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Electron Diffraction Study of Monolayers Adsorbed on Single Crystal Surfaces

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Some monolayers adsorbed on galena cleavage faces are investigated by the reflexion method of electron diffraction. The characteristic manners of monolayer adsorption previously revealed are reviewed. More complex adsorption manners are found from a cleavage face of galena. They are discussed in connection with those previously revealed. It is remarkable that in all these manners of monolayer adsorptions individsual molecules are adsorbed on one kind of the constituent atoms of the substrate.

In the course of the study of surface reactions involved in the technical process of 'flotation', diffraction patterns consisting of streaks normal to the substrate surface were observed by the reflexion method[1),2)]. This kind of patterns is considered as due to monomolecular adsorbed layers, every molecule being adsorbed on one kind of the constituent atoms of the substrate[1,2)].

The surface reactions investigated were those between sulphydric collectors (xanthate and dithiophosphate) and cleavage faces of galena (PbS; NaCl-type; cleavage, (001); Fig. 1). Since both the collector molecules have similar sulpher-bearing polar groups, they are most likely adsorbed on lead atoms of the substrate. Such a strong interatomic interaction between adsorbent and adsorbate was also studied by Mathieson[3)] in his investigation of monolayer of stearic acid on a single-crystalline silver surface.

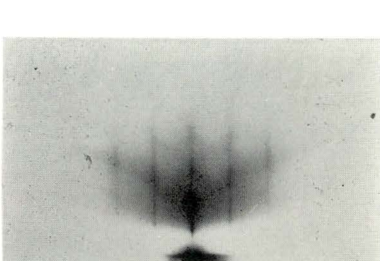


Fig. 1. Diffraction pattern from a cleavage face of galena. Beam along <100>.

Although a kind of streak pattern due to orientated monolayer was obtained also by Newman[4)], the interaction between deposited atoms and atoms of the substrate was not so

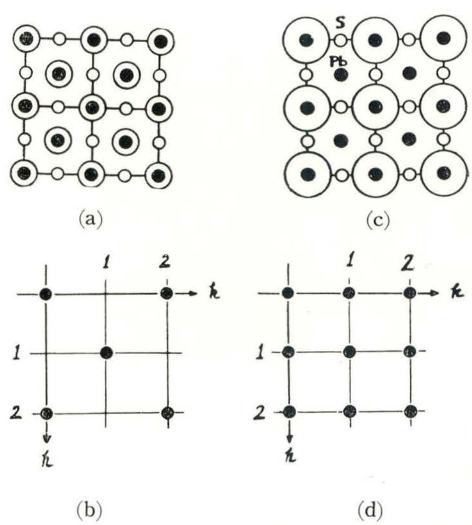


Fig. 2. (a) Arrangement of xanthate molecules in monolayer on galena cleavage face. Full circles represent lead atoms of the substrate, small open circles sulpher atoms, and large open circles adsorbate molecules. (b) Two-dimensional reciprocal lattice due to the monolayer adsorbed in the manner of (a). Indices refer to the unit cell of galena. (c) Arrangement of dithiophosphate molecules in monolayer on galena cleavage face. Regarding circles, see the legend (a). (d) Two-dimensional reciprocal reciprocal lattice due to the monolager adsorbed in the manner of (c).

strong in his case; no evidence of pseudomorphism was given, in contrast with the cases of the present authors[1,2] and Mathieson[3].

The xanthate molecules in monolayer are arranged as in Fig. 2 (a); every lead atom on galena cleavage face is occupied by a xanthate molecule, two dimensional arrangement of the adsorbate being just the same as that of adsorbent. The two dimensional reciprocal lattice is illustrated in Fig. 2 (b). Diffuse diffraction streaks due to adsorbed monolayer of xanthate fell on just the Kirchner-Raether lines of a galena cleavage face at any azimuthal setting of the substrate galena to incident beams. The diethyl-dithiophosphate molecules adsorbed are arranged as in Fig. 2 (c). It is remarkable that in this case the adsorbed molecules do not occupy every possible position, an occupied lead atom being surrounded by four occupied next-nearest neighbours. This is consistent with the fact that the cross section of dithiophosphate molecules is about twice as large as that of xanthate molecules. The reciprocal lattice is illustrated in Fig. 2 (d). A typical diffraction pattern due to monolayer of diethyl-dithiophosphate molecules is reproduced in Fig. 3. Diffuse superlattice streaks appear with a spacing just one half of that of Kirchner-Raether lines of the cleavage pattern of galena in the azimuth [100], being consistent with Fig. 2 (c).

It was to be noted that for an adsorbed patch as shown in Fig. 2 (c) anti-phas patches should be present in its environment as schematically shown in Fig. 4. Therefore, when small patches in anti-phase relation grow independently without phase relation, the reciprocal lattice of Fig. 2 (d) approaches to that of Fig. 2 (b). This situation was realized in an experiment using relatively high concentration of dithiophosphate[2]; in this case the patches will be small in size and large in number, since the adsorption is expected to start independently from a large number of lead atoms.

Very rarely (one instance out of obout one hundred specimens) another type of superlattice streak pattern, which cannot be accounted for by the adsorption manner of Fig. 2 (c), has been obtained (Fig. 5, (a) in the [100] azimuth and (b) in the [110] azimuth). The superlattice streaks persisted after soaking

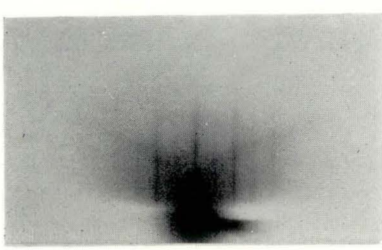


Fig. 3. Diffraction pattern from a galena cleavage face treated with diethyldithiophosphate solution. Beam along ⟨100⟩.

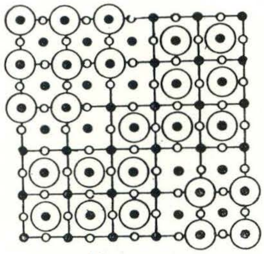
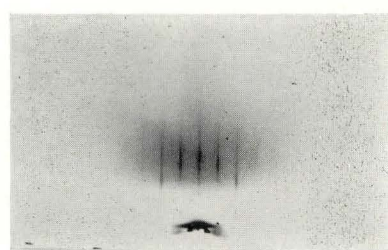
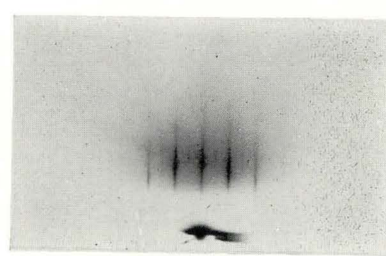


Fig. 4. Intermixing of small patches of two possible phases (A and B), both being in the manner of Fig. 2 (c).



(a)



(b)

Fig. 5. Diffraction pattern from a galena cleavage face, on which an unknown substance has been adsorbed before cleaving. Beam along ⟨100⟩ in (a), and along ⟨110⟩ in (b).

the specimen in either ether or acetone, but disappeared after soaking it in distilled water. (The diffuse streak patterns obtained with xanthate or dithiophosphate solution did not change by soaking the specimens in distilled water). The face seems to have adsorbed some unknown substance before cleaving. The streaks in Fig. 5 are extremely sharper than those in Fig. 3, implying that adsorbed patches responsible for the streaks are quite large in size.

The patterns can be accounted for in outline by the adsorption manner as shown in Fig. 6 (a). The remarkable aspect of the manner is that an occupied lead atom is surrounded by four occupied third-nearest neighbours. However, positions of weak streaks in the first Laue zone of Fig. 5 (a) and those of streaks appeared in the [310] azimuth suggest the presence of an adsorption manner of Fig. 6 (b). In it an occupied lead atom is

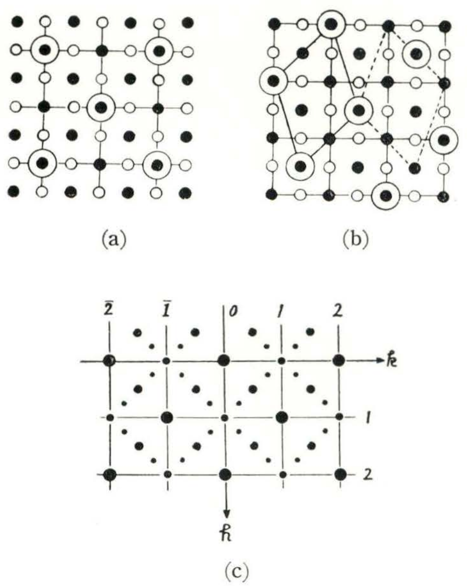


Fig. 6. (a) Arrangement of scattering centres in monolayer on galena cleavage face, which accounts for the diffraction patterns of Fig. 5. (b) Arrangement of scattering centres in monolayer on galena cleavage face, which is postulated to accunt for the diffraction patterns thoroughly. Wide solid and dashed lines represent two equivalently possible unit cells of the adsorbed substance. (c) Resulting two-dimensional reciproal lattice derived from simple coexistence of adsorption menners of (a) and (b). Areas of circles approximately represent relative intensities.

surrounded by two occupied third-nearest neighbours and four occupied fourth-nearest ones. Since the third-nearest distance is nearly equal to the fourth-nearest one (the ratio of distances in 2 to $\sqrt{5}$), the occurrence of the manner of Fig. 6 (b) is quite reasonable. It is to be noted that the densities of adsorbed molecules in the adsorption manners of Fig. 2 (a), Fig. 2 (c), Fig. 6 (a) and Fig. 6 (b) are, 1, 1/2, 1/4 and 1/4, respectively (taking that in Fig. 2 (a) as the unit). If patches of last two manners are present in eqal amount, and the sizes of each patches are quite large, the resulting reciprocal lattice can be derived as in Fig. 6 (c). It is seen there that several indices become fractional (quarter or quarters) with respect to the unit cell of the substrate, in contrast to the cases of Fig. 2. The presence of these fractional indices were also supported by experiments using incident beams along ⟨210⟩ and ⟨510⟩. Some faint streaks in the first Laue zone (Fig. 5 (a)), which are not givenin Fig. 6 (c), can be accounted for by assuming double diffractions between strong streaks in the zeroth and streaks in the first Laue zone, all of which assume the arrangement of Fig. 6 (c). Although streak intensities (Fig. 5) are somewhat inconsistent with the adsorption manner proposed above, the discrepancy is well understood, if weak phase interaction among patches, whose adsorption manners are shown in Fig. 6 (a) or Fig. 6 (b), are taken into account.

Thus, the present study has experimentally confirmed that in some cases monolayer adsorption is influenced so strong by an interaction between adsorbent and adsorbate that individsual adsorbate molecules are attracted to substrate atoms, resulting in particular manners of arrangement of adsorbate molecules, which have simple relations to the arrangement of substrate atoms.

The authors thank to Dr. R. Sato, Mitsubishi Metal Mining and Metallurgical Laboratory, for his useful discussion.

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DISCUSSION

L. D. BROCKWAY: Several years ago we were also interested in the adsorption of xanthates on galena and sphalerite and looked especially at the sphalerite, which was polycrystalline in our specimen. Being aware of the preferential adsorption of xanthate on galena until after the sphalerite has been tested with a dilute solution of copper sulphate, we examined the sphalerite after treatment with the xanthate. The copper solution caused an isomorphous replacement of some zinc atoms with copper atoms, after which there was a chemical reaction with the xanthate resulting in an unoriented layer of cuprous xanthate. The same product appears on the surface of the mineral form cupric sulphide when it is treated with xanthate.

H. UCHIKOSHI: Electron diffraction investigations of surface reactions taking place on copper-treated sphalerite cleavage faces (single crystalline) were carried out some years ago by Dr. R. Sato, Mitsubishi Metal Mining and Metallurgical Laboratory. His results are in accordance with what Prof. Brockway stated.

In order to reveal such an adsorbed monolayer as I mentioned, it is neccessary to use a single crystal surface as flat as possible like cleavage faces used by us, or reformed surfaces of silver studied by Dr. Newman or Dr. Mathieson. The copper-treated sphalerite cleavage face does not seem to meet this purpose, as Dr. Sato already pointed out. We have emphasized that the combination of sulphydric collectors and galena cleavage is suitable for such kind of observation.

A. GOSWAMI: We have observed extra spots (super-lattice) when the beam was along $\langle 100 \rangle$ of the etched galena crystal. Have you observed anything like it?

H. UCHIKOSHI: No, we have never observed superlattice spots from etched cleavage surface of galena. Superlattice streaks, which we found from a fresh cleavage face, also disappeared after the specimen was soaked in distilled water.