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X-RAY EMISSION SPECTRA STUDIES OF SOME SULPHUR CONTAINING MINERALS BY ELECTRON MICROPROBE

(Fig. 1—2)

Abstract: The chemical shift measurement of X-ray emission $SK_{\alpha_{1,2}}$ lines on the samples sulphides, sulphosalts and anhydrite were carried out. The electron microprobe JXA-5A was used for the measurements of chemical shift. The same instrument was used for the checking of chemical composition of measured area. Using the data of chemical shift of $SK_{\alpha_{1,2}}$ lines the effective charges of sulphur atoms in measured compounds were determined.

Резюме: В работе подаются результаты точечного анализа некоторых сульфидов, сульфосолей и $CaSO_4$. Особое внимание уделено измерению химических сдвигов линии $SK_{\alpha 1,2}$ в приведенных образцах использованием электронного микроанализа JXA-5A и эффективных заряц атомов серы. Исходя из результатов эфективных набойов авторы обсуждают характер химической связы в минералах и дальнейшие возможности использования результатов рентгеноспектрального исследования минералов с помощью электронновогo микроанализа в геологии.

Introduction

The microanalysis by electron microprobe has become one of the most important methods of geochemical research, and at present it is rather classical method for determining of chemical composition of minerals.

Recently some authors has made effort to use the electron microprobe for the purpose of X-ray spectral research (V. A. Batyrev — A. V. Šatunova 1967, R. Theisen 1967, Ch. D. Dodd — G. L. Glenn 1968, I. Takayoshi — T. Hideo 1970).

They tried to find out the relation between the X-ray emission spectra of pure chemical elements and the X-ray emission spectra of chemical element bound in a compound. It is known that the energy of X-ray radiation of a chemical element depends slightly upon the character of chemical bound among the atoms of a molecule. If ionic character of a chemical bond is high then the shift of X-ray line peak is high and on the contrary there is none chemical shift if the chemical bond is purely covalent.

The degree of ionic character of a chemical bond of compound can be quantitatively expressed by an effective charge of the atoms of an element. The effective charge of an atom provides of the redistribution of its valence electron. The redistribution occurs when atom enters the molecule. The effective charge of considered atom is positive if its valence electrons are shifted towards the adjacent atoms and on the contrary the effective charge of an atom is negative if the valence electrons of adjacent atoms are shifted towards the considered atom. The effective charge is usually expressed in units ^{+}e $(= 1.602 . 10^{-19}\ C)$.

In the case of elements of the third period (C. A. Coulson — C. Zauli 1963, W. I. Nefedow 1962, G. Leonhardt — A. Meisel 1970) there is direct coherence between the chemical shift of X-ray lines and the effective charge of atoms

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in a molecule of compound. If the effective charge of the atom in a molecule is positive then $K\alpha_{1,2}$ line peak is shifted towards the higher energy and on the contrary if the effective charge is negative $K\alpha_{1,2}$ line peak is shifted towards lower energies. As the reference position for $K\alpha_{1,2}$ peak it is usually used that of the pure element.

We tried to use the instrument JXA-5A for the determination of chemical shift of sulphur atoms in some minerals. As we are informed the electron microprobe has not been used for the purpose of determination of atomic effective charge up to this time.

Experimental part

We chose for the studing the minerals: argentite (Ag_2S), galena (PbS), chalcopyrite ($CuFeS_2$), bismutite (Bi_2S_3), stibnite (Sb_2S_3), pyrite (FeS_2), emplectite ($CuBiS_2$), aikinite ($CuPbBiS_3$) and anhydrite ($CaSO_4$).

We used the Jeol microprobe JXA-5A for the identification and the determination of chemical composition of measured area. The experimental conditions during analysis were: accelerating voltage 15 kV, sample current 4.10^{-8} A, LiF and quartz crystals. The various corrections were evaluated by computer CDC 3300 using the computer program SONDA 03 (F. Škvára — V. Hulinský 1972).

We measured the chemical shift of $SK\alpha_{1,2}$ lines using the pentaerithritol (PET) and quartz crystals. The $SK\alpha_{1,2}$ lines were recorded by method „step by step". We had to construct the attachment for this purpose because the model JXA-5A allows only the continual recording of X-ray spectra.

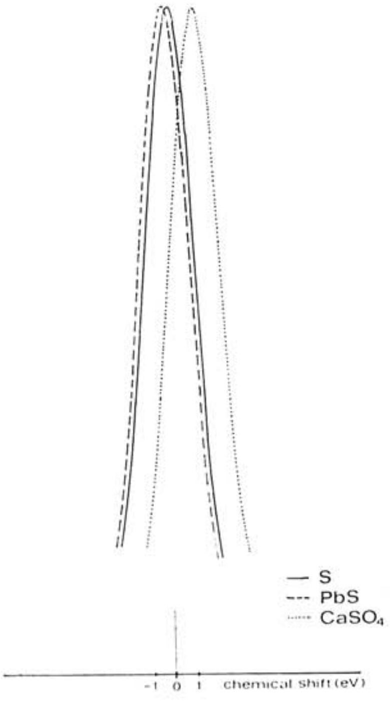

Fig. 1. Chemical shifts of $SK\alpha_{1,2}$ lines in $CaSO_4$ and PbS.

The experimental conditions during the measuring of chemical shift were: accelerating voltage 10 kV, sample current 1—4.10^{-8} A, the diameter of electron beam 20—50 μm. As the standard for the position of $SK\alpha_{1,2}$ peak we used the pressed powder sulphur. The surface of all samples were evaporated by carbon layer. Every sample was measured 3—5 times in order to diminish the experimental bias.

The example of chemical shift of $CaSO_4$ and PbS where the chemical shift was highest is shown at fig. 1.

We used for the evaluation of effective charge the semiempirical formula of Nefedow (R. L. Barinskij — V. I. Nefedow 1966) (Fig. 2).

$$\triangle E\, K\alpha_{1,2} = k\,.\,E\, K\alpha_{1,2} \overset{q}{\Sigma} \sqrt{I_i}$$

$$\triangle E' K\alpha_{1,2} = k\,.\,E' K\alpha_{1,2}\, \Sigma \sqrt{F_i}$$

where $\triangle E\, K\alpha_{1,2}$ is the energetic shift of $SK\alpha_{1,2}$ line [eV], $E'\, K\alpha_{1,2}$ is the energy of $SK\alpha_{1,2}$ line [eV], k is the constant ($= 5.1\,.\,10^{-5}\, eV^{-1/2}$ and Ii, Fi are ionization potentials resp. electron afinities of sulphur atoms.

Discussion

The quantitative analysis confirmed that we dealt with the homogeneous minerals of general chemical composition (see table 1). This justified to measure the chemical shift and to evaluate the effective charges of sulphur atoms. The results of effective charges q and the degrees of ionic character of chemical bond i are in the table 2. The degree of ionic character of chemical bond is defined as the ratio $i = \frac{q_{eff}}{q_{max}}$, where q_{eff}

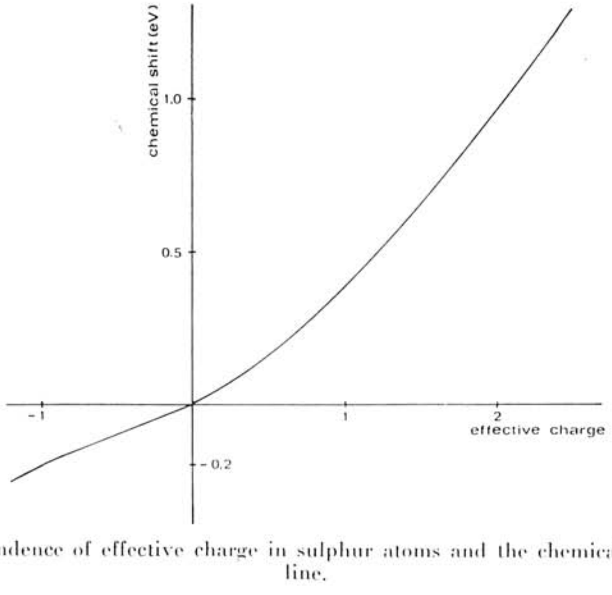

Fig. 2. The dependence of effective charge in sulphur atoms and the chemical shifts of $SK\alpha_{1,2}$ line.

Table 1. The results of quantitative analysis by electron microprobe JXA-5A

	Bi	Pb	Sb	Ag	Cu	Fe	S	CaO	SO_3
argentite Ag_2S	—	—	—	88,11	—	—	11,34	—	—
galena PbS	—	87,64	—	—	—	—	12,85	—	—
stibnite Sb_2S_3	—	—	72,14	—	—	—	28,85	—	—
bismutite Bi_2S_3	82,92	—	—	—	—	—	17,58	—	—
chalcopyrite $CuFeS_2$	—	—	—	—	35,20	29,25	32,83	—	—
pyrite FeS_2	—	—	—	—	—	45,62	53,81	—	—
emplictite $CuBiS_2$	61,43	—	—	—	19,21	—	17,82	—	—
aikinite $CuPbBiS_3$	35,86	34,28	—	—	12,12	—	16,62	—	—
anhydrite $CaSO_4$	—	—	—	—	—	—	—	40,12	56,32

is the effective charge and q_{max} is the theoretic charge of an atom in condition of purely ionic bond.

We can see from table 2. that none of the minerals has the pure covalent chemical bond. In both sulphides and sulphosalts (oxidation stage — 2) are effective charges negative, it means that the density of valence electrons is higher in the region of sulphur atoms. The different situation we can see in $CaSO_4$ (oxidation stage + 6). The valence electrons of sulphur in SO_4^{-2} group are shifted towards the oxigen atoms. We can explain this phenomena by high electronegativity of oxigen atoms.

In some minerals (PbS, Bi_2S_3, $CuPbBiS_3$) the ionic character of chemical bound is quite high. The values of effective charges of sulphur atoms in Bi_2S_3, $CuBiS_2$ and $CuPbBiS_3$ confirme the idea about the relationship among the minerals and their salts.

Conclusion

We emphasize the complete interpretation of effective charges of atoms in molecules is very difficult. In spite of this fact we are convinced the chemical shift measuring method is very perspective and can explain the mutual relation of elements of minerals.

The X-ray microanalyser is suitable instrument also for X-ray spectral studies of minerals. We compared our results with the results of Nefedow (V. I. Nefedow 1962). The results are in good agreement. We point the all results untill this time were obtained by fluorescence X-ray spectrometers which had been designed for this purpose and therefore one must expect the higher precision of results than when X-ray microanalyser is used.

Table 2. The results of chemical shifts of $SK_{\alpha_{1,2}}$ lines and the effective charges of sulphur atoms

Mineral	Chemical shifts $\Delta EK\alpha_{1,2}$ [eV]	effective charge q_{eff} ^{+}e	ionic character chemic. bond $i = \frac{q_{eff}}{q_{max}}$
argentine Ag_2S	−0,19	−0,67	−0,33
galena PbS	−0,27	−1,2	−0,60
stibnite Sb_2S_3	−0,19	−0,92	−0,46
bismutite Bi_2S_3	−0,27	−1,2	−0,60
chalcopyrite $CuFeS_2$	−0,19	−0,92	−0,46
pyrite FeS_2	−0,17	−0,87	−0,43
emplective $CuBiS_2$	−0,20	−1,00	−0,5
aikinite $CuPbBiS_3$	−0,20	−1,00	−0,5
anhydrite $CaSO_4$	+1,2	+2,29	+0,37

On the other hand the X-ray microanalyser is the only instrument when it is necessary to measure the chemical shift in very small areas (less than 100 μm).

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