ESR study of p-type natural 2H-polytype MoS₂ crystals: The As acceptor activity

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ABSTRACT

Low-temperature ($T = 1.7\text{--}77\text{ K}$) multi frequency electron spin resonance (ESR) study on p-type 2H-polytype geological MoS₂ crystals reveals p-type doping predominantly originating from As atoms substituting for S sites in densities of $(2.4 \pm 0.2) \times 10^{17}\text{ cm}^{-3}$. Observation of a “half field” ($g \sim 3.88$) signal firmly correlating with the central Zeeman As acceptor signal indicates the presence of spin $S > 1/2$ As agglomerates, which together with the distinct multicomponent makeup of the Zeeman signal points to manifest non-uniform As doping; only $\sim 13\%$ of the total As response originates from individual decoupled As dopants. From ESR monitoring the latter vs. T , an activation energy $E_a = (0.7 \pm 0.2)\text{ meV}$ is obtained. This unveils As as a noticeable shallow acceptor dopant, appropriate for realization of effective p-type doping in targeted 2D MoS₂-based switching devices.

Over the recent years, two-dimensional (2D) materials, in particular, the transition metal dichalcogenides (TMDs) have enjoyed a resurgence of research interest driven by their potential for replacing traditional semiconductors in next generation nanoelectronic devices.^{1–6} Among the TMDs, 2D molybdenum disulfide (MoS₂), specifically, has been widely studied for its outstanding photocatalytic, optoelectronic, and mechanical properties.^{3,6}

Bulk MoS₂ (molybdenite) is an abundant soft mineral consisting of three-layered S-Mo-S sheets of hexagonal structure and strong in-plane ionic-covalent bonding, held together by van der Waals forces; It is a semiconductor with indirect band gap of $\sim 1.3\text{ eV}$, turning to a direct (optical) gap of 1.85 eV in monolayer form.^{1,2} Obviously, to enable full exploitation of the

unique properties of atomically-thin MoS₂ films, reliable production methods of large area 2D MoS₂ films will be essential. Accordingly, various methods have been explored [See, e.g., Refs. [1](#), [2](#), and [7](#)]. Yet, as with other layered materials such as graphite and boron nitride, pristine, clean high-quality 2D flakes can be produced by micromechanical exfoliation^{[1-3](#)}—in fact the method first applied, in the case of graphene, has triggered the start of a new research field.^{[6](#)} The flake serves as a bench mark for 2D MoS₂ research, and therefore, understanding its fundamental physical and chemical properties, down to atomic detail, is of basic importance. Devices realized using exfoliated flakes figure as the ones with the highest mobility achieved.^{[3,8,9](#)} Similar to traditional semiconductor technology, realizing stable n and p-type conduction is indispensable for all the applications for which MoS₂ is intended, such as heterojunction bipolar transistors, light emitting diodes, and photodetectors.^{[1](#)} Yet, the bipolar doping strategy needs to be refined. For the MoS₂ material is mostly reported as being intrinsically n-type,^{[2,3,5,9-12](#)} which, in one view, is ascribed to the amphoteric doping nature of native point defects in combination with the low lying conduction band (CB) minimum and valence band (VB) maximum in MoS₂ referenced to the vacuum level;^{[13](#)} The n-type doping propensity is commonly attributed to S vacancies operating as donors.^{[2,14,15](#)} This, however, has recently been countered theoretically,^{[16](#)} concluding that, while S vacancies are found to be the most abundant defects, they should behave as acceptors; Alternatively, good n-type doping of natural MoS₂ might arise from substitutional Re impurities.^{[16-18](#)} Yet, in aiming applications, there appears a lack of robust and tunable “conventional” p-type doping of MoS₂ based on substitution of host atoms by covalently-bonded acceptor impurities.^{[13](#)} Decades ago, Nb substituting for Mo in 3R MoS₂ grown by the chemical vapor transport method had been concluded to operate as acceptor,^{[10,11](#)} as recently experimentally confirmed^{[13,19](#)} and

supported theoretically.¹⁸ Recent work has found that geological (geo-) MoS₂ may unite both p and n-type regions in one sample.²⁰

Obviously, the choice of doping—type and level—plays a key role in device development, which can strongly affect the performance. In aiming to contribute to the characterization of the natural MoS₂ reference material, the current work deals with the nature of doping of p-type crystals. An in depth low-temperature (T) electron spin resonance (ESR) characterization of the As acceptor is carried out, including analysis of its ESR spectral composition and determination of the As thermal activation energy; As emerges as a most efficient acceptor dopant. It thus appears that, different from what is mostly reported, the current study deals with MoS₂ crystals that are genuine p-type—to be ascribed to the particular “spectrum” of impurities innate to the MoS₂ excavation site, an asset that can show drastic variations over the earth.

The samples studied are two commercially obtained,²¹ within a ~ 1 Y time span, bulk geo-MoS₂ crystals (A and B) of, as it appears, 2H polytype (hexagonal symmetry, two MoS₂ layers per repeat unit, and Mo in trigonal prismatic coordination bonded to 6 S atoms [see. e.g., Ref. 1]). Both crystals are found to be largely p-type as evidenced (see below) by the observed As acceptor ESR spectra, and the samples show much similar ESR properties. The p-type doping nature has been independently firmly ascertained by the thermoelectric test.²² Of these crystals, thin ESR-sized slices of $\sim 2 \text{ mm} \times 8 \text{ mm}$ were cut with the c axis (stacking direction) along the main face normal $\mathbf{n}$. Observations were made on the samples in the as-received state and after heating in vacuum ($< 5 \times 10^{-5}$ Torr) at 400 °C for ~ 20 h. The latter treatment, however, was found not to affect the ESR response within experimental accuracy, neither qualitatively nor quantitatively.

Conventional cw absorption-derivative X- and K-band measurements were carried out at low temperatures ($T = 1.68\text{--}77$ K), using sinusoidal modulation, $B_m \cos \omega_m t$ ($\omega_m/2\pi \sim 100$ kHz), of the

applied magnetic field $\mathbf{B}$. Use was made of a calibrated comounted Si:P marker sample [$g(4.3\text{ K}) = 1.99869$; spin $S = 1/2$] serving as accurate g and spin density marker. Defect densities were determined through orthodox double numerical integration of as-observed dP_{μ}/dB spectra (P_{μ} is the reflected microwave power), measured under distortion-avoiding spectrometer settings (i.e., reduced incident power P_{μ} , B_m).

The current work deals with two ESR signals: the As-acceptor signal and a so far unreported “half-field” line stemming from an $S > 1/2$ center, both signals showing distinct anisotropy with respect to ϕ_B , the angle $\mathbf{B}$ makes with $\mathbf{n}$.

Figure 1 shows representative K-band ESR spectra (stemming from As impurities, as will appear) observed at 4.3 K for $\mathbf{B}||$ (panel a) and $\mathbf{B} \perp c$ -axis (panel b). From the inferred g map, shown in Fig. 2, it is found that the spectra correspond to a center of axial symmetry about the c axis characterized, at 4.3 K, by $g_{||} = 2.027 \pm 0.001$ and $g_{\perp} = 2.309 \pm 0.001$, in excellent agreement with initial work:²³ There, based on the observed g values and g matrix symmetry together with the observed ^{75}As (100% natural abundance; nuclear spin $I = 3/2$) hyperfine (hf) structure, the signal has been demonstrated to originate from holes localized around As acceptor impurities substituted for S sites in bulk 2H MoS₂. The excited holes are in the d_{z^2} band, the one generally accepted (see, e.g., Refs. 1, 23, and 24) as the highest filled VB in 2H MoS₂. Within experimental accuracy, the As g value appears constant over the T range covered.

FIG. 1. Derivative-absorption K-band ESR spectra of the non-ionized As acceptor observed at 4.3 K, using $P_{\mu} = 2.5\text{ nW}$ and $B_m = 0.6\text{ G}$, in sample geo-2H MoS₂ (B) for $\mathbf{B}||c$

axis (panel (a)) and $\mathbf{B} \perp c$ axis (panel (b)). In panel (a), NCL indicates the narrow central line, whereas the dashed curve represents a computer simulation of the broad center line. The dotted lines mark the total width of the ^{75}As hf quartet.

- [PPT](#)

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- [High-resolution](#)

FIG. 2. g map of the As acceptor, obtained from K band observations at 4.3 K for $\mathbf{B}$ rotating over an angle of 90° with respect to the c axis. The solid curve represents an optimized fitting of expression $g(\varphi_B) = [g_{\parallel}^2 \cos^2(\varphi_B) + g_{\perp}^2 \sin^2(\varphi_B)]^{1/2}$ for a center of axial (C_{3v}) symmetry using $g_{\parallel} = 2.027$ and $g_{\perp} = 2.309$.

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As illustrated by Fig. [1\(a\)](#), the ^{75}As hf structure is most clearly observed for the $\mathbf{B} \parallel c$ direction, showing a prominent hf quartet of splitting $A_{\parallel} = 28.0 \pm 0.2$ G, well in agreement with previous work.²³ X-band observations give the same results. Yet, a closer look reveals the As spectrum to be of richer nature, being comprised of (at least) three components: In addition to the ^{75}As hf

quartet, there is a weak narrow central line (NCL), and underneath, a broad signal (broad center line, BCL) of peak-to-peak width $\Delta B_{pp} = 21 \pm 2$ G and of Voigt shape (Lorentz factor ~ 0.7) as concluded from computer assisted spectra simulation [cf. dashed curve in Fig. [1\(a\)](#)]. The width of the weak NCL, $\Delta B_{pp} = 11 \pm 2$ G, is comparable to that of each of the quartet lines. All three constituent spectral components appear centered at the same g value ($g_{\parallel} = 2.027$) and shift in tandem, together making up the total of the As Zeeman ESR spectrum; It corresponds to an As impurity density (sample A; 1.65 K) of $(2.4 \pm 0.2) \times 10^{17}$, of which the ^{75}As hf quartet constitutes $13 \pm 1.5\%$.

If only dealing with a dilute system of uniformly distributed, single As acceptordopants, one would normally expect, given the 100% natural abundance of the ^{75}As isotope, as hole ESR signal only the ^{75}As hf quartet. However, the emerging, more complicated, spectrum may be understood by, e.g., referring to the known properties of donors in Si, e.g., the extensively studied case of P donors, providing useful information on the dopant arrangement. Also in this case, depending on the P concentration, three major ESR components may generally be observed: that is, in the doping range $[\text{P}] \sim (3\text{--}30) \times 10^{16} \text{ cm}^{-3}$,^{[25](#)} the ^{31}P hf doublet ($I = 1/2$; 100% abundance) of ~ 42 G splitting, a NCL—there referred to as central pair line (CPL)—and the broad center line. While the hf doublet stems from electrons centered around isolated, mutually non-interacting P sites, the single NCL arises from two electrons at a pair of close P impurities (cluster pair) for which the hf splitting is averaged out by antiferromagnetic exchange narrowing,^{[26](#)} the two electrons now acting as one unit.^{[26–28](#)} The BCL, in turn, is attributed to electrons exchanged over larger-sized, yet decoupled, clusters of P atoms (three or more); these clusters are not electron interconnected in the metallic sense^{[29](#)} (P doping well below the critical level for impurity band formation).

As essential general message, the exposed ESR spectral composition bears out details of the donor distribution in the semiconductor, the signal emerging as a mix of responds arising from electrons at individual (hf pattern) and clustered (NCL, BCL) dopant atoms. The currently observed As acceptor spectrum in MoS₂, thus, appears to reflect a similar situation.

One more relevant piece of information may come from the observation of a, albeit weak, half field line at $g \approx 3.88$ of $\Delta B_{pp} = 9.0 \pm 1$ G as illustrated in Fig. 3 for $\mathbf{B} \parallel \mathbf{n}$, signaling the presence of a $S > 1/2$ spin system. The signal, of intensity $\sim 0.65\%$ of the total As Zeeman signal, shows prominent anisotropy: Starting from its highest g value, observed for $\mathbf{B} \perp \mathbf{n}$, the signal g gradually decreases (cf. Fig. 3), a behavior coherent with the central As Zeeman signal. Moreover, monitoring its intensity vs. increasing T shows, within experimental error, an identical decay (see below) as the As Zeeman signal which makes us conclude the half field line to pertain to As acceptors. The obvious interpretation then would be that, as heralded by the presence of the NCL and BCL in the AsZeeman spectrum, there are localities in the MoS₂ crystal where two or more Asdopants have agglomerated so as to end up in the formation of a $S \geq 1$ defect through exchange interaction. This finding adds one more element attesting to the complexity and manifest non-uniformity in As doping over the sample volume.

FIG. 3. Typical K-band “half field” ESR signal ($\Delta B_{pp} \sim 9$ G) observed at 4.7 K using $P_{\mu} = 80$ nW for $\mathbf{B} \perp \mathbf{c}$ axis ($\phi_B = 90^\circ$); The inset shows the decrease in g as $\mathbf{B}$ tilts away from the c axis. The signal is ascribed to As clustering with $S > 1/2$ spin system formation as a result of electron-electron interaction.

- [PPT](#)

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- [High-resolution](#)

Once the unique defect spectrum has been isolated, ESR appears as one of the most powerful techniques to accurately monitor its intensity vs. a varying external parameter. With respect to semiconductors, this would in principle enable straightforward monitoring, strict individually for each type of dopant present, of its excitation behavior. Then, if at hand an expression adequately describing the dopant occupation statistics vs. T , it would, e.g., for the case of an acceptor in principle enable direct assessment of the corresponding thermal activation energy, $E_a = E_A - E_v$, referenced to the top, E_v , of the valence band (VB), where E_A represents the acceptor energy level.

Apart from the T -dependent variation of the ESR signal intensity due to the change in statistical occupation of the acceptors by paramagnetic electrons, the acceptor impurity spin system intensity on top will also be subjected to the usual T dependence inherent to its specific magnetic behavior, e.g., paramagnetic, ferromagnetic, etc. So, correct dopant occupation monitoring will require proper separation of the T dependences.

Most useful in this respect, in ESR terms, appears the observation of explicit “first-order” hf structure originating from interaction of the unpaired electron with the nuclear spin of the atom at which it is (partially) localized, as is the case for the current As signal showing the prominent ^{75}As hf quartet pattern. Similarly, turning to dopants in Si, there is the well known example of P donors with characteristic ESR signal showing the distinctive 42-G split ^{31}P ($I = 1/2$) doublet for non-degeneracy doping levels $[\text{P}] \leq 1.3 \times 10^{18} \text{ cm}^{-3}$.^{[25,28](#)} As outlined, such hf structure

authenticates “ideal” dilute distribution of decoupled P dopants, the corresponding spin system being known to exhibit Curie-type susceptibility $\chi_C \propto 1/T$.

Accordingly, the intensity of the ^{75}As hf ESR spectrum (highest field peak) has been monitored over as wide a T range possible, starting from the lowest T experimentally attainable (~ 1.68 K) up to $T \sim 70$ K. Pertinently, the closely correlated increasing damping of the microwave cavity as T is raised points to As hole excitation to the VB. The results are shown in Fig. 4, where the data have been normalized for the admitted $\chi_C \propto 1/T$ dependence. Thus, for clarity, in aiming to correctly assess the As dopant activation, the ^{75}As hf component has been carefully monitored rather than the total, yet more intense, As ESR spectrum. As outlined, the latter, in addition to ^{75}As hf, bears several additional components (NCL, BCL) with different and/or unclear magnetic behavior vs. T , which would leave an unacceptable uncertainty.²⁵

FIG. 4. Temperature dependence of the intensity (double integral of dP_{μ}/dB spectra) of the ^{75}As hf ESR pattern stemming from single decoupled non-activated As acceptor atoms substituting for S in sample geo 2H MoS₂ (A). Due to the fast fading of the hf signal, the data at the higher T end are considered less reliable. The dashed curve represents an optimized fit of Eq. (1), from where the activation energy $E_a = 0.7 \pm 0.2$ meV is obtained.

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The data are interpreted by the expression for the ratio of neutral, N_A^* , to total, N_A , acceptor densities³⁰

$$N_A^*/N_A = 1 - 2(1 + K)^{-1/2}, \quad N_A^*/N_A = 1 - 2(1 + K)^{-1/2},$$

with $K = 4g_d N_A / N_v = (4g_d N_A / N_{v0}) T^{-3/2} \equiv K_0 T^{-3/2}$, where $N_v = 2(2\pi m_v kT/h^2)^{3/2} \equiv N_{v0} T^{3/2}$ is the VB effective density of states; here, k is the Boltzmann constant, h Planck's constant, and m_v is hole effective mass taken for MoS₂ as³¹ $m_v = 0.56m_0$ (electron rest mass) from which we obtain $N_{v0} \approx 2.02 \times 10^{15} \text{ cm}^{-3} \text{ K}^{-3/2}$; g_d represents the impurity level spin degeneracy factor, which for bulk MoS₂ is taken as $g_d = 2$ as there appears no band degeneracy at the top of the VB.^{30,31} Equation (1), reflecting an ideal case situation, can be rigorously derived within the standard semi-classical description of solid state band structure³⁰ for the conditions of a semiconductor non-degenerate throughout the whole of the T range considered, and doping absolutely dominated by one principle kind of impurity with negligible amount of compensation or intrinsic excitation. As to the current case of As dopants in MoS₂, admitting, as likely, that As is by far the overruling type of dopant, the measured As density would reliably meet the condition of non-degeneracy,¹³ and moreover, adduce reasonable support to the requirement of negligible compensation.

Optimized fitting of Eq. (1) to the data in Fig. 4 (cf. dashed curve) gives $E_a = (0.7 \pm 0.2) \text{ meV}$, revealing As as a very shallow acceptor. For completeness, to be added is that in light of the rather large As concentration dealt with, the actual low-dopant concentration E_a value may be somewhat higher.^{30,32} This result may be compared with the value of $\sim 80 \text{ meV}$ predicted for *monolayer* MoS₂.¹⁸ In the current case, the actual E_a value may also be somewhat lowered due to strain-induced level broadening.

In further going into the applied fitting model represented by Eq. (1), the low- T data of Fig. 4 have been addressed in more detail. For the low- T condition, $K \exp(E_a/kT) \gg 1$ (say > 10), when relatively few holes are excited, Eq. (1) approximates to

$$N^*_A/N_A = 1 - N_v/g_d N_A \exp(-E_a/2kT) \approx 1 - K' \exp(-E_a/2kT), N^*_A/N_A = 1 - N_v/g_d N_A \exp(-E_a/2kT) \approx 1 - K' \exp(-E_a/2kT),$$

which, in bringing out the full T dependence, is rewritten as

$$(1 - N^*_A/N_A) T^{-3/4} = K'_0 \exp(-E_a/2kT), (1 - N^*_A/N_A) T^{-3/4} = K'_0 \exp(-E_a/2kT),$$

with prefactor $K'_0 K'_0 \equiv \sqrt{(N_v/g_d N_A)}$. Eq. (2) comes as a versatile expression as it would enable one to read E_a directly from the slope of the plot $\ln(1 - N^*_A/N_A)$ vs. $1/T$ —a usual custom in the interpretation of transport data,³⁰ with Eq. (2) then written for the density of charge carriers in the VB or CB.

For the current As-in-MoS₂ case, Eq. (3) would hold for $T \lesssim 10$ K. Then, from a plot of $\ln[(1 - N^*_A/N_A) T^{-3/4}]$ vs. $1/T$ of the As signal intensity data according to Eq. (3), we obtain, as directly read from the slope of the fitted straight line, $E_a = (0.63 \pm 0.15)$ meV, in agreement, as expected, with the result from fitting Eq. (1) over the entire T range covered. And, importantly, we obtain $K'_0 = 0.15 \pm 0.03 \text{ K}^{-3/4}$, close to the value $\sim 0.07 \text{ K}^{-3/4}$ expected on the basis of the values estimated for N_v and measured N_A . This overall good quality and self consistency in fitting, notably regarding K'_0 , adduces support to the appropriateness of applying Eq. (1) for the current data analysis.³³

There is one more description of interest. As outlined elsewhere,³⁴ for the usual conditions of absolute dominant doping by one kind of dopant, say acceptors, and no appreciable compensation nor intrinsic excitation, a relation for the occupation of the acceptor impurities can be derived valid for the high- T part of the acceptor activation region, i.e., $E_F - E_A \gg kT$ (say $\gtrsim 3 kT$, where E_F is the Fermi level), given as

$$N^*A/NA=(1+N_{\text{vgd}}NAe^{-E_a/kT})^{-1}\equiv(1+K''0T^{3/2}e^{-E_a/kT})^{-1}, NA^*/NA=(1+N_{\text{vgd}}NAe^{-E_a/kT})^{-1}\equiv(1+K0''T^{3/2}e^{-E_a/kT})^{-1}$$

with $K''0K0'' = (N_{\text{vgd}}/g_dNA) = K'0K0'$. Such formula, except for using a T -independent exponential prefactor and with E_a replaced by $E_a/2$, has been applied before to interpret ESR-monitored donor activation behavior.^{35,36} Optimized fitting of Eq.(4) to the data in Fig. 4 for the $T > 10$ K part gives, in agreement, $E_a = 0.68$ meV and $K''0K0'' \sim 0.07 \text{ K}^{-3/2}$.

In summary, an extensive low- T ESR study of p-type geo-MoS₂ bulk crystals reveals dominant p-type doping by As acceptor atoms substituting for S sites in 2H polytype MoS₂, to an overall density of $\sim 2.4 \times 10^{17} \text{ cm}^{-3}$. The ESR spectral features unveil marked non-uniform doping in general, with only a fraction of $\sim 13\%$ of the As impurities doping in the desired “isolated” manner, as rendered by the ⁷⁵As hf structure. From T -dependent monitoring of the latter, an activation energy $E_a = 0.7 \pm 0.2$ meV is deduced, herewith establishing As an efficient p-type dopant in MoS₂. The obtained insight should contribute to developing appropriate doping strategies—implying both unipolar tunable n and p-type doping—for few-layer MoS₂ application in future electronic nano-devices.

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Monitoring the intensity of the ^{31}P hf doublet vs. T over the range 4.3–37 K and fitting of Eq. (1) to the data gives $E_a(\text{P}) = (42 \pm 4) \text{ meV}$, to be compared with the commonly accepted value of $\sim 45 \text{ meV}$.³⁴

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