0001 \AA) in the length of nonequivalent Pt-S bonds cannot explain the considerable discrepancies in the degree of electronic shielding. Most likely, they coincide with bisectrices of S-P-S angles. However, the axis passes inside a small four-membered metallacycle

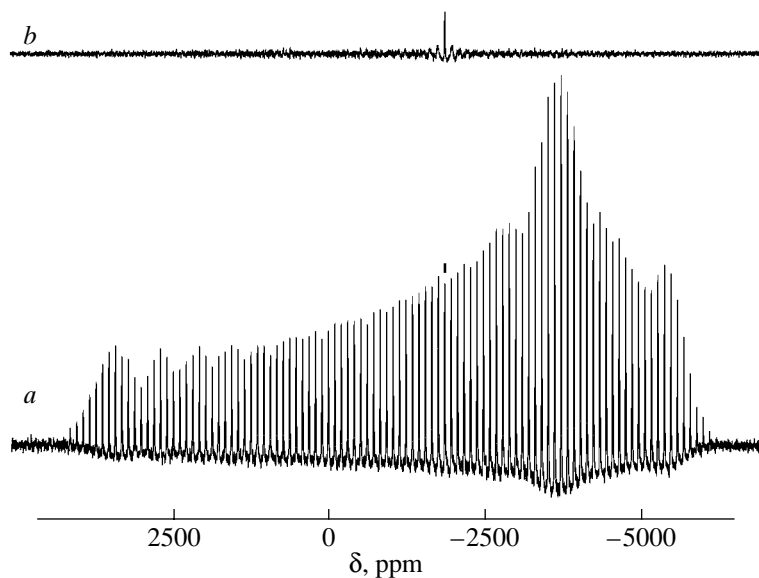


Fig. 3. (a) The resultant MAS MNR ^{195}Pt spectrum of cooperite monocrystals. The upper vertical mark indicates the centerband. The sample rotation frequency is 8000(1) Hz. (b) Spectrum recorded under conditions of smooth swinging of rotation frequency.

$[\text{Pt}_2\text{S}_2]$ (more shielded position) in one case and through an extended eight-membered cycle $[\text{Pt}_4\text{S}_4]$ (less shielded position) in another case.

Thus, we have scrutinized for the first time cooperite monocrystals based on X-ray diffraction, microprobe, and high-resolution SEM data. Despite the considerable ^{195}Pt chemical shift anisotropy nuclei in cooperite, we have demonstrated the principal possibility of the application of static and MAS ^{195}Pt MNR spectroscopy for the study of natural platinum minerals.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research and the Far East Division of the Russian Academy of Sciences (joint program "The Russian Far East," project no. 06-03-96009) and the Presidium of the Far East Division of the Russian Academy of Sciences (project no. 06-III-A-08-339). A.V.I. acknowledges financial support from the Agri-

cola Research Centre, Luleå University of Technology, Sweden.

REFERENCES

1. L. P. Plyusnina, G. G. Likhoidov, and I. Ya. Nekrasov, *Dokl. Earth Sci.* **370**, 86 (2000) [*Dokl. Akad. Nauk* **370**, 99 (2000)].
2. L. P. Plyusnina, G. G. Likhoidov, and A. I. Khanchuk *Dokl. Earth Sci.* **405**, 1235 (2005) [*Dokl. Akad. Nauk* **405**, 105 (2005)].
3. G. A. Kirakosyan, *Koord. Khimiya* **19**, 507 (1993).
4. M. Gianini, W. R. Gaseri, V. Gramlich, and U. W. Suter, *Inorg. Chim. Acta* **299**, 199 (2000).
5. O. E. Yushko-Zakharova, V. V. Ivanov, L. N. Soboleva, et al., *Minerals of Noble Metals: A Handbook* (Nedra, Moscow, 1986) [in Russian].
6. V. V. Ivanov, *Environmental Geochemistry of Elements: A Handbook* (Ekologiya, Moscow, 1997), Vol. 5: *Rare Elements* [in Russian].
7. W. Kraus and G. Nolze, *J. Appl. Crystallogr.* **29**, 301 (1996).