PHYSICAL REVIEW VOLUME 140, NUMBER 2A 18 OCTOBER 1965

Optical Absorption of a Few Unit-Cell Layers of MoS_2

R. F. FRINDT*
Physics and Chemistry of Solids, Cavendish Laboratory, Cambridge, England

(Received 26 March 1965)

An experimental study of the absorption edge of single crystals of MoS_2 down to a thickness of a few unit-cell layers has been carried out. With crystals less than 30 Å thick, the strong absorption peak in the red part of the spectrum disappears. Structure on the short-wavelength side of this peak disappears at a thickness of about 125 Å. These changes may be due to exciton size effects. The strength of a peak in the orange part of the spectrum is independent of thickness, down to the thickness of a few unit-cell layers. A new peak is observed with crystals less than 50 Å thick.

INTRODUCTION

As the thickness of a crystal decreases, the influence of the surfaces on the crystal properties should become apparent. It should be possible to study the surface regions directly with very thin crystals, since a favorable surface-to-bulk ratio can be obtained. With this end in view, a study of very thin crystals of layer structures was undertaken, and the work presented here summarizes an experimental study of the optical absorption of the layer structure MoS_2 down to a thickness of a few unit-cell layers (the thickness of a unit-cell layer is 12.3 Å).

The optical absorption of MoS_2 crystals has been studied in some detail by Frindt and Yoffe.[1] At room temperature, strong peaks are observed on the main absorption edge in the red part of the spectrum at 6660 and 6050 Å (called peak A and peak B respectively). At low temperatures, more structure (A_2 and A_3) is observed on the short-wavelength side of peak A. The absorption peaks have been attributed to the formation of exciton states close to the conduction band. Assuming spherical symmetry and Mott's model of an exciton,[2,3] exciton radii of 20 and 80 Å have been calculated for peaks A and A_2.[1] If these radii are correct, a weakening of the absorption peaks is expected with decreasing crystal thickness; however, no changes have been observed in the spectrum of a MoS_2 crystal slightly less than 100 Å thick at room temperature.[1] The main absorption edge of cooled MoS_2 crystals has now been studied down to a thickness of about two unit cell layers. It is found that the absorption changes with decreasing crystal thickness.

EXPERIMENTAL METHODS

Very thin single crystals of natural MoS_2 have been prepared by a cleavage technique. Crystals in the thickness range 500 to 1000 Å can be obtained by cleaving them from the face of a large crystal.[1] When such crystals are put onto a smooth transparent substrate such as fused quartz or mica, they are flattened to the substrate surface by strong attractive forces. If a crystal is then peeled away from the substrate using adhesive tape, extremely thin crystal layers sometimes remain intact on the substrate. Crystal thickness measurements down to about 100 Å have been made using multiple-beam interference techniques,[1] and platinum shadowing and electron microscopy has been used to measure thicknesses less than 100 Å (a detailed description of such thickness measurements is given elsewhere).[4] Because of mechanical instability, crystals less than about 1000 Å thick must be supported by a substrate. Various glues and cements can also be used as crystal substrates; crystals of $Bi_8Te_7S_5$ having a thickness less than one unit-cell layer have recently been prepared in this way.[5]

Only small crystal areas of MoS_2 have been obtained, so that for absorption measurements a microscope objective was used to produce a magnified image of the crystal on the slit of a monochromator. With such an arrangement, the incident light intensity can be measured by moving the image of the crystal away from the monochromator slit, so that absolute values of the transmission could be measured with a crystal area as small as 0.3μ by 10μ. In general, the areas studied were about 1μ wide and 30μ long. A Hilger and Watts D187 glass monochromator was used along with a tungsten-filament light source, a mechanical light chopper, a photomultiplier and an amplifier tuned to the frequency of the chopped light. The spectra were studied with the crystal cleavage plane perpendicular to the direction of the incident light ($E\perp c$) and unless otherwise stated the crystals were lying on a fused quartz substrate. The crystals could be cooled by mounting the quartz substrate over a hole in the cold finger of a Dewar. The actual crystal temperatures were estimated from the positions of the absorption peaks (a shift of 160 Å to shorter wavelengths is observed[1] for peaks A and B when an 800 Å-thick MoS_2 crystal on a quartz substrate is cooled from room temperature to 77°K).

The thicknesses of the crystals used for Figs. 1 to 5

---

* Present address: Department of Physics, Simon Fraser University, Burnaby 2, British Columbia, Canada.

[1] R. F. Frindt and A. D. Yoffe, Proc. Roy. Soc. (London) **A273**, 69 (1963).

[2] N. F. Mott, Proc. Roy. Soc. (London) **A167**, 384 (1938).

[3] S. Nikitine, *Progress in Semiconductors*, edited by A. F. Gibson, F. A. Kröger, and R. E. Burgess (Heywood and Company Ltd., London, 1962), Vol. 6, p. 248.

[4] R. F. Frindt, J . Appl. Phys. (to be published).

[5] H. H. Soonpaa, Bull. Am. Phys. Soc. **10**, 364 (1965).

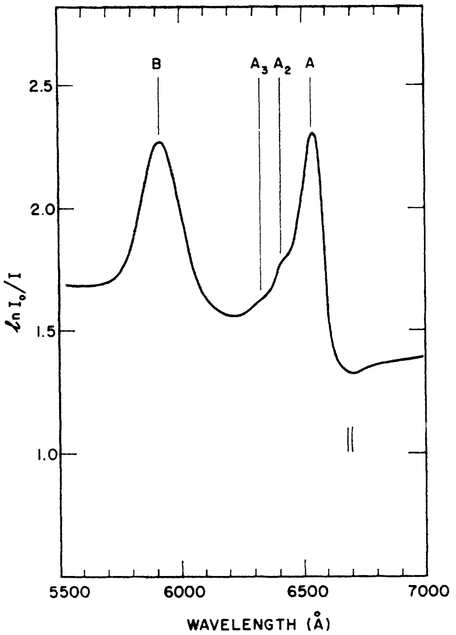

FIG. 1. Plot of absorption against wavelength for a cooled MoS_2 crystal about 500 Å thick. The ratio $I_0/I = 100/T$, where T is the percentage transmission. Peak A is at 6545 Å and B is at 5925 Å. Vertical lines indicate the expected wavelengths of A_2 and A_3. The experimental resolution which is shown below the curve is the same for all of the remaining curves. Estimated crystal temperature is 135°K.

were obtained from a plot of the room temperature transmission against thickness at a wavelength of 6400 Å.[1]

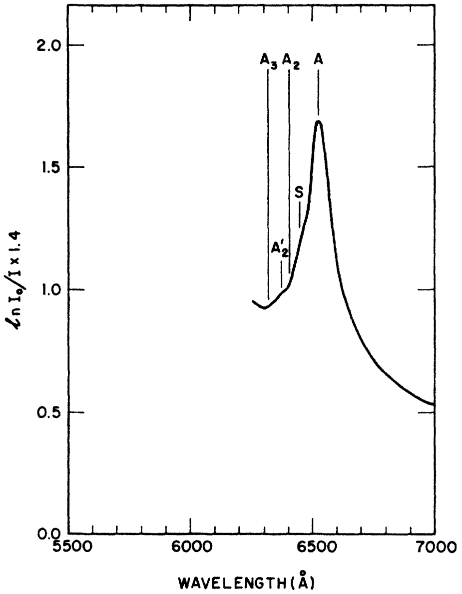

FIG. 2. Plot of absorption against wavelength for a cooled MoS_2 crystal about 100 Å thick. A is at 6530 Å, S is at 6450 Å and A_2' is at 6375 Å. The expected wavelengths of A_2 and A_3 are also shown. Estimated crystal temperature is 120°K.

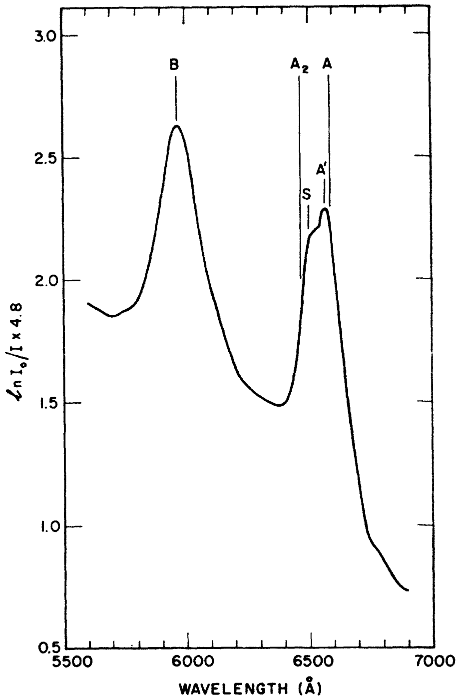

FIG. 3. Plot of absorption against wavelength for a cooled MoS_2 crystal about 55 Å thick. A' is at 6575 Å, S is at 6510 Å, and B is at 5980 Å. The expected wavelengths of A and A_2 are also shown. Estimated crystal temperature is 175°K.

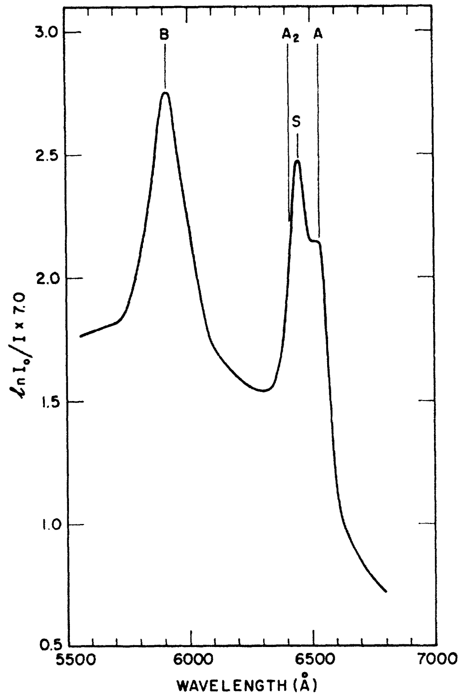

FIG. 4. Plot of absorption against wavelength for a cooled MoS_2 crystal about 45 Å thick. S is at 6455 Å and B is at 5920 Å. The expected wavelengths of A and A_2 are also shown. Estimated crystal temperature is 120°K.

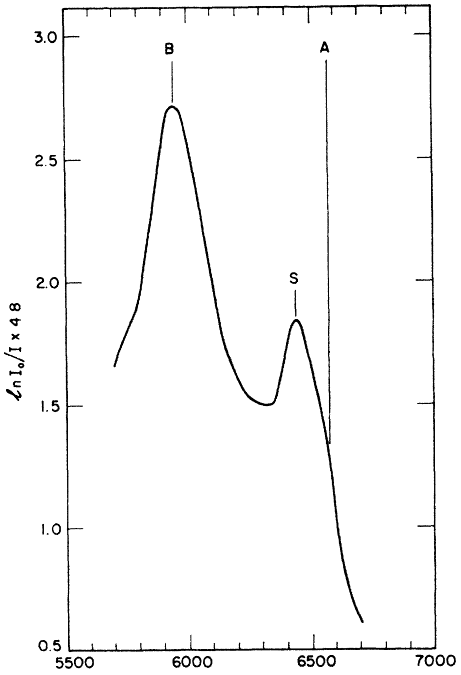

FIG. 5. Plot of absorption against wavelength for a cooled MoS_2 crystal about 30 Å thick. S is at 6440 Å and B is at 5955 Å. The expected wavelength of A is also shown. Estimated crystal temperature is 170°K.

EXPERIMENTAL RESULTS

The absorption of a cooled MoS_2 crystal about 500 Å thick is shown in Fig. 1. As observed previously, two strong absorption peaks called A and B are seen, with more structure (A_2 and A_3) on the short-wavelength side of A. The expected wavelengths of A_2 and A_3 are shown in Fig. 1 using data for thicker crystals at 77 and 4°K, where the spacing of A and A_2 is about 125 Å and the spacing of A_2 and A_3 is about 85 Å. Peak A_2 in Fig. 1 is observed at the expected wavelength, but A_3 is not well resolved.

Figure 2 shows the absorption of a crystal about 100 Å thick. Peak A_2 is no longer observed at the expected wavelength, but a very weak peak (A_2') is seen about 30 Å to shorter wavelengths. A weak absorption (S) is also seen. With a crystal about 200 Å thick, A_2' is considerably stronger, the shift of A_2' is only about 15 Å and no absorption is seen at S. The value of $\ln I_0/I$ is multiplied by a constant in Figs. 2 to 5 to allow a comparison of the spectra to be made.

The absorption of a crystal about 55 Å thick is shown in Fig. 3. Peak S is now quite strong and A_2 is no longer observed. The expected wavelength of A was obtained from the separation of A and B in Fig. 1. In Fig. 4, which shows the absorption of a crystal about 45 Å thick, S is now stronger than A. Peak A has practically disappeared in Fig. 5, which shows the spectrum of a crystal about 30 Å thick. The uncooled positions of S and B for this crystal are 6535 and 6130 Å, so that cooling shifts S by 95 Å and B by 175 Å.

The spectrum of an uncooled crystal 25 to 30 Å thick supported only by a platinum film has been studied and peaks B and S are observed at 6110 and 6485 Å. The crystal thickness was measured in an electron microscope using platinum shadowing.[4]

DISCUSSION

The peaks A, A_2, A_3, and B observed on the absorption edge of MoS_2 have been attributed to the formation of exciton states close to the conduction band.[1] If spherical symmetry and Mott's model of a hydrogen-like exciton[2,3] are assumed, the radius of the $n=1$ exciton (peak A) is about 20 Å, and the radius of the $n=2$ exciton (peak A_2) is about 80 Å.[1] With very thin crystals, some dependence of peak strength on thickness might be expected. The results show that the spectrum does depend on crystal thickness. Peak A starts to weaken at a thickness of about 50 Å and is no longer seen with a crystal about 30 Å thick. At a thickness of about 200 Å, peak A_2 starts to weaken and at 100 Å, it is no longer observed. This thickness dependence suggests that the weakening of peaks A and A_2 may be an exciton size effect. A similar weakening of exciton lines with decreasing crystallite size has been observed in the spectrum of CuI films.[6] Exciton size effects and other factors which could influence the spectrum of small crystallites have recently been discussed by Satten and Nikitine.[7]

In contrast to the behavior of peaks A and A_2, there is no indication that the absorption at peak B is strongly dependent on crystal thickness, down to a few unit-cell layers. This is consistent with recent results which indicate that the exciton radius for peak B is about 8 Å.[8] It is of interest that a transmission minimum at 6000 Å has been observed with crystals of the layer structure $Bi_8Te_7S_5$ having a thickness of one-third of a unit cell.[5]

A new absorption peak (S) has been observed with very thin crystals of MoS_2. For crystals less than 50 Å thick, the absorption coefficient at peak S is about 10^5 cm^{-1}, and as the thickness increases from about 50 Å, the absorption at S decreases. It can be said therefore, that either the absorption at S is present only with crystals less than about 50 Å thick, or that S is present at all thicknesses, but is only observable with very thin crystals. The latter possibility implies an absorption that extends into the crystal from the surfaces to a depth of about 25 Å or two unit cell layers. The shift in the position of S on cooling is about half that observed for peak B (Fig. 5). The origin of the

---

[6] S. Nikitine, L. Wenger-Wursteisen, and J. P. Eberhart, Physik Kondensierten Materie 2, 355 (1964).

[7] R. A. Satten and S. Nikitine, Physik Kondensierten Materie 1, 394 (1963).

[8] B. L. Evans and P. A. Young, Proc. Roy. Soc. (London) A284, 402 (1965).

absorption at S is not clear. The possibility of a strain effect must be considered since strain introduced by the contact between a crystal and its substrate can shift the positions of the absorption peaks. The separation of peaks A and B is 610 Å at 273 and 77°K for an unstrained crystal[1]; the separation of A and B in Fig. 1 is 620 Å, so that the strain introduced by cooling does not significantly affect the peak separation. This indicates that the absorption at S is not caused by crystal strain. The spectrum of a 25 to 30 Å thick crystal which was not on a quartz substrate gives support to this.

Brebner[9] has suggested that the absorption peaks observed with layer structures may be due to the excitation of electrons to "self-trapped" states in the conduction band, however it is not known if such a model could explain the thickness effects observed with MoS_2. There is a need for detailed theoretical work on the optical properties of MoS_2 and other related layer structures.

ACKNOWLEDGMENTS

The author would like to thank Dr. F. P. Bowden, C.B.E., F.R.S., and Dr. A. D. Yoffe for their interest in this work, the Royal Commissioners for the Exhibition of 1851 for the award of a Senior Studentship, and D.S.I.R. for a grant to the laboratory.

---

[9] J. L. Brebner, J. Phys. Chem. Solids 25, 1427 (1964).

PHYSICAL REVIEW VOLUME 140, NUMBER 2A 18 OCTOBER 1965

Influence of Lead Impurity on the Low-Temperature Color-Center Production in KCl†

E. Sonder and W. A. Sibley
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received 21 May 1965)

The growth of optical absorption bands in the visible and ultraviolet as a function of 1.5-MeV electron irradiation at liquid-nitrogen temperature has been measured for high-purity and lead-doped KCl. Dissolved lead causes the coloration near 360 nm to be enhanced; the rate of growth increases monotonically with Pb concentration, in agreement with previous studies of trapped holes. The *F* coloration is also enhanced by small amounts of impurity; however, the *F*-growth enhancement saturates at impurity levels of 20–100 ppm lead. An actual lowering of the *F*-center production rate is observed when samples doped with more than 100 ppm lead are used. This lowering is shown to be due to an increase in the α-center-to-*F*-center ratio in highly doped KCl. An explanation is proposed for the increased *F*-center coloration in terms of interstitial–*F*-center recombination and interstitial stabilization by the impurities.

INTRODUCTION

In this paper we report results of a detailed investigation of the liquid nitrogen temperature coloration of pure and doped alkali halides. The room temperature *F*-center colorability has been studied rather extensively[1] so that the impurity dependence of the early stage,[2] as well as the intensity dependence[3] and trace impurity suppression of the late stage,[4] have been amply demonstrated. Alkali halides irradiated at low temperatures have been shown to exhibit greatly diminished cation impurity dependence,[2] especially when the irradiations were performed at liquid helium temperatures. Recent evidence for iodides[5] indicates that even at these very low temperatures there is a degree of sample dependence. Moreover, below liquid nitrogen temperature, stable alpha centers (negative ion vacancies) are formed. They are the predominant radiation defect at 5°K, i.e., *F* centers are produced in relatively smaller numbers. The production behavior and stability of alpha centers is complex and depends upon anion impurities.[6,7] A very small change in the α center/*F* ratio, due to purely electronic effects would thus greatly influence the measured *F*-center production efficiency. Above 50°K, very few α centers are produced.[7] Therefore, we restrict our attention to the effect of impurity on *F*-center production at liquid nitrogen temperature.

Many of the samples are from ingots previously used for room temperature irradiations[4] in order to make comparison more meaningful. The production of trapped holes[8] (V_K centers) as well as of *F* centers was measured. There is a surprisingly large influence of impurity on *F* colorability and, where at room temperature impurities suppress the late stage,[4] we observed that they

---

† Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[1] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962).

[2] H. Rabin and C. C. Klick, Phys. Rev. 117, 1005 (1960).

[3] E. Sonder and W. A. Sibley, Phys. Rev. 129, 1578 (1963).

[4] W. A. Sibley, E. Sonder, and C. T. Butler, Phys. Rev. 136, A537 (1964).

[5] T. P. P. Hall, D. Pooley, and P. T. Wedepohl, Proc. Phys. Soc. (London) 83, 635 (1964).

[6] H. Bauser and F. Lüty, Phys. Status Solidi 1, 608 (1961).

[7] N. Itoh, B. S. H. Royce, and R. Smoluchowski, Phys. Rev. 137, A1010 (1965); 138, A1766 (1965).

[8] W. Kanzig and T. O. Woodruff, J. Phys. Chem. Solids 9, 70 (1958).