Electron Spin Resonance of Water Adsorption on Amorphous Molybdenum Sulfide

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The interaction between molybdenum trisulfide and water vapor has been studied by ESR. The trisulfide was obtained from the thermal decomposition of $(NH_4)_2MoS_4$. The observed spectra are characteristic of two distinct paramagnetic species. The first one corresponds clearly to sulfur chain radicals; the second is due to Mo^{5+} sites. The behavior of the Mo^{5+} signal amplitude is complex and depends on the water-vapor pressure in MoS_3 sample and the temperature. The ESR signal of Mo^{3+} disappears under the action of water-vapor pressure when condensation is possible. Gases like O_2 , N_2 , and CO_2 do not act upon this material at room temperature. An explanatory mechanism proposed involves adsorption with decomposition of water and disappearance of the Mo^{5+} ions, leading to Mo^{6+} and H^+ ions with the transfer of one electron.

Introduction

Many studies have been done on amorphous chalcogenides¹⁻⁴ in order to understand the elementary mechanisms involved in their transport properties and the nature of the sites which are involved.

Among these compounds, the amorphous molybdenum sulfides MoS_{2+x} have a wide industrial interest because they influence many hydrogenation and hydrodesulfurization catalytic processes.^{5,6} More recently, MoS₃ has been utilized as a cathode in the making of batteries, reacting reversibly with lithium.⁷

Therefore, it seems interesting to study more closely the physical properties of these sulfides by using new hypotheses^{2,3,8} in order to explain the behavior of amorphous chalcogenides.

In this manner, the study by means of electron spin resonance (ESR) has shown the presence of various types of paramagnetic centers in these compounds. A few of them have already been identified: some seem to be sulfur chains,^{4,9} and our work bears out this result, the other could be Mo^{5+} ions.^{3,4,10}

Previously, we studied the conductivity of molybdenum sulfides and showed that, in compounds such as MoS_{2+x} (0 < x < 1), the transport of current is due to discontinuous hops of electrons between localized states.¹¹ These localized sites are divided into two distinct classes. Then we tried to establish a relationship between the centers shown by ESR and the centers responsible for the conductivity. In addition, we noted that this last property was strongly influenced by water-vapor adsorption on these compounds regardless of the value of x.

The first stage of this present work consists of looking at the possible modifications in the ESR spectra of the molybdenum sulfides when they adsorb water vapor.

For this study we chose amorphous compounds, MoS_{2+x} , which are similar in composition to MoS_3 .

The Amorphous Molybdenum Sulfides

Preparation. The preparation of molybdenum sulfide has been widely studied.¹²⁻¹⁵ It is produced in the thermal decomposition

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of ammonium thiomolybdate $((NH_4)_2MoS_4)$ in an inert atmosphere. This starting material is commercially available or can be synthesized by using the method of Corleiss¹⁶ described by Bernard and Tridot.¹⁷ The molybdenum trisulfide thermally decomposes according to the following reaction:

$$(NH_4)_2MoS_4 \rightarrow MoS_3 + 2NH_3 + H_2S_3$$

The temperature is significant and allows one to obtain, depending on the case, compounds such as MoS_{2+x} . Thus, a thermal treatment at 195 °C maintained for 48 h under nitrogen gives, with both the synthetic and commercial ammonium thiomolybdate. a powdery sulfide whose composition is close to MoS₃.

The sulfides produced from the synthetic and commercial ammonium thiomolybdates will be represented as T and K, respectively.

It is probable that commercial thiomolybdate is less pure than that prepared in our laboratory; thus, it can lead to amorphous sulfides containing small quantities of oxides. However, the study of the product obtained from the commercial compound is justified by its potential industrial applications. The composition of the two sulfides (T and K) is MoS_3 given the errors of analysis.

ESR Spectra of MoS₃. The measurements have been performed using a conventional spectrometer operating at the X band. A Bruker dual-sample cavity allows the use of an inner standard for the determination of the g values (g = 2.0036 of pure DPPH, exempt from solvent). The ESR spectra were recorded in the temperature range 77-300 K, which was set by means of a Varian variable-temperature controller.

The ESR spectra of T (Figure 1a) and K (Figure 1b) molybdenum trisulfide were taken upon immediate exposure to the air. We can see that in both cases the spectrum results from the contribution of at least two distinct signals indicated by A and **B.** In all spectra shown in Figure 1, two components B_1 and B_2 appear for signal B. The nature of the chemical species responsible for these signals will be stated later on. The g values characterizing the components of signals A and B are shown in the figures.

These spectra correspond to compounds which are subjected to the action of the atmosphere. The degassing of the samples only allowed us to establish the interaction between the product and one of the air components. The samples were degassed by treatment at 180 °C under a vacuum of 4×10^{-5} torr, during 24 h. The ESR spectra of the products thus treated are represented in Figure 1 ((c) MoS₃, T; (d) MoS₃, K). The times of treatment were judged to be sufficient when the spectra remained unchanged

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Figure 1. ESR spectra of MoS_3 : (a) T, in the air; (b) K, in the air; (c) T, degassed under vacuum at 180 °C; (d) K, degassed under vacuum at 180 °C.



Figure 2. ESR spectra: (a) amorphous sulfur irradiated at 77 K; (b) MoS_3 , T degased at 180 °C.

after any further treatment at the same temperature. We found that the intensity of the spectrum related to signal A is strictly unchanged. This was the case for all treatments.

Sample T shows signals A and B which are resolved more easily. A very distinct doublet (g = 2.045 and 2.034) appears in signal A, and its spectral characteristics allow us to assign this axial signal, without ambiguity, to sulfur chains. In fact, the irradiation of amorphous sulfur at 77 K in a field of wavelengths corresponding to the maximum of optic absorption creates a distinctive resonance signal^{4,18} that we easily found (Figure 2, spectrum a). The values of tensor **g** components are identical with those observed elsewhere and are very close to those we have observed in the case of trisulfide T and K. The latter, the signal of which is more distinct, has been selected to make the comparison (Figure 2, spectrum b).

Sample K presents, after treatment, a significantly altered signal **B** which is likely due to reasons indicated under preparation.

As a matter of fact, we have verified that the different behavior of samples T and K cannot be ascribed to small variations of composition. The signal is composed, as mentioned above, of two

Figure 3. Amplitude variation of the ESR signal B of MoS₃, K as a function of time $(P < P_0)$: (1) P = 3 torr, $P_0 = 20$ torr; (2) P = 9 torr, $P_0 = 20$ torr; (3) P = 12.7 torr, $P_0 = 20$ torr; (4) P = 16 torr, $P_0 = 20$ torr; (5) P = 17.5 torr, $P_0 = 20$ torr; (6) P = 20 torr, $P_0 = 92.5$ torr.

parts, B_1 and B_2 . Only the fraction B_2 is significantly modified (Figure 1d, g = 1.9406 and 1.8900). Therefore, we found it interesting to choose sample K, the line modification of which can be easily analyzed, for the study of the solid-gas interaction (signal B_2). It should be noted that the measurements at 77 K do not provide any perceptible modification in the various spectra observed; no additional lines are detected at low temperature.

It is well established that gaseous oxygen often has a great influence on free radicals created in the substance. Its action is also very distinct on paramagnetic centers diluted in an inert matrix. Therefore, we made certain that only the water vapor was responsible for the observed phenomenon, e.g. the appearance, disappearance, and enhancement of the component. For this reason, after degassing as described, the product was brought together with N₂, CO₂, and O₂ without any modification in the B component. The results related to N₂ and CO₂ were expected, but it is nevertheless surprising that oxygen is totally inert regardless of the pressure and time of contact.

Thus, the water vapor seemed to play an essential part in the bearing of the spectra (as well as in the properties of electrical transport).

Action of Water Vapor on Molybdenum Trisulfide

We carried out the contact of MoS_3 and water vapor after the samples were degassed at a pressure of 4×10^{-5} torr. The desired vapor pressure was achieved by stabilizing the temperature of a small tank connected to the sample assembly containing carefully degassed water.

In all that follows, P_0 will be the saturated vapor pressure above the sample (defined by the temperature of the solid) and P will be the saturated water pressure generated by the temperature of the water tank.

 $P < P_0$. The temperature of the water was lower than the temperature of the sample for these studies. We studied as a function of time, t, the amplitude variation of signal B after a solid-water vapor contact was made: by defining I_0 as the amplitude of the signal for the gas-free product and I as the amplitude of this component at a contact time t, we were able to draw the diagram $(I - I_0/I_0 = f(t)$ (Figure 3). In all cases, the amplitude of signal B increases during the first minutes of contact before

Figure 4. amplitude variation of the ESR signal B of MoS₃, K as a function of time $(P = P_0)$: (1) $P = P_0 = 16.5$ torr; (2) $P = P_0 = 68$ torr.

Figure 5. ESR spectrum of MoS₃, K after a contact of with water vapor $(P = P_0)$.

becoming steady after 3 or 4 h. In addition, for a given pressure P_0 , $\Delta I/I_0$ is much higher than P is low (curves 1-5 of Figure 3). When the water-vapor pressure is nearly the same as the pressure corresponding to the saturated water pressure above the sample, the phenomenon strongly decreases; that is, signal B remains practically unchanged.

We then proceeded with the experiment by strictly keeping the sample and the water source at the same temperature.

 $P = P_0$. In this case the sample and the water reservoir are maintained at the same temperature. The results obtained under these conditions are shown in Figure 4. It is noteworthy that at the beginning of the MoS₃-Water vapor contact the amplitude of the signal increases, reaches a maximum, and then quickly decreases between 1 and 3 h, after which the decrease is more gradual. This maximum coincides with a distinct appearance of a doublet (g = 1.9187 and 1.9000; Figure 5).

In completion of the study of the influence of water vapor on MoS_3 , we have set the sample at a temperature which is lower than the temperature of the water source.

 $P > P_0$. Figure 6 shows the result of such an attempt. We note a rapid and simple reduction of signal B. As in the case where $P < P_0$, we were never able to observe the doublet mentioned in section 3.2.

Discussion

It is clear that the results allow us to assign the evolution of component B_2 for the ESR signal of MoS_3 exclusively to the adsorption of water vapor. The observed phenomenon is reversible.

Figure 6. Amplitude variation of the ESR signal B of MoS₃, K as a function of time $(P > P_0)$: P = 75.5 torr; $P_0 = 16.5$ torr.

We have found that there are two fields of pressure where the action of water vapor is different. When $P_0 > P$, there is no condensing phenomenon of the water vapor and signal B is either unchanged or slightly enhanced. On the other hand, in the cases where $P = P_0$ and $P > P_0$, condensation may occur and signal B₂ falls to zero.

As far as we know, the effect of the water vapor on degassed products is unusual. It is carried out according to a kinetic process which always causes, in conditions when $P > P_0$, signal B₂ to vanish.

Interpretation and Identification of Paramagnetic Centers. Signal A is not sensitive to any contact with a gaseous phase at 298 K as we have already mentioned. We made it clear that it is probably due to chains of sulfur atoms long enough to exclude any interaction between the centers as has already been suggested.⁴ This fact is corroborated by the striking similarity of the spectrum with that of the irradiated amorphous chains (Figure 2), the main values of the g factor matching perfectly.¹⁸

We attempted to modify the amplitude of signal A by irradiating the sulfide in the field 600-800 nm (lamp or laser beam), the conditions being the same as those that have been used in the case of amorphous sulfur. No modification has been observed. We conclude that the number of the centers created by irradiation would be too small because the sulfur chains responsible for the resonance signal would not be exclusively distributed on the surface by a simple adsorption phenomenon. This result seems to confirm the lack of action linked to the washing of the products by CCl_4 and CS_2 . It seems necessary to reject the hypothesis of an adsorbed species which would not be integrated to the structure.

Former work has ascribed signal B_1 to the paramagnetism of Mo^{5+} ions attributable to a MoS^{3+} species.⁴ The signal does not change noticeably with the adsorption of water vapor in the compounds which are being studied.

The characteristics of signal B_2 , position in the spectrum¹⁹ and line width, show that it can be assigned to the oxygenated Mo species corresponding to the oxidation number V.

Contrary to the work on oxides or some sulfides prepared on supports, 2^{0-22} only a few authors have mentioned the existence of sites of this nature in crystallized or amorphous unsupported sulfides.^{4,10} Besides, some results in this field show sites MoO³⁺ in compounds containing MoO₃ and in sulfides closely related to the composition MoS₃ but prepared in a slightly different way

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than ours (precipitation method).^{4,22,25-27} The signal of axial symmetry that we detected is totally indifferent to oxygen pressure at room temperature. We also think that the observed signal B_2 , the parameters of which are in agreement with those mentioned in the previous works, is due to the MoO³⁺ species. The sensitivity to saturated water vapor has already been indicated^{20,23} without any disappearance of the signal in supported bismuth molybdates. The authors have suggested the existence of superficial sites, the signal being restored after being put under vacuum. The action must be complex, and most likely, the kinetic phenomena must not be neglected. For example, the appearance of the doublet when $P = P_0$ at the very beginning of the impregnation might indicate a preferential process of physisorption. In such a case the water molecules would reduce the dipolar interaction between the paramagnetic centers; the structure would consequently be better resolved. The doublet disappears after a contact of approximately 1 h.

The action of water vapor is, in the limits of this work, shown after degassing at a higher temperature. It only shows one pattern of site Mo^{5+} , the doublet, which does not appear to be the manifestation of an additional signal related to another species. Furthermore, the water vapor has a much more complex action.

A likely action diagram could be represented by the following electrochemical process:28

 $Mo^{V}O^{3+} + 2H_2O \rightleftharpoons Mo^{VI}O_3 + 4H^+ + e^{-1}$

It assumes a decomposing adsorption of the water. As the ion Mo^{6+} is not paramagnetic, no signal should then be detected, as we can verify. The fact that degassing restores the signal means that the process is reversible. This equilibrium should be strongly shifted in direction 1 (and thus favor the formation of H⁺ ions)

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when water condensation occurs $(P \ge P_0)$, allowing the H⁺ ions to migrate. This hypothesis is confirmed by electrical conductivity measurements as a function of frequency $\sigma(\omega)$ on a series of MoS_{2+x} sulfides. The conductivity is an increasing function of water pressure.²⁴ Before any contact with water, the experimental values are correctly fitted by the equation $\sigma(\omega) = A\omega^s$, where A and s are parameters characteristic of the compounds studied. This type of law has already been emphasized in the study of other chalcogenides.^{29,30} It confirms, according to a generally accepted interpretation, the existence of charge-carrier hops between localized sites. The elementary mechanism seems to be related to the hop of one electron over a potential barrier to move from a localized site to another. Indeed, one can observe for the dc conductivity of these materials a law of the form $\sigma_{dc} \sim \exp(T^{-1/4})$, specific of such a transfer. Under the conditions in which $P \ge$ P_0 , σ_{dc} increases strongly (about a factor of 25). Simultaneously, there is an important modification of the experimental curves σ = $f(\omega)$ revealing a maximum in dielectric losses, $\omega \epsilon'' = \sigma(\omega)$, located at 2.2 \times 10⁴ Hz. This behavior is generally ascribed to the existence of an ionic conduction. The relaxation time of the ionic carriers would be approximately 7×10^{-6} s at 350 K. This result seems to be in accordance with the hypothesis of a creation of H⁺ ions in the medium under the action of the water.

The research of elementary mechanisms occurring in the transport phenomena caused us to propose such a mechanism which, in the limits of a hopping conduction between localized states, is perfectly explanatory and shows the self-consistency of both physical methods of observation. These experiments are currently under study and should provide explanations on the catalytic properties of these compounds.

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