

Magnetic Susceptibility and Electron Spin Resonance as Probes of Different Magnetic Species in MoS₃

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Magnetic susceptibility and electron spin resonance (ESR) measurements at 10 GHz are reported for amorphous MoS₃ between 5 K and 300 K. The densities of paramagnetic centers inferred from the two types of measurements differ by an order of magnitude (~1 and 0.1 mol%, respectively), demonstrating that the ESR measurements probe a subset of the magnetic species detected by the susceptibility measurements. The magnitudes of the susceptibility and ESR parameters place severe constraints on the possible origins of this phenomenon. These results are discussed in relation to previous work on similar materials, and the implications with regard to the detection and characterization of magnetic defects in other transition metal sulfides are pointed out.

INTRODUCTION

The compound MoS₃ is a member of a small class of transition metal sulfides which have only been prepared in an amorphous state. A combination of vibrational spectroscopy measurements and X-ray related observations (extended X-ray absorption fine structure, X-ray photoelectron spectroscopy, and radial distribution function analysis) have recently shown that MoS₃ has a short-range structure containing Mo-centered trigonal sulfur prisms which share triangular faces to form chains (1-3), similar to crystalline trichalcogenides. The Mo atoms dimerize along the chains, and both sulfide and disulfide (S₂)²⁻ species are present in the ratio 4 to 1. These structural features suggest the formal chemical formula (Mo⁵⁺)₂S₄²⁻(S₂)²⁻ for MoS₃, in which the remaining valence electron on each Mo⁵⁺ cation participates in forming spin-paired Mo-Mo dimers (1, 2).

The noncrystalline long-range structure of MoS₃ suggests that this compound may contain an appreciable concentration of

electronic surface states, defects and/or dangling bonds which may also carry local magnetic moments. Electron spin resonance (ESR) measurements have been used to the virtual exclusion of magnetic susceptibility measurements to examine low-density magnetic species in MoS₃ (4-6) and in other amorphous or poorly crystalline transition metal sulfides (6-13). In this report, we present the results of absolute ESR spin density measurements as well as high precision magnetic susceptibility measurements on carefully prepared samples of MoS₃. We find that X-band ESR detects a relatively small fraction of the total number of magnetic moments in these samples, a phenomenon also observed previously for reduced molybdenum oxides (14, 15). This result has important implications with regard to understanding the nature and density of the active sites on transition metal sulfide hydrotreating catalysts, since correlations between magnetic defect densities and catalytic rates have previously relied almost exclusively on ESR to determine the magnetic defect densities.

METHODS

Sample preparation. Magnetic susceptibility and ESR data were obtained on four different samples of MoS₃. Samples A, B, and C were synthesized by thermal decomposition of crystalline (NH₄)₂MoS₄. This precursor was prepared using the method of Ref. (2). Either ammonium paramolybdate (NH₄)₆Mo₇O₂₄ · 4H₂O or MoO₃ was dissolved in aqueous ammonia and red crystals of (NH₄)₂MoS₄ formed upon passing H₂S through the solution. The crystals were removed by vacuum filtration, washed and dried, and the product stored in a He-filled dry box until use. MoS₃ was then obtained by thermal decomposition in a He stream for four hours at 275°C; the MoS₃ was subsequently handled and stored under dry He atmosphere. The sulfur contents were determined from the weight losses upon decomposition of the (NH₄)₂MoS₄ precursors and by elemental analyses, yielding nearly stoichiometric compositions MoS_{3.02-3.03} in each case. In order to investigate the influence of the purity of the starting materials on the magnetic properties of the final MoS₃ products, three different sources of the Mo were used: reagent grade ammonium paramolybdate with 0.02% cation impurities (MoS₃(A)); reagent grade MoO₃ with 50 ppm cation impurities which was sublimed in O₂ at 750°C before use, yielding large MoO₃ crystals (MoS₃(B)); and Johnson–Matthey “Puratronic” ammonium paramolybdate where the only impurity cation detected was Mg at less than 1 ppm (MoS₃(C)). Finally, a fourth MoS₃ sample (MoS₃(D)) was prepared by chemical decomposition of (NH₄)₂MoS₄ according to Ref. (16). This sample was exposed to air following the synthesis, then stored in a He dry box. The MoS₃ samples B and D were subjected to trace cation analysis by semiquantitative optical emission spectroscopy (17).

Magnetization measurements. Static magnetization data were obtained using a modified commercial Faraday magnetome-

ter (18) from about 10 K to 300 K for each of the four MoS₃ samples. The sample capsule consisted of two opposing concentric delrin cups which could be press-fitted together; the MoS₃ samples were loaded into the capsule in a dry box under He gas. Data were also obtained for the (NH₄)₂MoS₄ precursor to MoS₃(B). Magnetization (M) versus applied magnetic field (H) isotherms were taken to correct the observed magnetization data for the contribution of ferromagnetic impurities. High precision susceptibility data were obtained in a fixed H of 6.35 kG upon sweeping the temperature at less than 1 K/min.

ESR measurements. The ESR data were collected using a Varian E-Line Century Series spectrometer operating at 9.5 GHz. The data were accumulated and analyzed with a Nicolet 1180 Instrument Computer. Variable temperatures from 5 K to 300 K were provided as necessary with flowing gas systems. ESR spin densities (n_{ESR}) were derived from double integration of the derivative of the ESR absorption after baseline subtraction. The absolute values were calibrated against a Varian Weak Pitch Standard (2.25×10^{13} spins). The linearity of the calibration over the magnetic field scan and spin density ranges of interest here was verified using aqueous MnSO₄ solutions. Similar sample tube geometry and placement in the cavity is used throughout. The accuracy of the n_{ESR} values derived in this manner is estimated to be 10–15%.

RESULTS

Magnetization Measurements

The saturation moments (M_0) of the ferromagnetic impurities as found from the M(H) isotherms were nearly temperature independent and are listed in Table 1. The values observed for MoS₃ samples B, C, and D correspond to the saturation moment of only 2–4 molar ppm of iron metal impurities, whereas that of sample A was an order of magnitude larger.

TABLE I

Magnetic Susceptibility (χ) and Electron Spin Resonance (ESR) Parameters for Four MoS₃ Samples and One (NH₄)₂MoS₄ Precursor^a

Sample	M_0^b (10 ⁻² G - cm ³ /mol)	$\chi(RT)^c$ (10 ⁻⁶ cm ³ /mol)	χ_0^d (10 ⁻⁶ cm ³ /mol)	n_χ^e (mol% spins $\frac{1}{2}$)	n_{ESR}^e (mol% spins $\frac{1}{2}$)	$\langle g \rangle^f$	n_χ/n_{ESR}
MoS ₃ (A)	65(7)	-59	-78(2)	1.36(9)	0.17	2.0144	8
(NH ₄) ₂ MoS ₄	0.56(12)	-67.2	-67.5(8)	<0.009	0.0018	1.9809	—
MoS ₃ (B)	3.8	-37.6	-61(1)	1.87(11)	0.11	2.0139	17
MoS ₃ (C)	6.9	-42.0	-63(3)	1.63(19)	0.11	2.0177	15
MoS ₃ (D)	4.4(3)	-44.0	-61(1)	1.27(5)	—	—	—

^a The estimated accuracy in the least significant digit of a quantity is shown in parentheses.

^b Ferromagnetic impurity saturation magnetization.

^c Room temperature magnetic susceptibility.

^d Temperature independent contribution to the susceptibility.

^e Spin density derived from susceptibility (n_χ) and ESR (n_{ESR}) measurements.

^f Average g value of the ESR absorption.

The temperature dependent magnetic susceptibility (χ) of each of the four MoS₃ samples could be fitted well by the simple relation $\chi = \chi_0 + C/(T - \Theta)$, which is the sum of a temperature independent term (χ_0) and a Curie-Weiss term. The parameters χ_0 , C , and Θ were determined from least-squares fits to the data. An example of the quality of the fit obtained is shown in Fig. 1, in which the inverse molar susceptibility $(\chi - \chi_0)^{-1}$ is plotted versus temperature for sample D; the fit for sample B has been presented previously (2). In each case, the Weiss temperature Θ was found to be small and negative (~ -2 K, antiferromagnetic). From the values of the Curie constants $C = n_\chi g^2 S(S + 1) \mu_B^2 / 3k_B$, where k_B is Boltzmann's constant, the spin densities n_χ were derived assuming that the magnetic moments have spin $S = \frac{1}{2}$ with gyromagnetic factor $g = 2$, or $n_\chi = 100C/0.375$ in units of mol% spins $\frac{1}{2}$ if C is the molar Curie constant. The values of χ_0 and n_χ for each sample are shown in Table 1.

The MoS₃ samples B, C, and D exhibited χ_0 values which are identical to each other within experimental error, whereas that for MoS₃(A) is significantly more negative. The origin of the latter difference is not clear, although we note that MoS₃(A) also exhibited an order of magnitude larger M_0 value (cf. Table 1) and was synthesized using the

lowest purity starting materials. To facilitate comparison with χ data obtained by other workers, we have included our measured room temperature values in Table 1. These values are comparable with the values previously reported for MoS₃ (-48×10^{-6} (4, 19) and -50×10^{-6} cm³/mol (20)).

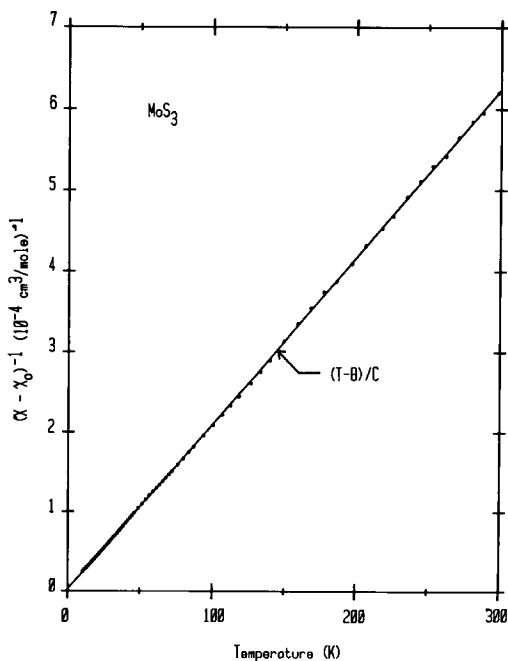


FIG. 1. Inverse magnetic susceptibility $(\chi - \chi_0)^{-1}$ versus temperature for MoS₃ sample D.

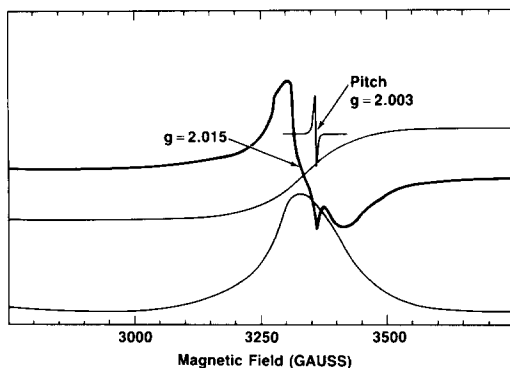


FIG. 2. ESR spectrum for MoS₃ sample B. From the right of the figure, the middle curve is the absorption derivative, the bottom curve the absorption, and the top curve the integral of the absorption.

The n_x values in Table 1 for the MoS₃ samples are comparable, ranging from 1.3 to 1.9 mol%. These values are at least 200 times larger than that of the nominally diamagnetic (NH₄)₂MoS₄ precursor to MoS₃(B). They are also at least an order of magnitude greater than can be accounted for by the concentrations (17) of potentially magnetic cation impurities. The n_x values must therefore arise from a paramagnetic Mo specie, from a Mo-anion complex, and/or from some kind of anion radical. The n_x values are small in comparison to the number of Mo atoms, but are similar to the maximum density of surface sites probed by oxygen chemisorption measurements on MoS_{2+x} materials (6, 21).

Electron Spin Resonance Observations

The (NH₄)₂MoS₄ precursor has no obvious signal other than a small feature near $g = 1.98$ which most probably results from a minor amount of surface decomposition. Intensity estimates are difficult to make because the signal is weak and poorly defined, but it is nearly two orders of magnitude smaller than for MoS₃, as shown in Table 1. In contrast, the ESR spectra taken at room temperature for the three batches of MoS₃ prepared by thermal decomposition of (NH₄)₂MoS₄ have a common shape, as

shown in Fig. 2, and comparable intensities (Table 1), but the g values are now near 2.01. As a precaution, these MoS₃ samples were sealed in quartz ESR tubes under vacuum after their preparation, with no exposure to air. Searches at magnetic fields from 0 to 20 kG and temperatures from 5 K to 300 K did not detect any other paramagnetic signals. Subsequent exposure to air did not change the shape of the ESR absorption or the magnetic susceptibility data, consistent with previous ESR observations (4, 5). However, n_{ESR} did decrease by about 30% for the one air-exposed sample examined here by ESR; it is not clear why this decrease was not observed by previous workers, and we do not yet understand the origin of the decrease.

The ESR absorption of MoS₃ in Fig. 2 is asymmetric, with an average g value of about 2.014. The sharp negative spike on the absorption derivative varies in intensity from sample to sample; its contribution to the total integrated intensity is insignificant. The average g value for the broader signal is similar to that observed for high surface area MoS₂; however, the zero crossing of the derivative curve occurs on the low field side of the absorption spectrum rather than on the high field side as in MoS₂, indicating an asymmetry parameter for MoS₃ opposite in sign to that for MoS₂ (6). Similar spectra have been previously reported in other ESR studies of molybdenum sulfides (4, 5). Perhaps the most important observation is that the spin densities n_{ESR} observed by X-band ESR lie between 0.11 and 0.17 mol% of the molybdenum, roughly an order of magnitude lower than detected by our susceptibility measurements on the same samples. There is no obvious correlation between the n_{ESR} and n_x values.

DISCUSSION

As noted above, the large disparity between the density of magnetic defects in MoS₃ as determined by magnetic susceptibility and ESR has also been observed in

reduced molybdenum oxides (14, 15). The source of the disparity is not clear. A preliminary M(H) isotherm at 1.4 K up to 66 kG obtained on MoS₃ using a Princeton Applied Research vibrating sample magnetometer could be fitted well by a Brillouin function modified to take into account a negative Weiss temperature and with $S = \frac{1}{2}$, $g = 2$, and $n_x = 1.3$ mol%, consistent with the assumptions used to derive the n_x values in Table 1, and with the n_x values themselves. Thus, the disparity does not appear to arise from these assumptions. As mentioned above, ESR searches for other absorptions at 9.5 GHz have not been successful. It appears that there are inequivalent magnetic species, at least one of which is not observable by ESR.

After considering various alternatives, we have formulated a model for the magnetic properties of MoS₃ which is consistent with the available magnetic data, as follows. We propose that the paramagnetic species in this compound are two groups of Mo⁵⁺ (d¹) defects. The first type of Mo⁵⁺ is isolated from the other Mo⁵⁺ cations and is observable by both ESR and susceptibility. The second occurs in magnetically coupled (Mo⁵⁺)₂ dimers forming a coupled two-electron system, and is observed only in the susceptibility. Anisotropy in the coupling of the two unpaired electrons within a dimer would lead to a zero-field splitting of the triplet ($S = 1$) magnetic energy levels which could be larger than the ESR microwave quantum and thus prevent ESR transitions from taking place or broaden the resonance so much as to render the resonance unobservable. This model can be tested by extending the susceptibility measurements to temperatures which are low compared to the energy of the 10 GHz microwave quantum (0.3 K).

In conclusion, ESR has been extensively used in the past to characterize the density and nature of magnetic defects on supported and unsupported transition metal sulfides. These measurements have been important in hydrotreating catalysis be-

cause the spin densities obtained by ESR on a number of such systems have been found to correlate with catalytic desulfurization (6, 13, 22) and hydrogenation (9) reaction rates. Our findings show that the magnetic species detected by ESR in one such compound constitute a minor fraction of the total number of magnetic sites actually present, a result which has also been found to occur elsewhere in the MoS_{2+x} system (22). It is clearly important in this context to extend coordinated susceptibility/ESR/catalytic rate studies to other unsupported binary and promoted systems as well as to supported catalysts, in order to clarify the conditions under which the susceptibility and ESR spin densities differ and to clarify the relationship of these data to the activity and selectivity of the catalysts.

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