**Variations of paramagnetic defects and dopants
in geo-MoS₂ from diverse localities probed
by ESR**

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ABSTRACT

Exfoliated flakes from molybdenite crystals often still serve as benchmark substrates for two-dimensional MoS₂ fundamental and device-oriented research. In this article, results are reported of a multi-frequency electron paramagnetic resonance (EPR) study on a series of natural 2H MoS₂ crystals taken from various (seven) geological sites with the intent to explore the variations in quality and properties in terms of occurring paramagnetic point defects, with particular focus on the assessment of the predominant type of impurity dopant. The sample set covers three types of overall doping regimes, i.e., p-type, n-type, and mixed (n-type and p-type parts in one sample). The doping type appears primarily governed by substitutional impurities as evidenced by the observed As and N acceptor (both substituting for S) and Re donor (substituting for Mo) signals. For all p-type specimens, doping is found to be ruled by As where, however, a strong variation is revealed in doping uniformity, which appears not directly correlated with the As dopant density. Without specific precautions taken, surface contamination related EPR signals are observed in virtually all As-excavated geo-MoS₂ specimens. While several of these signals are of unassigned origin, two prominent ones are identified, one as concerning oxo-Mo⁵⁺ compounds and the other Mn²⁺ centers. The geo-MoS₂ sample with the foremost n-type doping shows, besides the prime Re donor EPR signal, an intense powder-pattern signal, tentatively typified by $g_{||} = 2.076$, $g_{\perp} = 2.253$, which is suggested to originate from intercalation-related defects. The results bear out the necessity of rigorous surface cleaning, even including invasive removal of surface layers, to obtain pristine MoS₂ parent crystals suitable for enabling exfoliation of high quality flakes.

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I. INTRODUCTION

There is ongoing intense research activity on two-dimensional (2D) layered transition metal dichalcogenides (TMDs) for potential revolutionary applications in future novel nanoelectronic devices, including a “beyond complementary metal–oxide–semiconductor (CMOS)” target.^{1,2} Among those, the prototypical molybdenite (MoS₂), in particular, has enjoyed much interest for its outstanding

properties, including superb electrostatic behavior, good mechanical robustness, flexibility, and thermal and chemical stability.^{1–3} The material has been touted as a competitive candidate for next-generation logic devices:^{4,5}

bulk MoS₂ is a semiconductor

(SC) with an indirect band gap of ~1.3 eV, evolving into a direct gap of ~1.85 eV in a covalently bonded S–Mo–S monolayer form, thus enabling electronic tunability via thickness control.

Obviously, wide range nanoelectronic integration will require reliable production methods of wafer scale high quality MoS₂ monolayers (MLs) on select substrates, either by direct growth on the target substrate or by first growing on a template substrate followed by a layer transfer process. Yet, as it appears, layer synthesis techniques globally fall short on meeting expectations, e.g., regarding carrier mobility, due to intolerable excess of grain boundaries and structural defects.¹

In part, because of this in combination with the ease in fabrication, mechanical exfoliation of (few) ML flakes from natural or synthetic crystals is habitually practiced in pioneering basic and proof-of-principle applied research.^{3,6,7}

Pertinently, explorative

devices using exfoliated flakes still figure as the best ones leading in J. Chem. Phys. 152, 234702 (2020); doi: 10.1063/5.0002046 152, 234702-1
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terms of carrier mobility. Obviously, in dealing with flakes, it would appear indispensable to have solid insight on the quality of the parent crystal, e.g., regarding purity and n-type/p-type nature, much dependent on the crystal's origin.

The current work reports on a study by multi-frequency electron spin resonance (ESR) of the variations in the quality of various natural MoS₂ crystals in terms of occurring (paramagnetic) point defects, including both bulk and surface contamination imperfections and (dopant) impurities, with special focus on the assessment of the predominant type of impurity dopant. In this respect, ESR takes an exclusive position, enabling fundamental evaluation, both atomically and structurally, and quantification of defects, in a true defect-specific selective way.

The latter may be apparent from emerging ESR studies on molybdenite, implying work on contamination, such as acceptor impurities in bulk natural 2H-MoS₂

8–14 and synthetic 3R-MoS₂

8

and

donor impurities¹⁵ in natural 2H-MoS₂, the latter work also dealing with structural imperfections (VS) as also addressed in other

ESR work on synthetic 2H-MoS₂.

16 Besides the investigation of bulk crystals, stimulated by technological interest, pioneering effort has expanded to the study of intrinsic imperfections in polycrystalline large-area few-layer synthetic 2D 2H-MoS₂ films¹⁷ and in such films after a layer transfer process.¹⁸ Finally, the realm of ESR investigation has also explored other morphologies, including, e.g., Li-doped MoS₂ nanotubes,¹⁹ fullerene-like MoS₂ nanoparticles,²⁰ and (MoS₂)_{1-x}(C₆₀)_x entities.²¹

II. EXPERIMENTAL DETAILS

As indicated in Table I, bulk MoS₂ specimens, admittedly of 2H type, from seven geological localities spread over six countries were studied. The dopant nature (n or p type or domain-wise mixed) of the samples was independently assessed by the thermoelectric test (see, e.g., Ref. 22).

Of the as-received crystals, thin (~0.2 to 0.5 mm) slices of ~2 × 5 mm²

area were cut with the c-axis along the main area normal *n*, appropriate for ESR observations. The latter was carried out at cryogenic temperature (*T* = 4.2–77 K) using conventional continuous wave X and K-band spectrometers, equipped with adequate allowance for analysis of magnetic field vector anisotropy of signals. The latter was monitored through varying the angle ϕ_B that the applied magnetic field *B* makes with *n* over a broad range (~180°).

First derivative $dP_{\mu r}/dB$ spectra, where *P_{μr}* is the reflected microwave power, were recorded using periodic modulation, *B_m cos(ω_mt)*, at $\omega_m/2\pi \sim 100$ kHz of *B*. The reported ESR spectra were typically averaged over ~20 field scans. Aiming to maximally trace the ESR signals, care was taken to make sufficiently broad field scan spectra, spanning a *g*-value range from ~4.9 to 1.55. Extending field scans to the sufficiently high-*g*-value range (low *B* values) was given due attention. This is because besides the plain interest in tracing possibly present “new” high-*g*-value ESR signals, the concern not to miss potentially present “half-field” signals typical for *S* > 1/2 centers, the detection of whose responses is outlined before (see, e.g., Refs. 10, 12, and 23), may significantly contribute to the characterization of the corresponding defects.

In striving for reliable evaluation of defect densities and signal *g*-values, co-mounted marker samples were used, i.e., LiF:Li [g(4.3 K) = 1.998 69 ± 0.000 02; spin *S* = 1/2],²⁴ with an isotropic signal well calibrated in terms of both the total numbers of spin centers enclosed and *g*-value. Defect densities were determined through double numerical integration of the as-observed $dP_{\mu r}/dB$ signals.

Some samples were subjected to annealing in vacuum (<7 × 10⁻⁶ mbar), a treatment that may serve two purposes: one, removal of possibly ESR-active surface adsorbates and, two, maximally ESR-activate

imperfections/impurities through defect-H bond dissociation (H removal) of centers over time possibly left inactivated (diamagnetic) by hydrogen, a treatment inspired by previously accumulated experience in dealing with passivation by hydrogen of defects/dopants in semiconductors.^{25,26}

III. EXPERIMENTAL RESULTS AND ANALYSIS

Multiple types of ESR signals are observed, some of which, in terms of origin, have previously been well identified and characterized before, while others appear newly observed. Generally, we may classify the observed signals' nature as being of bulk, surface (interface), or surface contamination layer origin. Generally,

TABLE I. Semiconductor type and prevailing impurity dopants detected by ESR at 4.2 K in natural MoS₂ specimens taken

from different geological sites.

Label Sample origin n-type/p-type^a Dopant impurity Density (cm⁻³) (±10%)

A Canada^b

p As 2.4×10^{17}

B Austria (Zillertal) p As 1.9×10^{17}

C Czechia (Krupka) p As 3.0×10^{17}

D Chili (Chuquicamata) n Re 1.6×10^{17}

E Norway (Bandakslia) Mixed^c N $\geq 2.2 \times 10^{15}$

F Norway (Knaben) n . . .

d

. . .

G France (Château-Lambert) Mixed N $\geq 2.6 \times 10^{16}$

^aDetermined thermoelectrically.

^bObtained from SPI Supplies, USA.

^c

Both p-type and n-type regions in one sample.

^dOnly a weak surface contamination signal ($g \approx 2.047$) observed.

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discrimination between “bulk” and “surface” nature could be attained by comparing measurements on samples split off from the outer part [prolonged exposure to (geo) environment] of the parent crystal with the ones freshly cleaved from the “interior.” This approach was preferred rather than having recourse to submitting the sample surfaces to an etch back process.

Presenting an exhaustive description of all (often, complex) signals observed will not be attempted. Rather, in the first instance, we will focus on “known” defect signals, i.e., those of identified origin, and next, as to the remainder, concentrate on some considered “characteristic” in terms of spectral properties with a possible hint for assignment.

A. Dopant and bulk defect associated signals

As to the first class, there are the known impurity dopants, including, along current observations, the acceptors As^{8,10} and N,^{12–14} and the donor Re.¹⁵ Assessment of these would provide access to the kind of MoS₂ semiconductor type (n or p) one is dealing with, knowledge of which may be much desired in the application of exfoliated flakes.

As summarized in Table I, the SC type over the specimens studied varies: samples fully p-type or n-type throughout or “mixed,” that is, p-type and n-type regions being united in one sample, a feature reported before for geo-MoS₂.

27 Three specimens (A, B, and

C) appear prominently p-type, originating, as spotted by ESR, from substantial doping by As acceptors (As substituting for S),⁸ ranging

from $1.9 \times 10^{17} \text{ cm}^{-3}$

(sample B) to $3 \times 10^{17} \text{ cm}^{-3}$

(sample C); for

the three types of specimens, observed (4.3 K; B n) K-band As acceptor spectra are illustrated in Fig. 1. Two specimens (D and F)

are distinctly n-type, which, in the former case, is explained by the observed, albeit rather weak, ESR Re donor signal.¹⁵ In specimen F,

however, no donor type signal could be traced (vide infra). In the

mixed doping type specimens E and G, the N acceptor is revealed,

accounting for the n-type regions. Figure 2 illustrates the N-acceptor

signal observed in specimen G (Château-Lambert, France) for the

“extreme” field orientations $B \parallel c$ -axis and $B \perp c$ -axis, respectively,

FIG. 1. Derivative-absorption K-band ESR spectra of non-ionized As acceptors

(incident microwave power $P_{\mu} \sim 2.5 \text{ nW}$) observed in geo-MoS₂ specimens A, B,

and C (cf. Table I) for the configuration with the applied magnetic field $B \perp c$ -axis.

FIG. 2. Low-temperature (4.3 K; $P_{\mu} = 2.5 \text{ nW}$) K-band ESR spectra of N acceptor

dopants (N substituting for S) observed in the geo-MoS₂ specimen G (Château Lambert,

France) of n, p mixed-type doping for the “extreme” field orientations

$B \perp n$ and $B \parallel n$, the signals being observed at $g = 2.270$ and $g \parallel = 2.032$,

characteristic for the axial symmetric g matrix of N acceptors in 2H MoS₂.

12,13

positioned at the g-values 2.032 and 2.270, the ones characteristic for the N acceptor in 2H MoS₂.

12

1. Acceptors

Regarding the p-type specimen (A, B, and C), apart from As dopant density, more details about the doping can be obtained from the corresponding ESR signal. As disclosed previously,¹⁰ in the range of non-degenerate doping, the As ESR signal generally emerges as a “complex” signal composed of three major components, i.e., the ⁷⁵As (nuclear spin $I = 3/2$; 100% natural abundance) hyperfine (hf) quartet of splitting $A \parallel = 28 \text{ G}$; $A \perp = 18.1 \text{ G}$, a narrow (N) and broad (B) center line (CL). The narrow center line (NCL) stems from two electrons at a pair of close As impurities of which the

hf splitting is averaged out by antiferromagnetic exchange narrowing,²⁸ whereas the broad center line (BCL) is attributed to unpaired electrons exchanged over larger-sized, yet decoupled, clusters of As atoms. The latter two signals expose non-uniformity in dopant distribution. Clearly, a comparison of the As signals (4.3 K; B n) shown in Fig. 1 for samples A, B, and C bears out strong specimen (geological locality) dependent variation in dopant homogeneity, which, notably, appears not to be directly correlated with the observed As dopant densities: For comparable As densities, the As distribution in sample C appears far more inhomogeneous (intense BCL) than in the B one, knowledge useful when dealing with flakes.

2. Donors

As indicated above, the Re donor has been detected by ESR in specimen D (Chili). This is illustrated in Fig. 3, showing a “full,” i.e., a broad field scan-X-band ESR spectrum observed in specimen D at 4.3 K for B n. The presumed Re donor spectrum is situated in the higher field part ($B \gtrsim 3100$ G), the Re donor spectrum itself extending over a broad field interval ($B \approx 3200$ to ≈ 4700 G, corresponding, approximately, to the g-range 1.987–1.353). Zoomed-in observations of the spectrum are presented in Fig. 4. The latter spectrum much resembles the one observed in Ref. 15 under similar experimental conditions (i.e., X-band ESR, low T, and B n), where J. Chem. Phys. 152, 234702 (2020); doi: 10.1063/5.0002046 152, 234702-3

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FIG. 3. Low-temperature broad-field scan X-band ESR spectrum observed in ntype geo-MoS₂ specimen D (Chuquicamata, Chili) for B n using $P_{\mu} \sim 50 \mu\text{W}$, revealing at the right part ($B \gtrsim 3100$ G), the spectrum attributed to the Re donor (Re substituting for Mo) in 2H MoS₂, characterized, as the first eye-catching feature, by a sextet arising from single-nucleus hf interaction of the unpaired electron with a Re nucleus ($I = 5/2$).

the originating center has been identified as an unpaired electron localized at a Re impurity substituting for a Mo atom, i.e., the ReMo center (of spin $S = 1/2$) operating as a donor. It has been inferred to exhibit an orthorhombic g matrix characterized by the principal values g_1 (c-axis) = 1.726, $g_2 = 1.618$, and $g_3 = 1.401$, the values being down shifted with respect to the free electron g-value $g_e = 2.0023$, as expected for donor centers in semiconductors (see, e.g., Ref. 29). The down shifts are substantial, which is ascribed to the large spin–orbit coupling involved.²⁹ The spectral appearance further bears out the presence of a prominent hf interaction of the unpaired electron with the Re nuclei naturally being comprised of the isotopes ¹⁸⁵Re and ¹⁸⁷Re (natural abundance $\eta = 37.4\%$ and 62.6% , respectively), both

FIG. 4. Comparison of zoomed-in X-band ESR spectra of the Re donor observed in geo-MoS₂ specimen D (Chili) for B n and using $P_{\mu} \sim 2 \text{ mW}$, illustrating the steadily augmenting substantial broadening of the constituent peaks with increasing T, resulting in turning the spectrum to become virtually undetectable for

T → 35 K.

with a nuclear spin $I = 5/2$ and with nearly identical nuclear magnetic moments and electric quadrupole moments, an hf interaction that, for an isotropic center, would, to first order, result in a sextet signal pattern. Furthermore, more complication is added to the Re donor signal due to considerable quadrupole interaction (nuclei of $I > 1/2$), all in all resulting in a complex, highly anisotropic multi-peak signal as appearing in Fig. 3.

Having isolated the ReMo donor ESR spectrum, one might wish to infer the corresponding donor thermal activation (ionization) energy, E_d (i.e., $E_d = E_C - E_A$, where E_A and E_C represent the dopant energy level and the bottom of the conduction band, respectively), a basic characteristic of a dopant, through monitoring the donor ESR signal intensity vs T, as successfully demonstrated in previous work on dopants in semiconductors, such as the As and N acceptors in MoS₂

10,12,13 and the P donor in Si.³⁰ As outlined elsewhere,¹⁰ for the sake of reliability, most appropriate for this purpose would be to carry this out on a prominent spectrally well “isolated” hf peak in the ESR spectrum. For the current intention, we may choose the third peak from right (denoted as peak x) in Fig. 3. However, it turns out that such monitoring is much limited as it can be reliably carried out only over a limited T range (up to ~30 K) due to rapidly decreasing signal-to-noise (S/N) ratio with an increase in T. As illustrated in Fig. 4, showing a comparison of the X-band Re spectra observed for B_n at four different T's (4.3 K, 13 K, 19 K, and 25 K), the latter results from drastic line broadening with increasing T, admittedly due to phonon-assisted spin-lattice relaxation. The figure exposes increasing substantial overall spectral broadening (broadening of all constituent spectral peaks) with raising T, the Re spectrum becoming virtually undetectable for $T \gtrsim 35$ K.

Reliable intensity monitoring of peak x could only be carried out up to ~25 K, above which the signal becomes too feeble to enable reliable analysis. The results, plotted in Fig. 5 as inverse signal intensity I_s (area under the absorption curve, proportional to the magnetic susceptibility χ) vs T, expose a nearly paramagnetic ($\chi \propto T$

–1

) behavior; least square fitting of the Curie–Weiss law,

FIG. 5. Plot vs T of the inverse intensity (double integral of $dP_{\mu r}$ /dB response) of

the X-band Re spectrum (peak labeled x in Fig. 3) taken for B_n. The dashed line represents an optimized least-square linear fit, demonstrating a Curie–Weiss law type [$\chi \propto (T - T_C)$

–1

] behavior with a close to zero T_C of 1 ± 1 K, indicative of a

paramagnetic system of negligibly (weakly) interacting spins. Error bars represent the spread in the data over multiple observations.

(cf. dashed line in Fig. 5), gives a Curie temperature

$T_C = 1 \pm 1$ K, pointing within errorbars to a paramagnetic defect system of mutually negligibly interacting spins.

Clearly, over the T-range covered, the data in Fig. 5, thus, do not show any evidence for extra decay of the signal intensity I beyond the paramagnetic $1/T$ decrease with increasing T as would occur in the case of thermal donor activation. Yet, however limited, the fact that no noticeable donor activation occurs up to ~ 30 K bears some information about the attendant $E_a(\text{Re})$. Indeed, if stepping from the previous ESR-based inference of acceptor (As, N in MoS₂) and donor (P in Si) activation energies,^{10,12,14} where the interpretation is based on the expression for the ratio of the neutral [electron paramagnetic resonance (EPR)-active], ND

*

, to the total, ND, dopant

densities rigorously derived from quantum state dopant occupation statistics for the ideal case, i.e., a non-degenerate semiconductor with doping absolutely dominated by one kind of species and with negligible compensation or intrinsic excitation, it is estimated that $E_a(\text{Re}) > 20$ meV. Previous work¹⁵ based on dc Hall effect measurements has inferred $E_a(\text{Re}) = 89$ meV.

Obviously, assessment of $E_a(\text{Re})$ through ESR would need the possibility for Re signal intensity monitoring up to much higher T , perhaps up to room temperature, covering a substantial range of thermal donor activation, the latter requirement being similar for all other experimental methods aiming determination of E_a through monitoring the carrier density. Unlike the case of acceptors (As, N) in MoS₂, this appears so far prevented for the current Re donor case due to unfortunate EPR signal traits. The latter includes unavoidable naturally raised hurdles such as the broadness of the Re spectrum, widely spread out over numerous peaks, and the disastrous rapidly decreasing S/N ratio with increasing T due to signal broadening. With respect to ESR sensitivity, some rescue might come from optimized MoS₂ samples with much enhanced Re impurity density, as studied before.¹⁵ It herewith bears out some limitations of the EPR method, obviously intimately linked with the magnitude of the involved E_a to be determined.

Furthermore, worth noticing is that although the material is found to be indisputably n-type (cf. Table I), no donor-type signal (or dopant characteristic spectrum in general) could be traced in sample F (Knaben, Norway). In fact, only a weak, almost isotropic signal characterized by $g = 2.047$ could be observed, whose spectroscopic

properties, thus, do not meet those expected from a donor center in MoS₂. The signal likely concerns a surface contamination related center. There may be several reasons for failing detection of a donor-type ESR signal in this specimen F. First, of course, there is the point about sensitivity. Although clearly being n-type, the overall total number of donor sites (density) in a typical ESR sample may be below the ESR spectrometer sensitivity limit, which would be the case the more so if one would be dealing with a complex (multi-peak) spread out ESR spectrum (as is, e.g., the case for the Re donor). In that sense, the dominant donor dopant could still be Re, but with dopant density insufficient to enable ESR tracing. Low dopant density is, thus, well feasible: although determinedly pointing out the type of dopant, the thermoelectric test appears merely a quantitative method rather than qualitative, with little information about actual dopant density. Second, as already alluded to and perhaps most likely, one might be dealing with a donor center (impurity related, or perhaps, an intrinsic defect) of so far still unidentified by ESR (unknown nature), with an inherently complex, highly broadened ESR spectrum, prohibitively unfavorable for enabling standard ESR detection. Third, and finally, one might also suggest that the major part of the total donor system would be activated already at the lowest temperature (i.e., 4.3 K) reached in the current ESR observations. This, however, would imply an extremely small donor activation energy, which is kept unrealistic.

A final general remark here regarding observed impurityrelated dopants may concern the notion that, according to earth science investigation,³¹ Re emerges as a most common impurity encountered in geo MoS₂. It may then come somewhat as a surprise that, in the currently studied set of geo-MoS₂ specimens, covering seven different localities, an explicit Re EPR signal could be traced in only one type, i.e., specimen D (Chili). Part of the reason for this may be a “lucky shot” effect in the sense of a non-representative selection of covered geo-MoS₂ excavation localities; the impurity content in geo-molybdenite varies drastically over the Earth area. Yet, as a separate message from the current study, it appears that acceptor impurities play an important role as well, with As emerging as the most prominent one.

3. Bulk defect

One more remarkable signal drawing attention is observed in specimen D (Chili), more precisely the very intense and broad signal appearing in the left part of the X-band overview ESR spectrum depicted in Fig. 3 and of which Fig. 6 shows a zoomed in K-band observation. Repeated measurements on various freshly cleaved samples show that the signal, although clearly not being part of the Re spectrum, indisputably originates from centers located in the bulk. The signal is very intense, corresponding to a defect density ($S = 1/2$) of $\sim 2.8 \times 10^{19} \text{ cm}^{-3}$

. It behaves isotropic, its shape coming as a powder pattern, which would be confirmed by the broadening of the peak-to-peak width, ΔB_{pp} , from ~ 250 G to ~ 570 G in changing the observational frequency from the X-band to K-band
FIG. 6. Zoomed-in K-band ESR spectrum ($P_{\mu} \sim 8$ nW) of an intense signal of bulk, yet unknown, origin observed in n-type geo-MoS₂ specimen D (Chili). The signal appears as a powder pattern-like shape (randomly oriented spin system), where the superposed dashed curve represents an “optimized” powder pattern fitting for a center of axial symmetry, giving $g_{||} = 2.076$ and $g = 2.253$. The high-field part of the spectrum may be somewhat distorted by a weak overlapping broad cavity background signal.

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(factor $20.7/8.9 = 2.3$). Along this view, an “optimized” fitting of the spectrum for a center of axial symmetry results in the dashed curve shown in Fig. 6 from where the values $g_{||} = 2.076$ and $g = 2.253$ are obtained. The fitting is not perfect, but may serve as a start for typifying the signal (it should be added that the high-field part of the spectrum may be slightly perturbed by a weak cavity background signal on top).

Comparing with previous ESR results on molybdenum, the inferred g -values appear to be remarkably close to those characteristic for substitutional acceptor defects, such as V, Nb, and As in MoS₂. Indeed, when initially having been observed in the K-band ESR, there was the impression one was dealing with an acceptor. However, if this would be the case, it is not understood how an isotropic signal can be obtained from a substitutional acceptor dopant situated in a bulk, well ordered MoS₂ crystal, as manifestly demonstrated by the genuine anisotropic Re donor spectrum simultaneously observed in one and the same sample. Moreover, simultaneous observation by ESR (at low T) of both a significant donor (Re) and acceptor signal would seem only possible if the sample would be an agglomerate of both n-type and p-type doped parts, responding separately. However, as indicated in Table I, based on independent verification, there is no evidence for this. So, the origin of the signal remains elusive.

Perhaps, as one possibility instead, the broad signal’s nature may concern a layer intercalation matter related to impurities nested in the van der Waals interlayer regions, where as a result, for defects residing in that environment, the crystallographic restriction may be much relaxed. For a defect system residing in that neighborhood, a powder pattern-type signal might be obtained, the overall finding then still giving the impression one is dealing with a “bulk” defect.

B. Surface/surface layer related centers

As a first pertinent remark, we notice that if no specific precautions

are taken, surface contamination related ESR signals are observed, generally of unknown origin, in virtually all as-received geo-MoS₂ specimens.

Of all MoS₂ specimens studied, type C (Czechia) exhibits, besides the As signal, the richest spectrum of signals. An eyecatching one, labeled γ in Fig. 7, which presents a K-band spectrum observed for the B_n geometry, is characterized by zero-crossing $g = 1.9698$ and density $1.2 \times 10^{17} \text{ cm}^{-3}$ (or $\sim 2.0 \times 10^{15} \text{ cm}^{-2}$,

if calculated per unit area). One more, yet substantially less intense, narrow ($\Delta B_{pp} \sim 7 \text{ G}$) symmetric single-line peak is present at $g = 1.9260$, both spectra being found to remain unaffected after a vacuum anneal at 450°C ($\sim 2 \text{ h}$). Comparative measurements on different pieces of the sample cleaved off from the same parent geo-MoS₂ crystal indicate both signals to concern surface (layer) contamination defects. Yet, from ϕB -dependent measurements, it appears that the latter is uncorrelated with spectrum γ and is, henceforth, left unattended.

As we may perceive from spectrum γ in Fig. 7, major spectral characteristics include that the main (central) peak is distinctly asymmetric and as hinted by the six arrows, it appears centered amid and flanked by a sextet of equidistant weak lines split by $A = 20.7 \pm 0.2 \text{ G}$. The sextet and the central line behave in the same way to variations in T and P_μ , indicating these to be part of one spectrum.

FIG. 7. Derivative-absorption K-band ESR spectrum (4.3 K) of a most likely Mo⁵⁺ centered surface contamination related defect (γ) observed at zero-crossing $g_c = 1.9698$ in geo-MoS₂ specimen C (Czechia) using $P_\mu \sim 2.5 \text{ nW}$ for B_c-axis.

The arrows mark six attendant weak equidistant signals of about equal intensity, well linked to the main signal γ , whose structure is seen as concerning an hf sextet of splitting $A = 20.7 \text{ G}$ arising from single-nucleus hf interaction with ⁹⁵Mo and ⁹⁷Mo isotopes. The peak at $g = 1.9260$ appears to be unrelated with spectrum γ . The narrow signal at $g = 1.99869$ stems from a co-mounted Si:P marker.

If, as likely, dealing with a sextet hf structure, within the context of the natural isotopic constituents of MoS₂, this then likely concerns a primary single-nucleus interaction hf structure arising from ⁹⁵Mo and ⁹⁷Mo isotopes (natural abundance of $\eta = 15.9\%$ and 9.6% , respectively, both having $I = 5/2$ and about the same nuclear g factor; other stable isotopes have $I = 0$) as S has only one stable isotope with nuclear spin (³³S: $I = 3/2$; $\eta = 0.75\%$). So, the spectrum appears as a notably asymmetric main signal amid a sextet of much weaker lines of splitting $A = 20.7 \pm 0.2 \text{ G}$.

In an attempt to unveil the nature and locality of the originating defects, we may focus on these spectral features. Spectroscopically, signal asymmetry may arise from various causes. As a first suggestion, and perhaps most obvious, for a defect in an amorphous environment, the signal could be seen as (part of) a powder patternlike main signal flanked by an hf sextet of lines that should exhibit

the same line shape as the main one. In closer look, it might concern a powder pattern of an axially symmetric center characterized by $g > g_{||}$. (see, e.g., Ref. 23), and accordingly, computer assisted fitting of the spectrum has been attempted, with inclusion of the presence of an hf sextet of which the total intensity should, according to the natural Mo isotopic composition, be $25.5/74.5 = 34.2\%$ of the main central line. Although, as shown in Fig. 7, fitting could be quite successfully achieved for the main pattern, it may generally be inconclusive in the lack of an experimentally resolved high-field spectral structure.

As a second possibility, for a defect system residing in a more crystalline (ordered) surrounding, ESR signal asymmetry for an axial symmetric center may arise from a spread in the orientation of the unpaired orbitals, as might arise, e.g., from stress-induced small site-to-site variations in local defect geometry (see, e.g., Ref. 32). However, for changing the field direction (B tilting away from the B_n direction; decreasing ϕ_B), the signal should undergo a g shift with concomitant change in the line shape, none of which is observed (cf. Fig. 8), thus ruling out this conjecture.

Further search as to the atomic origin of the signal and its specific (asymmetric) structure may be guided by assuming that the resolved additional multi-peak structure, i.e., presumably a sextet, concerns hf interaction from one Mo nucleus. The signal should then stem from a Mo-centered defect, and more insight might be gained from previous ESR work on such centers over a wide range of Mo compounds. Indeed, perusal of the pertinent literature indicated that various paramagnetic ESR signals have been observed from Mo-centered defects, which, rather generally, can be divided in two groups:^{33,34} Mo⁵⁺ centers surrounded by sulfur atoms (thio-Mo⁵⁺ group)³⁵ and Mo⁵⁺ centers surrounded by oxygen ions (oxo-Mo⁵⁺ group). A comparison with previous results, in particular dealing with supported Mo-oxide catalysts systems, indicates that similar, yet not identical, signals with close g-values as the one currently observed have been reported from Mo⁵⁺ (i.e., Mo in the 5+ oxidation state with one unpaired electron) complexes of molybdenyl (short Mo=O group) character (molybdenyl compounds), i.e., containing a short M=O bond, such as encountered in Mo⁵⁺ oxyhalide anions³⁶ and species comprised of Mo⁵⁺ with a first coordination sphere composed of, in addition to a molybdenyl group, five to three O atoms, the entities being denoted as Mo⁵⁺_{6c} (Mo⁵⁺ in hexacoordination), Mo⁵⁺_{5c}, and Mo⁵⁺_{4c}, respectively.³⁷ Various of such

complexes exhibit g matrices with $g > g_{\parallel}$ (as would seem the case for the current observation) and comparable g -values, i.e., $g = 1.944$, $g_{\parallel} = 1.892$; $g = 1.957$, $g_{\parallel} = 1.866$; $g = 1.926$, and $g_{\parallel} = 1.755$, for the Mo^{5+} 6c, Mo^{5+} 5c, and Mo^{5+} 4c species, respectively, so that the current signal might be a superposition of such types positioned in an amorphous environment.³⁷ The Mo^{5+} 6c is assigned an

hf matrix³⁸ with $A_{\parallel} \sim 98$ G and $A \sim 44$ G, about $2\times$ larger than currently inferred. On the basis of the discussed similarities, the signal illustrated in Fig. 7 likely results from isolated Mo^{5+} centered complexes. The corresponding high areal defect density would indicate the originating defects to be located in a surface compound

FIG. 8. Angular variation of the zoomed-in K-band ESR spectrum y (cf. Fig. 7) observed ($P_{\mu} \sim 25$ nW) in the geo-MoS₂ specimen C (Czechia) as a function of ϕ_B for B tilting away from $B \perp n$ ($\phi_B = 90^\circ$) toward the $B \parallel n$ direction, indicating the signal to fade away for $\phi_B \rightarrow 50^\circ$ with the spectral shape apparently remaining unchanged.

FIG. 9. K-band ESR spectrum observed at 4.3 K in the geo-MoS₂ specimen G (France) using $P_{\mu} = 25$ nW. The intense signal, centered at $g \sim 1.999$, originates from Mn^{2+} impurities residing in a disordered surface contamination layer. The narrow signal at $g = 1.99869$ stems from a co-mounted Si:P marker. contamination layer rather than just concerning pure (interface) surface defects.

On the spectroscopic side, however, one observation should be added. The signal intensity, apparently without the signal changing shape nor the g -value, drops drastically with decreasing ϕ_B (B tilting away from the $B \perp n$ direction), to disappear for $\phi_B \rightarrow 50^\circ$ (see Fig. 8). Such a behavior for a presumed powder pattern is currently elusive. Maybe, it could refer to the contamination layer, rather than fully amorphous, being of partially organized nature.

As a general concluding remark, observation of such Mo^{5+}

- centered complexes indicates, not quite surprisingly, that severe surface contamination of geo-MoS₂ surfaces may be encountered. Turning to another observation, also found is that the specimen G (France) suffers from a vast contamination, as revealed by the observation (cf. Fig. 9) of an intense isotropic specific Mn^{2+} impurity signal ($S = 5/2$) (see, e.g., Ref. 39). Measured at the K-band, it consists of a broad signal ($\Delta B_{pp} \sim 590$ G) centered at $g \sim 1.999$ with, on top, a main sextet arising from one nucleus hf interaction with ^{55}Mn ($I = 5/2$; 100%) isotopes. Simulation of the spectrum (cf. dashed curve in Fig. 9) indicates the hf sextet peaks to be characterized by $\Delta B_{pp} \sim 45$ G, with splitting $A_{hf} \sim 94$ G. The intense signal

had disappeared when measuring on a sample taken from the inner part of the mother crystal, indicating it to concern a surface layer contamination.

IV. CONCLUSIONS

In summary, comparative ESR analysis of various geomolybdenite specimens has exposed numerous kinds of both bulk and surface contamination related defects. Different overall dopant regimes (n, p, and mixed) are encountered, with As, N, and Re being traced as effectively dominant bulk impurity dopants. As for the ptype MoS₂ specimens, a drastic variation in As dopant uniformity is revealed, of interest when applying exfoliated flakes in prospecting nanoelectronic devices.

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Not surprisingly, various surface (layer) contamination related defects are observed in the geo-MoS₂ specimen with surfaces extendedly exposed over time to geological weathering conditions, including oxo-Mo⁵⁺ (molybdenyl) compounds and Mn²⁺ centers. Clearly, the latter observations bear out the necessity that surfaces should be thoroughly cleaned, with surface layers removed, before considering to exfoliate high quality flakes for intended fundamental intrinsic analysis or targeted innovative applications.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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