defect structure proposed by Cargill.[9] The understanding of electrical conduction in amorphous semiconductors will be hopefully improved by performing a similar study on Si and Si-Ge alloys. These experiments will be the subject of a future publication.

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[1] J. J. Hauser, Phys. Rev. Lett. **29**, 476 (1972).
[2] H. C. Theuerer and J. J. Hauser, J. Appl. Phys. **35**, 554 (1964).
[3] D. M. Maher and A. Staudinger (unpublished).
[4] T. M. Donovan and K. Heinemann, Phys. Rev. Lett. **27**, 1794 (1971).
[5] F. L. Galeener, Phys. Rev. Lett. **27**, 1716 (1971).
[6] F. L. Galeener, Phys. Rev. Lett. **27**, 421 (1971).
[7] K. L. Chopra and S. K. Bahl, Phys. Rev. B **1**, 2545 (1970).
[8] P. A. Walley and A. K. Jonscher, Thin Solid Films 1, 367 (1968).
[9] G. S. Cargill, III, Phys. Rev. Lett. **28**, 1372 (1972).
[10] V. K. S. Shante, Phys. Lett. 43A, 249 (1973).
[11] C. J. Adkins and E. M. Hamilton, in *Proceedings of the Second International Conference on Conduction in Low-Mobility Materials, Eilat, Israel, 1971* (Taylor and Francis, London, 1972), p. 229.
[12] E. M. Hamilton, Philos. Mag. **26**, 1043 (1972).

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Electron-Paramagnetic-Resonance Studies on Arsenic Acceptors in Natural (2*H*) and Synthetic (3*R*) MoS_2 Crystals

R. S. Title and M. W. Shafer
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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We have observed the EPR spectra of As acceptors in both natural MoS_2 crystals (2*H* polytype) and in synthetic MoS_2 crystals (3*R* polytype). The *g* values of the resonance signals show that the As acceptors are associated with a band that has d_{z^2} orbital character. Energy considerations indicate that the As acceptors are most likely substitutional on sulfur sites. The observation of d_{z^2} orbital character for the As acceptors on sulfur sites is only consistent with a MoS_2 band structures that has the d_{z^2} band as the highest filled band. In one of our samples the concentration of As acceptors was low enough so that some of the holes introduced by the As acceptors were localized at the As impurity. For these centers we were able to observe an As^{75} hyperfine structure in the EPR spectrum. We determine from this hyperfine structure a value of $\langle 1/r^3 \rangle = 2.99$ a.u. for the hole orbit around the As and a value for the nuclear electric quadrupole moment of As^{75}, $q = 0.28$ b.

INTRODUCTION

The wide range of electrical properties ranging from insulating through semiconducting to superconducting that are found in the structurally and chemically similar layered transition-metal dichalcogenides has attracted considerable experimental and theoretical interest.[1] There have been several proposals of band-structure models which attempt to explain the electrical, optical, and other properties of these materials. While none of these has been completely successful in explaining all the properties, the proposed band-structure schemes have been very useful in providing a framework for discussion and for establishing some physical understanding of the properties.

The band structures that have been proposed are made up of molecular orbitals composed from the orbital wave functions on the transition-metal and the chalcogen atoms. Some of the proposed models are shown in Fig. 1. In these models the valence band *V* is made up primarily of the chalcogen *s* and *p* orbitals; the conduction band *C* is made up primarily of the transition-metal *s* and *p* orbitals; and the nonbonding and antibonding transition-metal *d* orbitals are either in the forbidden gap or else overlap the conduction or valence bands. The ordering of the *d* orbitals is determined by the crystal symmetry at the metal site. The order shown in Fig. 1 is appropriate for the trigonal prismatic structure found for group-V and group-VI dichalcogenides such as NbS_2 and MoS_2. The number of

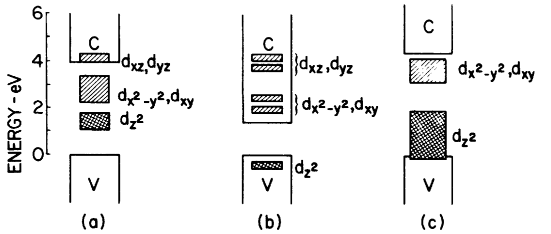

FIG. 1. Proposed band-structure schemes for MoS_2 (a) following Wislon and Yoffe (Ref. 1); (b) following Huisman *et al.* (Ref. 2); (c) following McMenamin and Spicer (Ref. 3).

electrons in MoS_2 is sufficient to fill the d_{z^2} band and this band is shown as filled in Fig. 1. NbS_2 has one less electron and the d_{z^2} band is only half-filled. Consequently it shows metallic conduction and is superconducting at low enough temperatures.

It is difficult to calculate the relative spacing of the various bands in Fig. 1 from first principles. The three proposals in Fig. 1 are attempts to use various experimental data to arrive at a band structure. Wilson and Yoffe,[1] using primarily optical-absorption data and electrical measurements, proposed the structure shown in Fig. 1(a). The d_{z^2} band lies approximately 1 eV above the valence band and is separated by approximately 0.25 eV from the empty $d_{x^2-y^2}$, d_{xy} band above it. In this model MoS_2 is a narrow-band-gap (0.25-eV) semiconductor.

Huisman *et al.*,[2] failing to observe some of the absorption peaks upon which Wilson and Yoffe based their model, and also from a reinterpretation of electrical-conductivity data in both *p*- and *n*-doped MoS_2, proposed the model shown in Fig. 1(b). In this model the forbidden gap is 1.3-eV wide and is located between the conduction and valence bands. The ordering of the *d* orbitals is similar to that of Wilson and Yoffe. All the *d* bands, however, overlap other bands. The d_{z^2} band overlaps the valence band. Both the $d_{x^2-y^2}, d_{xy}$ band and the d_{xz}, d_{yz} band overlap the conduction band. The upper two *d* bands show spin-orbit splitting.

McMenamin and Spicer[3] and Williams *et al.*[4] have recently measured the ultraviolet photoemission spectrum in MoS_2. From their data, McMenamin and Spicer propose the band model shown in Fig. 1(c). In this model only the bottom of the d_{z^2} band overlaps the valence band and the top is completely clear of the valence band. The top of the d_{z^2} band is separated by 1.3 eV from the bottom of the $d_{x^2-y^2}, d_{xy}$ band and this band does not overlap the conduction band. (McMenamin and Spicer do not discuss the d_{xy}, d_{yz} band.)

In addition to the models shown in Fig. 1 there have been two semiempirical band-structure calculations[5,6] which derive the *k*-space variation of the bands. Both of these use the same experimental data as Wilson and Yoffe[1] did and require revision to account for the ultraviolet photoemission data of McMenamin and Spicer[3] and Williams *et al.*[4]

We have recently shown that electron-paramagnetic-resonance (EPR) measurements on shallow acceptor defects may be used to identify the orbital character of the band with which the acceptor is associated.[7] For a semiconductor, Kohn and Luttinger[8] have shown that the wave function of a shallow donor or acceptor can be expressed as the product of a hydrogenic wave function and the Bloch function of the nearby conduction or valence band, respectively. The *g* values of the EPR signal from the donor or acceptor therefore depend on the nature of the Bloch function of the associated band. We have in this way determined from EPR measurements on Nb acceptors in MoS_2[7] that the holes on the Nb acceptors are associated with a band with d_{z^2} orbital symmetry. The EPR experiment measures the holes in their lowest-energy state. Figure 1 is of course drawn with the usual convention in which the energy of electrons increases upward. In this convention, holes will be in the lowest-energy state when they occupy the highest-filled band, i.e., holes "bubble" upward to reach their lowest energy. These EPR measurements indicate that the top of the highest-filled band has d_{z^2} character. This would tend to rule out the model of Huisman *et al.* [Fig. 1(b)] in which the filled d_{z^2} band overlaps the yet higher-lying filled valence band. There is, however, the possibility in this model that there exists no physical mechanism that has a nonvanishing matrix element for transfer of holes from the d_{z^2} band to the more energetically favorable valence band. Since Nb acceptors on Mo sites introduce holes associated with the Mo d_{z^2} band, the absence of a mechanism for transfer of holes to the energetically favored valence band in the Huisman model would tend to lock the holes in the d_{z^2} band. The lack of a transfer mechanism is, however, unlikely since electrical-dipole radiation would link a *d* and a *p* band. One method of checking on the transfer of holes from d_{z^2} to the valence band would be to study the orbital symmetry of holes resulting from the substitution of acceptor defects on the chalcogen sites. The holes on these sites would be associated with the valence band. If, however, there exists a mechanism for transfer of holes from the valence band to the d_{z^2} band and it is energetically favorable for the transfer to occur [as it is in the models of Wilson and Yoffe, Fig. 1(b), and McMenamin and Spicer, Fig. 1(c)], then the holes introduced by the acceptors on the chalcogen sites would be observed to have d_{z^2} orbital character.

In this paper we report EPR measurements on As acceptors both in synthetic MoS_2 (3*R* polytype) crystals and in a natural crystal of MoS_2 (2*H* polytype). The measurements in both types of crystals indeed show that the holes on the As acceptors have d_{z^2} orbital character.

The question of the site location occupied by an As impurity is a very important one in the interpretation of the data. In one of the EPR measurements reported below we observe a spectrum due to a single hole localized at an As impurity. One can conceive of several ways that this can occur. For the sake of simplicity in the discussion we shall denote the charge on the various atoms as if MoS_2 were ionic. MoS_2 is a semiconductor with bonding that is only partially ionic but the discussion is somewhat simplified and no errors made if ionic charge states are used for discussion purposes. One can have a single hole attracted to an As^{3-} ion substitutional on a S^{2-} site. A second possibility is for a single hole to be attracted to an As^{5+} ion on a Mo^{4+} site. Molybdenum in MoS_2 contributes four electrons to bonding bands and the two remaining valence electrons on the Mo are in the nonbonding d_{z^2} band. An As^{5+} ion on a Mo site would therefore result in a single hole. To decide between the two possible substitutional sites for As, one must consider the energetics involved in the substitution. Amongst the criteria to be considered are the bond energy differences (usually expressed in terms of electronegativity differences) and also the size mismatch between the impurity and the ion it replaces. The nature of the bonding, whether covalent or ionic, will affect these quantities. As previously mentioned, the bonding in MoS_2 is intermediate between covalent and ionic. In a table of electronegativities, Gordy and Thomas[9] assign As a value of 2.0 which is approximately halfway between Mo (1.6) and S (2.5). Electronegativity differences do not offer a clear choice between the two substitutional sites. In order to determine the size mismatch both the covalent and ionic radii for the various ions involved are listed in Table I. The radii are taken from the compilation of Dickinson.[10] For either ionic or covalent bonding it will be noticed that there is a much smaller size mismatch when As is substitutional at a sulfur site than at a molybdenum site. This would tend to favor arsenic to be substitutional at a sulfur site.

It is also possible that As occupies an interstitial site, either within an empty trigonal prism in a layer or in the van der Waal's gap between the layers. For As to have a single hole associated with it, an arsenic atom would have to accept two electrons leaving a single hole in its $4p$ shell. Whether the bonding is ionic or covalent, the size of an As^{2-} free ion (~3.5-Å diameter) is considerably larger than the interstitial site within a trigonal prism and it is unlikely that As would occupy that site. While the interstitial site in the van der Waal's gap is capable of expanding to accommodate an As^{2-} ion, there has to date been no success in incorporating acceptor defects into the van der Waal's gap of the transition-metal dichalcogenides. Many metals which donate electrons to the material have been incorporated as well as many organic molecules for which it is has been suggested[11] that electron transfer takes place from the molecule to the layer of the material.

TABLE I. Table of radii[a].

Covalent	Radii (Å)	Ionic	Radii (Å)
Mo	1.37	Mo^{4+}	0.70
As	1.18	As^{5+}	0.47
S	1.04	S^{2-}	1.83
		As^{3-}	1.96

[a]Reference 10.

We therefore conclude that this fact along with size considerations highly favor the S site as the site of an As impurity. Our observation by EPR that the hole attracted to an As impurity is associated with a band with d_{z^2} orbital character is only possible if the d_{z^2} band is the uppermost filled band in MoS_2 and definitely rules out the model of Huisman *et al.* For the EPR spectrum of As in the natural crystal of MoS_2 we were able to observe a hyperfine interaction with the As^{75} nucleus. From the interaction some features of the hole orbit around the As nucleus could be deduced.

EXPERIMENT AND RESULTS

The crystal structure of the layered transiton-metal chalcogenides and of MoS_2 in particular has been fully discussed in the review article of Wilson and Yoffe.[1] The coordination of the six S atoms around a Mo atom is trigonal prismatic. The trigonal prisms are hexagonally packed within a layer, with every other prism containing a Mo atom. The layers are bonded to one another by van der Waals forces. Two stacking polytypes are found for MoS_2. In the $2H$ polytype, two layers are required to form a unit cell. In this polytype the sulfurs in the upper layer are directly above a Mo atom in the lower layer. MoS_2 also has a $3R$ polytype in which three layers are required to form a unit cell. Crystallographic information for both polytypes is given by Wilson and Yoffe.

MoS_2 is about the only layered transition-metal dichalcogenide that is found naturally. Most of the natural crystals are the $2H$ polytype though the $3R$ polytype is sometimes observed in natural crystals.[1] The crystals grown synthetically are always of the $3R$ form.[1]

The natural crystal ($2H$ polytype) used in these experiments is from Queensland Australia with arsenic present as an impurity. Arsenic was first identified from the hyperfine structure in the EPR spectrum. From the intensity of the spectrum the concentration of As was estimated to be of the order of 10^{17} cm^{-3}. This was subsequently verified by optical-emission analysis which showed the As concentration to be about 30 ppm (5×10^{17} cm^{-3}).

The synthetic MoS_2 crystals containing As were grown by the usual vapor-transport techniques with bromine as the transport gas. The crystal growing techniques were reviewed by Wilson and Yoffe.[1] In order for As to be incorporated into the lattice we found it necessary to use As_2S_3 as the doping material. Attempts to grow MoS_2 crystals using As metal as the doping material were unsuccessful. Firing MoS_2 powders with As gave a powdered material which showed an EPR spectrum near $g = 2.0$ but which did not show any anisotropy in the g value.

X-ray analysis of the synthetically grown arsenic-doped MoS_2 crystals showed them to be the 3*R* polytype. The concentration of As in the synthetic crystals was an order of magnitude larger than in the natural crystal.

Both the synthetic and natural crystals were checked for conductivity type by a three-point probe and were found to be *p* type, which indicates that acceptor impurities are dominating the electrical properties in both cases. The EPR measurements were carried out at *X* band at 77 °K.

EPR signals were observed both for the natural MoS_2 crystal and for the synthetic As-doped MoS_2 crystal. In both cases the anisotropy of the g tensor reflects the axial symmetry of the crystals, with the extrema in the g values in directions parallel and perpendicular to the crystal c axis. The $g_\parallel$ and $g_\perp$ values for each case are given in Table II. The g values are accurate to ± 0.001. A small but experimentally significant difference beyond experimental error is noted for the $g_\perp$ values in the 2*H* and 3*R* polytypes. For both types the measured g values, $g_\parallel = 2.025$ and $g_\perp$ near 2.30, are very close to those we reported for Nb acceptors in MoS_2[7] ($g_\parallel = 2.034$ and $g_\perp = 2.279$). The g values in Table II indicate that the holes introduced by the As acceptors in MoS_2 are associated with the d_{z^2} band. The g values associated with the d_{z^2} orbital are altered by a spin-orbit interaction with the d_{xz}, d_{yz} located approximately 1.9 eV above the d_{z^2} band.[1,2] The g values of the spin-orbit modified d_{z^2} orbital are given by

$$g_\parallel = 2, \quad g_\perp = 2 - 6\lambda/\Delta \ , \tag{1}$$

where λ is the spin-orbit coupling parameter for a Mo d hole and Δ is the separation of the d_{z^2} from the d_{xz}, d_{yz} band (1.9 eV). From the g values of Table II and substitution of Δ into Eq. (1), one finds $\lambda = -760$ cm^{-1}. This value of λ for a free Mo d hole is -1030 cm^{-1}.[12] The large reduction is indicative of appreciable covalency in the bonding,[13] as expected for a semiconductor such as MoS_2.

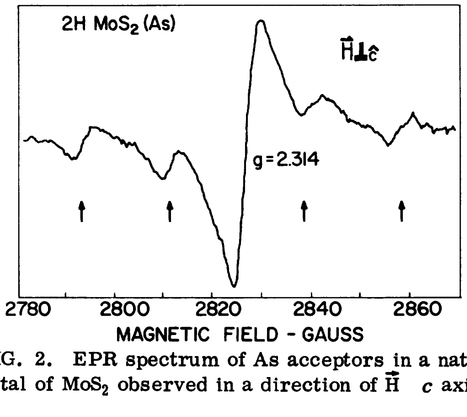

FIG. 2. EPR spectrum of As acceptors in a natural crystal of MoS_2 observed in a direction of $\vec{H}$ c axis.

TABLE II. Arsenic acceptors in molybdenum disulfide.

Crystal	$g_\parallel$	$g_\perp$	A	B (10^{-4} cm^{-1})	Q
2*H*	2.025	2.314	26.5	19.7	9.53
3*R*	2.026	2.302			

The EPR spectrum observed for the As acceptors in the natural crystal of MoS_2 (2*H*) is shown in Fig. 2. The spectrum is taken in a direction for which the magnetic field is oriented perpendicular to the c axis. In addition to the central peak four smaller peaks are observed and are attributed to a hyperfine interaction with the 100% abundant As^{75} nucleus which has a nuclear spin $I = \frac{3}{2}$. One would normally expect for this interaction that only the four hyperfine lines and no central peak would be observed. However, as first shown by Feher[14] for donors in silicon, if the concentration of donors is high enough, electron hopping between donors can occur. The hopping electrons are no longer localized near a donor nucleus and no hyperfine interaction is observed for these electrons. The combination of a central peak and the hyperfine pattern in Fig. 2 is interpreted as arising from both localized (the hyperfine peaks) and delocalized (the central peak) holes associated with a random distribution of As acceptors. To check this interpretation we looked at the EPR spectra in several different crystals taken from the same natural piece of MoS_2. The intensity of the central peak relative to the hyperfine peaks varied from crystal to crystal which would be expected if the concentration and/or distribution of As acceptors varied from sample to sample. Such a variation in intensities would not be expected for the hyperfine pattern associated with an impurity which has a mixture of isotopes, one of which has a nuclear spin-$\frac{3}{2}$ and the remainder with zero nuclear spin. For this case the ratio of the central-peak intensity to the hyperfine peaks would remain constant and be given by the relative isotopic abundance. The concentration of As in our synthetically grown crystals is too large for any holes to be localized around an As impurity. Only a single EPR peak is observed and is due to delocalized holes in these crystals.

The hyperfine spectrum that we observe in the natural crystals results from interactions between the nuclear magnetic-dipole moment and the nuclear electric-quadrupole moment of the As^{75} nucleus and a localized hole. From a study of the variation of the hyperfine spectrum as the angle between the magnetic field and the crystalline c axis is varied, the parameters A and B (magnetic dipole) and Q (electric quadrupole) that characterize the interaction may be determined and are given in Table II.

The theory of the hyperfine interaction for a d_{z^2}

hole was first given by Abragam and Pryce.[15] They express the parameters A and B in terms involving the nuclear gyromagnetic ratio γ, the Bohr magneton μ_B, the nuclear magneton μ_N, and $1/\langle r^3 \rangle$, where r is the radius of the hole orbit around the nucleus:

$$\begin{aligned} A &= \frac{2\gamma\mu_B\mu_N}{\langle r^3 \rangle}\left[(g_{\parallel}-2)+\tfrac{4}{7}-\kappa-\tfrac{1}{7}(g_{\perp}-2)\right] \ , \\ B &= \frac{2\gamma\mu_B\mu_N}{\langle r^3 \rangle}\left[(g_{\perp}-2)-\tfrac{2}{7}-\kappa+\tfrac{1}{14}(g_{\perp}-2)\right] \ , \end{aligned} \qquad (2)$$

where κ is a parameter that describes the contribution of unpaired s electrons to the interaction. This contribution arises because of a spin-dependent exchange between s and d electrons[16] which effectively unpairs the s electrons. The value of κ is usually observed to be near 0.25.[15]

From the experimental ratio of A/B (Table II) one can determine κ from Eqs. (2). The signs of A and B are not determined in the experiment. Assuming the ratio A/B to be negative, we find that $\kappa = 0.265$, in very good agreement with that found in other cases.[15] Substitution of κ back into either of the equations in (2) and substituting $\gamma = 0.96$ for As^{75},[17] we find that $\langle 1/r^3 \rangle = 2.99$ a.u. This value of $\langle 1/r^3 \rangle$ is considerably less than that expected for a free Mo $4d$ electron.[18] One should not, however, expect agreement. The experimental value of $\langle 1/r^3 \rangle$ is for a hole orbit around an As impurity. Although according to the hydrogenic model of Kohn and Luttinger[8] the wave function of the hole contains some d character of the nearby band, the radius of the hole orbit is, in the model of Kohn and Luttinger, given by ϵ/m^* times the hydrogen Bohr radius (one atomic unit), where ϵ is the dielectric constant of the host material and m^* the effective hole mass in units of the free-electron mass m_0. An average value of $\epsilon \sim 11$ is obtained from the data of Wieting and Verble.[19] The effective mass m^* is not known too well but is near unity or less.[1] The hole orbit therefore has a radius of about 11 a.u. which is considerably larger than the 1.3–2.5 a.u. observed for a Mo $4d$ electron depending on the bonding (see Table I). The smaller value of $\langle 1/r^3 \rangle$ that is observed for the hole orbit is consistent with the large radius of that orbit.

Abragam and Pryce[15] also give for a d_{z^2} orbital the equation relating the hyperfine parameter Q and the nuclear electric-quadrupole moment q:

$$Q = \tfrac{3}{7}\left[e^2 q / I(2I-1)\langle r^3 \rangle\right] \ , \qquad (3)$$

where e is the electronic charge and I is the nuclear spin equal to $\frac{3}{2}$ for As^{75}. Equation (3) can be written

$$Q = 1.13\,(q/\langle r^3 \rangle) \ , \qquad (4)$$

where Q is in 10^{-3} cm^{-1}, $1/\langle r^3 \rangle$ in a.u., and q in 10^{-24} cm^{-2}. Substituting $Q = 0.953 \times 10^{-3}$ cm^{-1} and $\langle 1/r^3 \rangle = 2.99$ a.u. we find

$$q = 0.28 \times 10^{-24}\ \mathrm{cm}^2 \ .$$

This value of q is in excellent agreement with the values found by optical spectroscopy by Murakawa[20] (0.27×10^{-24} cm^2) and by Koralkov and Makhanek[21] (0.29×10^{-24} cm^2). It was in fact the excellent fit of the hyperfine data to the nuclear magnetic-dipole moment and nuclear electric-quadrupole moment of As^{75} that led us to unambiguously identify As as the acceptor responsible for the EPR spectrum in our natural crystal of $\mathrm{MoS_2}$. The identification, as mentioned previously, was confirmed by optical-emission analysis and also by our ability to grow a synthetic $\mathrm{MoS_2}$ ($3R$ polytype) doped with As which had a similar EPR spectrum.

DISCUSSION

The important result from these experiments as far as the band structure of $\mathrm{MoS_2}$ is concerned is that the holes introduced by substitution of As impurities on S sites in $\mathrm{MoS_2}$ are associated with the d_{z^2} band. Since the valence band of $\mathrm{MoS_2}$ is made up primarily of electrons on the sulfur ions, substitution of As, with one less electron than S, on a S site should introduce holes into the valence band. If the band structure proposed by Huisman *et al.*[2] [Fig. 1(b)] is valid, then these holes at the top of the valence band would be in their energetically most-favored position and one would expect an EPR spectrum characteristic of holes in the p-like valence band. This is not observed. If, however, the model of Wilson and Yoffe[1] [Fig. 1(a)] or as modified by McMenamin and Spicer[3] [Fig. 1(c)] are the valid models, then holes introduced into the valence band would be expected to be found in the energetically more favored and filled d_{z^2} band, provided a suitable mechanism for transfer exists. The EPR data on the As acceptors in $\mathrm{MoS_2}$ therefore clearly establish the d_{z^2} band as the highest filled band in $\mathrm{MoS_2}$.

The establishment of the d_{z^2} band as the highest-filled band does point out a need for clarification of the nature of the conductivity processes in a d band in $\mathrm{MoS_2}$. Hole mobilities as high as 100 cm^2/V sec have been observed in p-type $\mathrm{MoS_2}$.[1,7] Mobilities as high as this are more usually associated

TABLE III. EPR data on acceptors in $\mathrm{MoS_2}$.

Acceptor	g	$g_{\perp}$	Ref.
Zr ($3R$) (powder sample)	2.03	2.24	a
Nb ($3R$)	2.034	2.279	b
As ($3R$)	2.026	2.302	c
As ($2H$)	2.025	2.314	c
V ($3R$)	2.030	2.268	a

[a] F. Mehran, R. S. Title, and M. W. Shafer (unpublished).

[b] Reference 7.

[c] This paper.

with a p-like band rather than a d band. There is a need for more experimental data on electrical conductivity in MoS_2 in order to clarify the nature of the conductivity.

The acceptors in MoS_2 for which EPR signals have been observed is summarized in Table III. The $g_\parallel$ values are all near 2.03, whereas $g_\perp$ varies from 2.24 to 2.314. The variation in the g values from acceptor to acceptor is similar to the chemical shifts observed for donors and acceptors in silicon and germanium.[14] Phillips[22] has shown that these shifts arise from strain perturbations. The small deviations of $g_\parallel$ from 2 are probably due to a number of factors such as hybridization of the d_{z^2} orbital and other second-order admixtures possibly as a result of dynamic Jahn-Teller effect.

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[1] J. A. Wilson and A. D. Yoffe, Adv. Phys. **18**, 193 (1969).

[2] R. Huisman, R. de Jonge, C. Haas, and F. Jellinek, J. Solid State Chem. **3**, 56 (1971).

[3] J. C. McMenamin and W. E. Spicer, Phys. Rev. Lett. **29**, 1501 (1972).

[4] R. H. Williams, J. M. Thomas, M. Barber, and N. Alford, Chem. Phys. Lett. **17**, 142 (1972).

[5] R. A. Bromley, R. B. Murray, and A. D. Yoffe, J. Phys. C. **5**, 759 (1972).

[6] D. R. Edmondson, Solid State Commun. **10**, 1085 (1972).

[7] R. S. Title and M. W. Shafer, Phys. Rev. Lett. **28**, 808 (1972).

[8] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).

[9] W. Gordy and W. J. O. Thomas, J. Chem. Phys. **24**, 439 (1956).

[10] S. K. Dickinson, Jr., Air Force Cambridge Research Laboratory (AFCRL) Report No. 70-0727, December,1970 (unpublished).

[11] E. Ehrenfreund, A. C. Gossard, and F. R. Gamble, Phys. Rev. B **5**, 1708 (1972).

[12] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. of Std. Circular No. 467 (U.S. GPO, Washington, D.C., 1958), Vol. III.

[13] J. Owen and J. H. M. Thornley, Rep. Prog. Phys. **29**, 675 (1966).

[14] G. Feher, Phys. Rev. **114**, 1219 (1959).

[15] A. Abragam and M. H. L. Pryce, Proc. R. Soc. A **205**, 135 (1951); Proc. R. Soc. A **206**, 164 (1951); see also A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford U. P., New York, 1970), p. 456.

[16] V. Heine, Phys. Rev. **107**, 1002 (1957); J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957); R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

[17] *American Institute of Physics Handbook*, 3rd ed. (McGraw-Hill, New York, 1972), pp. 8–21.

[18] A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1965), Vol. II A, p. 167.

[19] T. J. Wieting and J. R. Verble, Phys. Rev. B **3**, 4286 (1971).

[20] K. Murakawa, Phys. Rev. **110**, 393 (1958).

[21] V. S. Korolkov and A. G. Makhanek, Opt. Spektrosk. 12, 163 (1962) [Opt. Spectrosc. 12, 87 (1962)].

[22] J. C. Phillips, Phys. Rev. Lett. **24**, 1114 (1970).

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Millimeter-Wave Determination of Photoinjected Free-Carrier Concentrations in Highly Excited GaAs

R. F. Leheny, R. E. Nahory, and M. A. Pollack
Bell Telephone Laboratories, Holmdel, New Jersey 07733

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Measurements of millimeter-wave reflection are reported for optically injected free carriers in GaAs at 300 °K for high levels of uv laser excitation. This reflection responds directly to the total number of free carriers, giving 10^{14} electrons/cm^2 at an incident flux of 2.7×10^{23} photons/cm^2 sec. These results yield an injected free electron-hole lifetime $\tau\backsim0.5$ nsec for both pure and compensated material.

We report room-temperature time-resolved measurements of photoinduced changes in millimeter-wave reflection from *highly excited* GaAs. There is currently considerable interest in the properties of *highly excited* optically pumped semiconductors.[1] Measurements for such systems are made difficult because the high injected carrier densities only exist for short times and near the crystal surface.[2–4] Early reported attempts to determine carrier concentrations for high excitation levels are the measurements of Galkin *et al.*,[2] who describe reflection changes at $\lambda = 10.6$ μm in crystals pumped by a ruby laser. Vakhnenko and Strizhevskii[3] have analyzed these results using a plasma-reflection model, taking account of modifications required because the resonance occurs in a thin inhomogeneous layer. The method described here is similar in theory to these ir measure-