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THERMAL CHARACTERIZATION OF CHANGES IN STRUCTURE AND PROPERTIES OF CHALCOPYRITE AFTER MECHANICAL ACTIVATION

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ABSTRACT

Changes in specific surface area, surface layer composition, structural disorder, magnetic susceptibility and the rate of non-oxidative decomposition of chalcopyrite brought about by vibration grinding in air and methanol were investigated. Significant differences in structure and reactivity between systems ground in different environments enabled confirmation of the threshold phenomenon of mechanical activation, and led to the conclusion that plastic strain resulting in destruction of the long-range order in the structure may be considered as the source of changes in magnetic properties and excess reactivity.

INTRODUCTION

The effect of defects on solid-state reactions is often more significant than that of crystallochemical properties which stem from the type of lattice of the reacting solid. Therefore, by varying the preliminary treatments, storage conditions, or methods of preparation, defective solids with a high concentration of non-equilibrium defects may deliberately be created. Although the field of application for the majority of mentioned methods is confined to the given system, mechanical activation by fine grinding is universal in its potential application.

A wide range of physical and chemical processes occur during breakage and deformation, among which lattice disordering evoking changes in fine structure should be mentioned. The nature of disordering in mechanically activated minerals with a close-packed anion or cation sublattice has been

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the subject of detailed study since the early 1980s. Using Mössbauer spectroscopy, Pavlyukhin and co-workers [1–3] have shown that magnetic disordering is a threshold phenomenon and results in the destruction of long-range order in the structure. An unusual metastable state is formed when small cations from tetrahedral sites in the original structure pass into octahedral positions. The mechanism of this phenomenon is a crystallographic shear in the plane (111) of the close-packed oxygen spinel structure. Similar effects are observed for activation of phosphates and sulphides [4], among which chalcopyrite [5–10] is the object of our study.

EXPERIMENTAL

The investigations were carried out with chalcopyrite which originated from Slovinky (East Slovakia) and which had the following composition: 28.07% Cu, 28.36% Fe, 31.62% S, 0.65% As, 7.42% SiO_2 and 3.80% insoluble residue.

The samples (50 g each) were mechanically activated in a four-chamber vibration mill (Mining Institute, Slovak Academy of Sciences, Košice) with variable amplitude and variable speed of rotation, at 75% filling of the chamber with steel balls. The material was ground for 5–60 min either dry or in methanol (100 ml).

The structural disorder of mechanically activated samples was determined by X-ray diffraction phase analysis on a DRON 2.0 diffractometer (U.S.S.R.) using the following regime: radiation Cu $K\alpha$, 30 kV, 20 mA, time constant 1 s, limit of measurement 10 impulses s^{-1}, rate of detector 2° min^{-1}, paper drive 2.4 m h^{-1}. The degree of structural disorder F was calculated according to Patzak [11] from ratio of the integral half-width of chalcopyrite (112) X-ray diffraction lines:

$$F=\frac{B}{B_0} \tag{1}$$

where B and B_0 are the integral half-widths of mechanically activated and as-received samples, respectively.

The specific surface area, S_A, was determined from the adsorption isotherms of benzene vapour by the BET method [12]. The "granulometric" specific surface area, S_G, was calculated statistically from particle size distribution data measured on a Sartorius sedimentation balance (F.R.G.).

The morphology of the chalcopyrite particles was monitored by a BS 300 electron scanning microscope (Tesla, Czechoslovakia).

The specific magnetic susceptibility χ was measured with a KLY-1 instrument (Institute of Applied Geophysics, Czechoslovakia).

The IR spectra were obtained with a Specord 75/IR spectrometer (Carl Zeiss, G.D.R.), using the KBr-disc technique. The characteristic vibrations of chalcopyrite were observed at $\bar{\nu} = 360\ \mathrm{cm}^{-1}$ [13] and those of the sulphate group at $\bar{\nu} = 1144\ \mathrm{cm}^{-1}$ [14]. The occurrence of sulphate was quantified for the above vibration by the relationship

$$E = -\log T \qquad (2)$$

where E is extinction and T is transmittance.

X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCA 3 MK II instrument (VC Scientific, Gt. Britain) in 10^{-6} Pa vacuum. The electrons were excited by Al $K\alpha$ emission of $h\nu = 1486.6$ eV; the

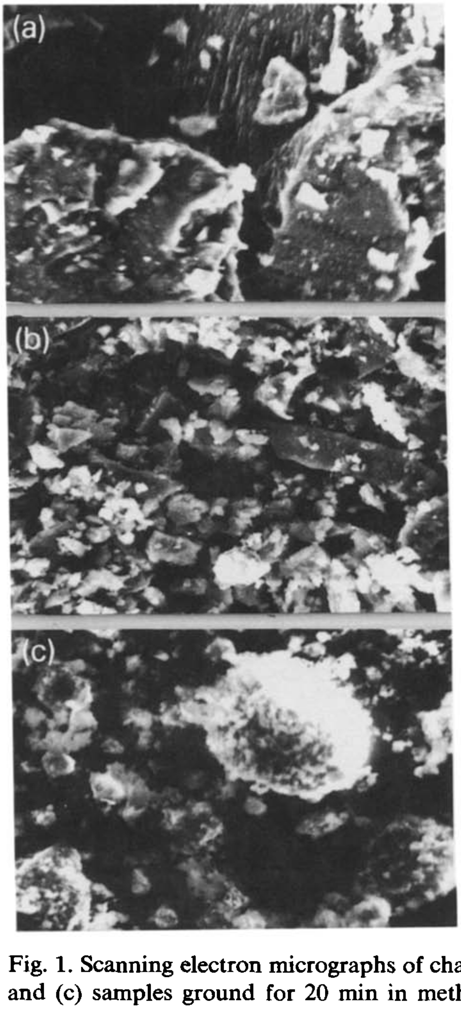

Fig. 1. Scanning electron micrographs of chalcopyrite: (a) as-received sample (20–32 μm); (b) and (c) samples ground for 20 min in methanol and air, respectively. Magnification 900×.

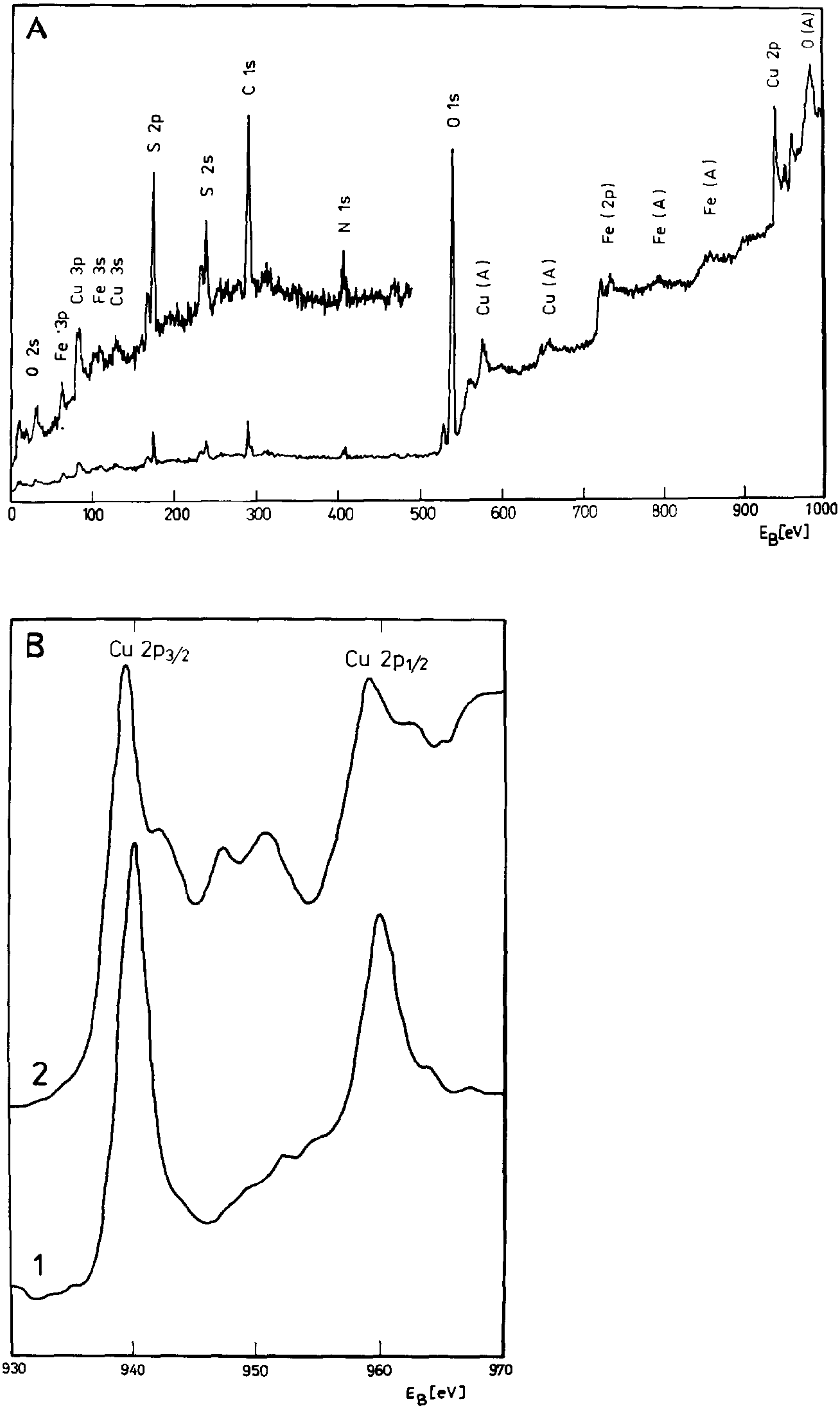

Fig. 2. XPS spectra of as-received (20–32 μm) sample (1) and for samples activated for 20 min in air (2) and in methanol (3). A, Review spectrum; B, Cu $2p_{3/2}$ and Cu $2p_{1/2}$ spectra; C, S^{2-} and S^{6+} spectra.

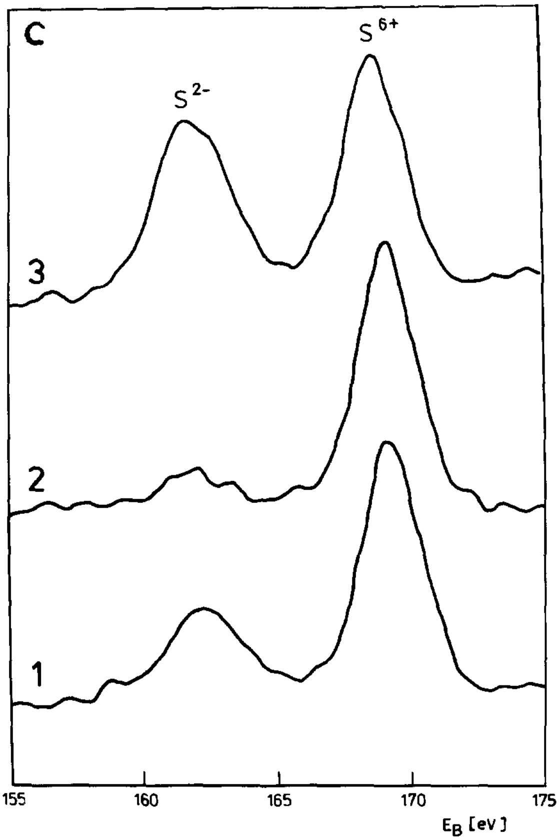

Fig. 2. (continued).

transmission energy of the electron analyser was 20 eV and the width of the entrance slit of the analyser was 4 nm.

The thermal decomposition of chalcopyrite

$$CuFeS_2 \rightarrow CuFeS_{2-x} + xS \qquad (3)$$

was investigated in a dynamic reactor with a static layer of the solid phase, under the following conditions: weighed amount 500 mg, volume flow rate of argon 3.3×10^{-1} m^3 s^{-1}, temperature 868 K. Experimental results were treated by the Kekam equation [15]:

$$\alpha = 1 - \exp(-k't^n) \qquad (4)$$

where k' is a constant related to the apparent rate constant k as follows [16]:

$$k = n(k')^{1/n} \qquad (5)$$

where α is the conversion degree and t is the reaction time.

RESULTS AND DISCUSSION

Changes in the secondary structure of the particulate assembly and mechanochemical transformations during the grinding process

Figure 1 shows scanning electron micrographs of dry- and methanol-ground chalcopyrite in comparison with the as-received (non-activated) sample. In Fig. 1a and 1b typical chalcopyrite grains may be identified and the only change brought about during methanol grinding is the size reduction. The micrograph of the air-ground sample (Fig. 1c) is characterized by the occurrence of agglomerates formed by clustering of fine particles.

Apart from the size reduction and changes in the secondary structure of the particulate assembly, changes in the chemical composition of surface layers brought about by grinding were determined.

Figure 2A presents the distribution of elements in the chalcopyrite surface layer, in the form of an XPS spectrum. As well as the basic elements (copper, iron and sulphur), other elements such as carbon, nitrogen and oxygen may be identified. The occurrence of carbon and oxygen in minerals is usual and is connected with adsorption of carbon dioxide. The XPS method allows information to be gained also on the oxidation states of the elements [17,18]. In Fig. 2B the copper $2p_{3/2}$ and $2p_{1/2}$ spectra are shown in the region $E_B = 950-970$ eV. The occurrence of shake-up satellites at 950 eV confirms that Cu^{2+} prevails over Cu^+ in the dry-ground samples. Similarly, it is possible to consider the distribution of the oxidation states of sulphur in differently disordered chalcopyrite samples from their measured peaks (see Fig. 2C); the ratio of S^{2-}/S^{6+} atomic concentrations decreased from 0.47 for the non-activated sample to 0.14 for the sample activated in air (Table 1).

The occurrence of S^{6+} forms in the surface layer of dry-ground samples was confirmed by measuring the extinction of the 1144 cm^{-1} band of SO_4^{2-} by IR spectroscopy. Figure 3 confirms the increasing extent of surface oxidation with the prolongation of grinding.

TABLE 1

Ratio of atomic concentration of elements in the surface layer of chalcopyrite (the layer thickness is ca. 5 nm)

Sample		Ratio of atomic concentrations		
Grinding time t_G (min)	Grinding environment	Fe/Cu	O/S	S^{2-}/S^{6+}
0	–	1.0	3.5	0.47
20	Air	1.8	4.1	0.14
20	Methanol	1.0	3.1	0.97

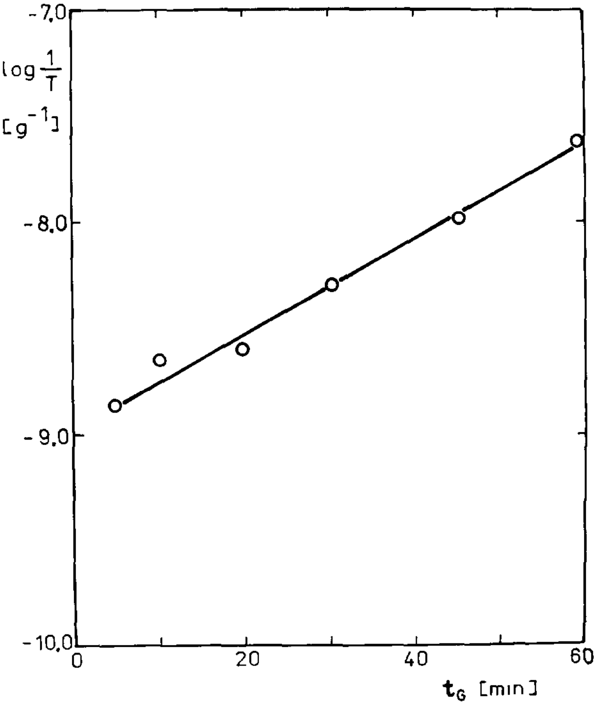

Fig. 3. Changes of the reciprocal value of transmittance T of the 1144 cm^{-1} band of SO_4^{2-} vs. grinding time t_G (dry grinding).

Remarkable changes take place also in the iron distribution. After 20 min of dry grinding the Fe/Cu ratio shows an almost two-fold increase in comparison with the as-received and methanol-ground samples.

On the basis of the results presented for XPS and IR analysis it is not possible to distinguish the form of the surface compounds of copper, iron, sulphur, and oxygen. However, it can be confirmed that the surface oxidation reaction on dry grinding was probably accompanied by formation of iron and copper sulphates and ferric oxides. Figure 4 presents complex information concerning the influence of grinding time and environment on the changes in the surface area, the degree of structural disorder, and the magnetic susceptibility.

The changes in specific surface area S_A and S_G (Figs. 4A and 4B) which result from dry grinding are more conspicuous than those which result from grinding in methanol. After 20 min of dry grinding the specific surface area, S_A, increases from an initial value of 0.35×10^3 m^2 kg^{-1} to a critical value of 4×10^3 m^2 kg^{-1}. At this value, a levelling-off of S_A and a decrease in S_G values indicate that intensive particle agglomeration has occurred. In the methanol grinding process the critical value of S_A is not reached in the observed time interval; apparently no significant agglomeration of particles takes place.

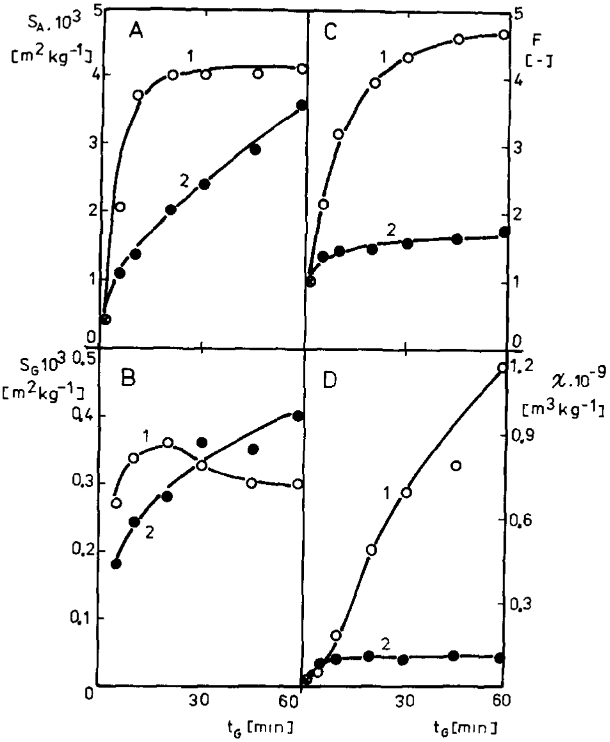

Fig. 4. Influence of grinding time t_G and environment on the specific surface area determined by the BET method, S_A (A), calculated from the dispersion analysis data, S_G (B), on the structural disorder F (C) and on the specific magnetic susceptibility χ (D). 1, Dry grinding; 2, grinding in methanol; ⊗, as-received sample.

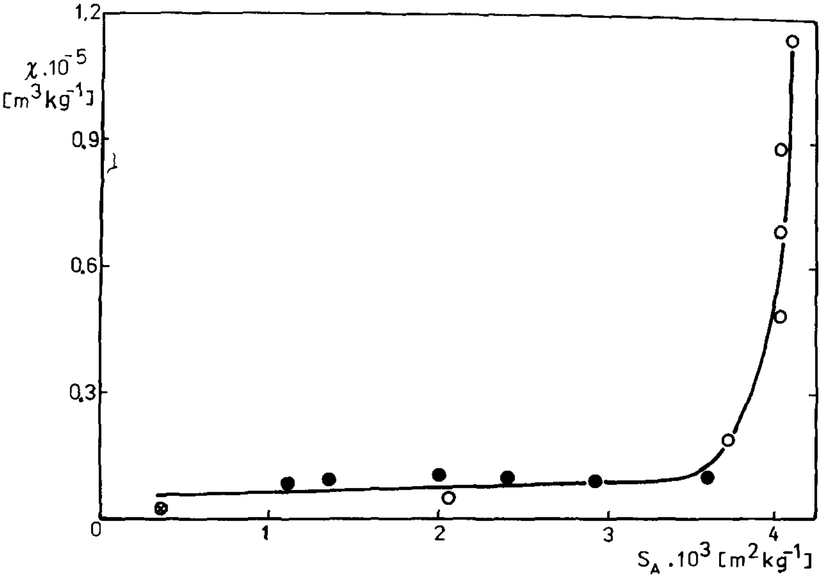

Fig. 5. Specific magnetic susceptibility vs. specific surface area values of chalcopyrite ground in methanol (●) and in air (○); ⊗, as-received sample.

The degree of structural disorder F (Fig. 4C), which gives integral information on the changes in lattice strain and in crystallite size, increases 3.7 times with the grinding time in air, but in methanol there is only a 0.8-fold increase.

The values of magnetic susceptibility, χ, are influenced by the grinding environment in the same way: the measured values of the specific magnetic susceptibility when grinding in methanol are negligibly small (Fig. 4D), whereas during dry grinding a 12-fold increase in χ occurs.

Low-temperature α-chalcopyrite has antiferromagnetic properties, i.e. it has a magnetically ordered structure. From the literature data [19] it is known that magnetic susceptibility of antiferromagnetic and ferromagnetic substances is independent of particle size.

The experimentally determined specific surface area dependence of the samples studied (Fig. 5) suggests that during grinding in methanol the

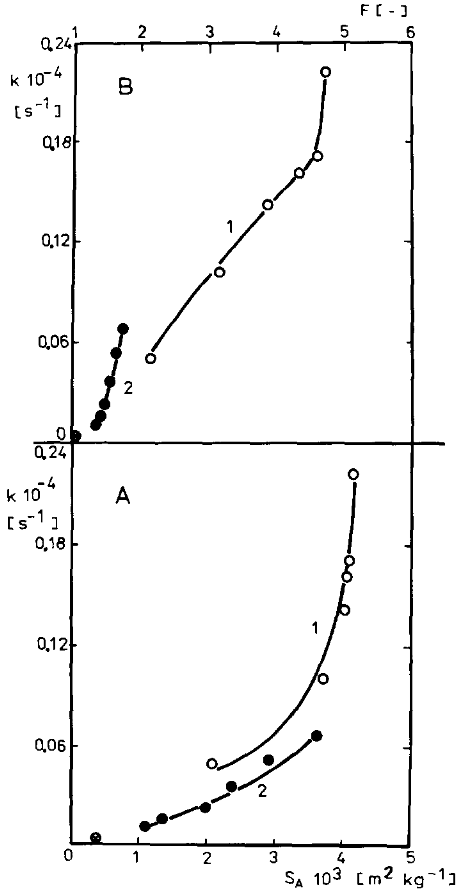

Fig. 6. Apparent rate constant k vs. specific surface area, S_A (A) and structural disorder F (B) for chalcopyrite samples ground in air (○) and in methanol (●); ⊗, as-received sample.

antiferromagnetic properties of chalcopyrite are unchanged. Increase in specific magnetic susceptibility of dry-ground samples in a narrow range of specific surface area may be explained partly by enrichment of the surface layer by paramagnetic Fe-oxide but mainly by the magnetic order–disorder transformation of chalcopyrite described in earlier papers [5,6].

Thermal decomposition of mechanically activated chalcopyrite

Figure 6 shows the changes in the apparent rate constant of the non-oxidative thermal decomposition reaction of chalcopyrite with the changes in S_A and F during grinding.

It is evident that the rate of thermal decomposition reaction changes with both of these variables. The determining influence of S_A and F may be expressed by an empirical "surface-structural" coefficient in the form of the product $S_A \times F$ by means of the following relationship (see Fig. 7):

$$k = a + bS_AF \tag{6}$$

For the samples investigated $a = 2.57 \times 10^{-3}$ and $b = 9.04 \times 10^{-3}$, and the correlation coefficient value $r_v = 0.9955$.

Thermal decomposition of chalcopyrite is a heterogeneous reaction the rate of which increases with the reaction surface. The mechanochemical effect caused by a structural and/or compositional metastability should therefore by observed as an excess reactivity over the ordinary effect of the reaction; the rate increase is caused by the increase in specific surface area caused by the particles' communication [20,21]. The excess specific reactivity

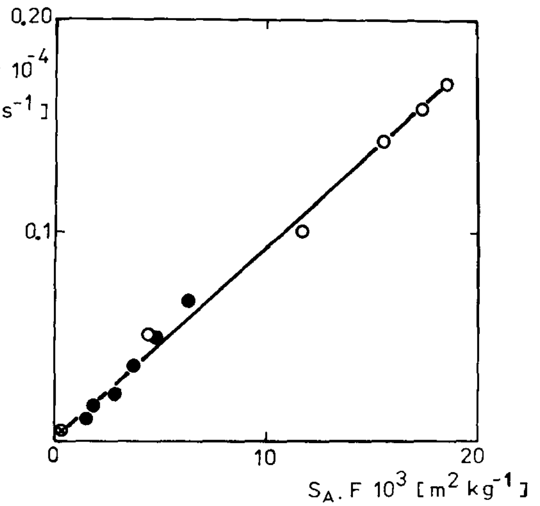

Fig. 7. Apparent rate constant k vs. "surface-structural" coefficient S_AF for chalcopyrite samples ground in air (○) and in methanol (●); ⊗, as-received sample.

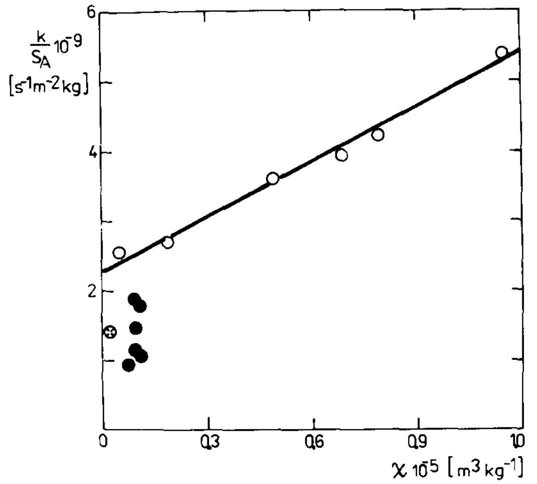

Fig. 8. Excess reactivity k/S_A vs. magnetic susceptibility χ: ⊗, as-received sample; ○, dry-ground samples; ●, methanol-ground samples.

for such cases may be expressed as the ratio of the apparent rate constant to the specific area of the activated powder, k/S_A.

In dry-ground powders a linear increase in the excess reactivity with increasing specific magnetic susceptibility was found (see Fig. 8). The values of k/S_A determined for powder ground in methanol oscillate, however, around that measured for the as-received sample.

The results obtained are in good agreement with the literature data [5,6]. Plastic strain leading to crystallographic shear in the sulphur sublattice and to a change in cation distribution between octa- and tetra- positions may therefore be considered as the source of the excess changes both in magnetic properties and in reactivity of mechanically activated chalcopyrite.

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