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Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR I. N. Plaksin and R. Sh. Shafeev

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Abstract

Full Text

Physical Chemistry

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The Influence of Certain Semiconductor Properties of the Surface on the Interaction of Xanthate with Galena

Galena, like many sulfide minerals, is a typical impurity semiconductor of mixed type; therefore, the sign of the electric-charge carriers is determined by the nature of the impurity in the mineral lattice. Lead atoms present in excess relative to the stoichiometric composition may serve as a donor impurity, while excess sulfur atoms, as well as oxygen adsorbed on the surface of the mineral, may serve as an acceptor impurity.

The behavior of the surface of electron and hole galena with respect to xanthate is not the same, owing to the fact that in the first case an increased concentration of electrons is observed on the mineral surface, whereas in the second case there is an increased concentration of holes, which, by recombination with the electron of the xanthate anion, are capable of forming a strong chemical bond with the mineral surface.

It should be noted that on the surface of galena, as well as of many other sulfides, one may expect the simultaneous presence of regions with electron and hole conductivity, which, owing to the requirement of equality of chemical potentials, creates nonequipotentiality of the electric field on the surface of the sulfide mineral. Earlier work by the authors (1) on carrying out cathodic polarization of the surface of sulfide minerals in a dilute solution of copper or silver ions established experimentally the existence of electrochemical heterogeneity of the surface of sulfide minerals.

In these investigations, regions with different electrochemical potentials were recorded by deposits of cathodic metal on the mineral surface, which were observed under a microscope. In addition, in studying changes in the outlines of deposits of cathodic copper as a function of the negative voltage applied to the surface of the sulfide mineral, it was established that on galena there exist regions with such a negative potential on which copper begins to deposit at zero surface charge, as well as regions on which copper is not deposited even at very high negative values of the voltage (−1.4 V).

Probably, xanthate is fixed with great difficulty on the surface of a sulfide having

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Fig. 1. Diagram of the apparatus for determining the thermoelectric e.m.f. of sulfide minerals

Figure 1: Fig. 1. Diagram of the apparatus for determining the thermoelectric e.m.f. of sulfide minerals

electron conductivity. This proposition is confirmed by the fact that sulfide minerals do not interact with xanthate if their surface has not been previously treated with oxygen (^{2}). In addition, it is known that on the surface of sphalerite (a typical electron semiconductor) xanthate is fixed to a lesser extent.

To determine the nature of the electric-charge carriers and the thermal coefficient of the thermoelectromotive force (thermo-e.m.f.) of sulfide minerals, an instrument with an electric thermoprobe was assembled according to the scheme shown in Fig. 1. The electric thermoprobe was made from a steel point heated by passing an electric

current through a nichrome coil wound on top of the thermoprobe. The temperature in the contact zone of the thermoprobe tip with the surface of the sulfide mineral was controlled by means of a thermocouple formed by the thermoprobe tip and a nickel wire welded near the very tip of the probe. Measurements of the thermoelectric e.m.f. were carried out at various temperatures from room temperature to 400° on galena, chalcopyrite, molybdenite, and pyrite. The results of the thermoelectric e.m.f. measurements are given in Fig. 2. The thermal coefficient was 200 μV/deg for galena, 160 μV/deg for chalcopyrite, 110 μV/deg for pyrite, and 70 μV/deg for molybdenite. High values of the thermoelectric e.m.f. indicate the impurity character of the sulfide minerals. In addition, by measuring the sign of the thermoelectric e.m.f. it was found that our samples of galena and chalcopyrite had electron conductivity, whereas molybdenite and pyrite had hole conductivity. In electron semiconductors the level of the chemical potential rises toward the lower boundary of the conduction band as the concentration of donor impurities increases, while in hole semiconductors this level approaches the upper boundary of the valence band, as a result of which the concentration of electrons in the conduction band decreases.

Fig. 1. Diagram of the apparatus for determining the thermoelectric e.m.f. of sulfide minerals

A simplified energy diagram of the process of xanthogenate fixation on galena in the presence of oxygen is shown in Fig. 3. In this diagram the energy of the boundary of the filled band is denoted by E_1, and the energy of the boundary of the conduction band by E_2. The donor level of the impurity lead atoms is E_d, and the acceptor level of the adsorbed oxygen is E_a. In addition, in the forbidden band there are the level of the chemical potential, corresponding to the transition of the mineral from electron type to hole type φ, and the energy level of the xanthogenate anions.

Fig. 2. Dependence of the thermoelectric e.m.f. of sulfide minerals on temper-

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Fig. 2. Dependence of the thermoelectric e.m.f. of sulfide minerals on temperature: 1—MoS2; 2—FeS2; 3—CuFeS2; 4—PbS

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Fig. 3. Diagram of the energy levels of galena

Figure 3: Fig. 3. Diagram of the energy levels of galena

ature: 1 —MoS_2; 2 —FeS_2; 3 —$CuFeS_2$; 4 —PbS

In galena of the electron type, the concentration of electrons in the conduction band (above E_2), as well as the position of the chemical-potential level, depends on the concentration of impurity interstitial lead atoms and can be calculated for each specific case on the basis of the dependence of the Fermi level on the concentration of free electrons. At low concentrations of impurity lead atoms, in the absence of electron degeneracy—which is quite probable for sulfide minerals—the Fermi-Dirac statistics may be replaced by the Maxwell-Boltzmann statistics. In this case the dependence takes the form:

$$n = N_{\mathrm{Pb}} \exp -(E_2 - \varphi)/kT,$$

where n is the concentration of electrons formed upon ionization of impurity lead atoms, N_{Pb} is the concentration of impurity lead atoms in galena, k is Boltzmann' s constant, and T is the temperature on the absolute scale.

As a result of the presence of free electrons on the surface of galena, a charge arises, the magnitude of which can be calculated by means of the Poisson equation. The increase in the magnitude of the surface potential caused by free electrons creates a potential barrier that xanthate anions must overcome in order to become fixed on the mineral surface. The fixation of xanthate on the surface of galena begins when the mineral passes from the electronic type to the hole type, owing to the appearance of acceptor oxygen levels in the forbidden band.

Adsorbed on the surface of galena, oxygen, in the process of ionization, absorbs electrons from the free band and thereby lowers the height of the potential barrier at the mineral surface

$$^1/_2 O_2 \to O^{2-}_{\mathrm{ads}} - 2e.$$

Fig. 3. Diagram of the energy levels of galena

It is probable that the decrease in electron concentration as a function of the oxygen concentration in the pulp follows a parabolic dependence ([3]). The height of the potential barrier, and consequently the level of the chemical potential of the electrons, gradually decreases with increasing concentration of dissolved oxygen in the pulp; at the same time, the probability that the barrier will be overcome by xanthate anions gradually increases.

When the level of the chemical potential corresponding to equality of the number of electrons and holes in galena is crossed, the potential barrier disappears, and in its place a potential well begins to arise, the depth of which increases with the growth in the number of holes in the filled band (section *bcd* in Fig. 3). From this moment, fixation of xanthate on the surface of galena begins, with the formation of a chemical bond with the lattice cation. With a further increase in the oxygen concentration, the concentration of holes increases to such an extent that xanthate electrons begin to be absorbed very intensively, and conditions are created for the oxidation reaction of xanthate to dixanthogen.

It should be noted that, owing to the inhomogeneity of the galena surface, the transition from the electronic type of mineral to the hole type proceeds unevenly; as a result, on the surface one may expect the simultaneous presence both of regions with hole conductivity and of regions with electronic conductivity, which creates a nonuniform, mottled character of the distribution of xanthate over the surface of galena particles.

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CITED LITERATURE

1. I. N. Plaksin, R. Sh. Shafeev, DAN, **121**, 145 (1958).
2. I. N. Plaksin, S. V. Bessonov, *Proceedings of the Second International Congress of Surface Activity*, **3**, London, 1957, p. 361.
3. S. R. Morrison, *Advances Catal. and Related Subjects*, **7**, 259 (1955).

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