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Anisotropic optical-absorption studies of NbS_2 single-layer suspensions aligned in a magnetic field

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Optical-absorption spectra for **E** parallel and perpendicular to the layers have been measured for NbS_2 single layers in the range from 1.8 to 3.1 eV by aligning particles in a water suspension using a magnetic field. A large weakening of the interband transition at 2.7 eV is observed in **E** perpendicular to the layers, consistent with recent theory on the absorption anisotropy of single-layer NbS_2. The particle alignment in the magnetic field indicates that the magnetic susceptibility perpendicular to the layers is enhanced over the bulk value, in agreement with recent theory for single-layer NbS_2.

I. INTRODUCTION

For some time there has been a wide interest in two-dimensional systems from both a theoretical and experimental point of view. We report here on a study of the optical anisotropy of oriented single-layer suspensions of the metallic layered compound NbS_2. We believe that this is the first study on the anisotropy of isolated single layers of a solid.

NbS_2 is one of the transition-metal dichalcogenide (TMD) layered compounds, a group of materials much studied because of their charge-density wave formation and intercalation properties.[1,2] The TMD's are often considered to be two dimensional because of the high anisotropy resulting from strong bonding in the layers and weak interlayer interactions. The effect of interlayer interactions on the band structure have been explored theoretically;[3–5] however, an experimental probe of layered compounds with and without interlayer interactions would be of considerable interest. In this regard we believe that studies on single layers can uniquely contribute to the understanding of layered materials. The NbS_2 structure studied here consists of stacks of molecular sheets or layers which we call "single layers." Each single layer is composed of a sandwich of Nb sheets between two S sheets. In the bulk NbS_2 starting material the unit cell consists of two single layers with the *ABAB* stacking.[6]

Optical studies of the TMD's have provided a great deal of information about the electronic properties and band structures of layered compounds.[6–8] But these studies are primarily confined to measurements with the incident light normal to the layers ($\mathbf{E}\parallel$ layers). The only measurements available on metallic layered compounds for $\mathbf{E}\perp$ layers are reflectivity measurements performed normal to the "edge" plane of as-grown crystals.[8] Such work is severely limited by the availability of suitable crystal edges. In this paper we use a novel method for studying the optical anisotropy of the layer materials—aligning small crystal platelets in suspension in a magnetic field—and report the experimental results for NbS_2 single-layer suspensions. It is well known that materials with a large anisotropy in the magnetic susceptibility χ tend to align with the greater χ direction parallel to the field. For example, $2H$-TaS_2 crystals have a greater susceptibility in the direction perpendicular to the crystal layers[9] ($\chi_\perp/\chi_\parallel$ is around 2.2–2.5) and thus TaS_2 platelets tend to align with the layers perpendicular to the field. A similar situation arises for NbS_2 platelets as is easily confirmed by suspending an NbS_2 single crystal in a magnetic field.

NbS_2 single-layer suspensions can be obtained by intercalation of hydrogen and water followed by ultrasonic dispersion.[10,11] The optical absorption of dilute NbS_2 single-layer water suspensions was measured from 1.77 to 3.1 eV at room temperature for both $\mathbf{E}\parallel\mathbf{B}, \mathbf{k}\perp\mathbf{B}$ and $\mathbf{E}\perp\mathbf{B}, \mathbf{k}\perp\mathbf{B}$ up to fields of 23 kG (for high fields this means approximately $\mathbf{E}\perp$ layers and $\mathbf{E}\parallel$ layers, respectively).

II. EXPERIMENT

Single-layer suspensions of NbS_2 were prepared by intercalation of hydrogen and deionized water into NbS_2 crystals followed by ultrasonic dispersion as described elsewhere.[11] For optical absorption studies dilute suspensions of about 0.05 mg of NbS_2 per ml were used. The particle lateral sizes, measured in an electron microscope, were in the range 50–300 nm with a typical lateral size of about 200 nm. The suspensions studied lasted for two weeks without serious flocculation. The basic optical arrangement used a double-beam setup with two chopping frequencies. A pair of quartz optical cells with a 10-mm path length were used as the sample and reference cells. They were fixed one over the other in the same vertical plane in the horizontal magnetic field. A schematic diagram showing the alignment of

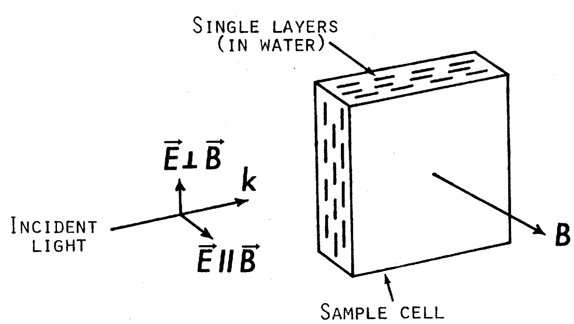

FIG. 1. Schematic diagram showing the alignment of single-layer NbS_2 (represented by short lines) in water in a magnetic field. The directions of the polarized incident light and the magnetic field are also shown. The diagram indicates that the layers tend to orient such that they are nearly perpendicular to the magnetic field.

NbS_2 single layers in a magnetic field and the relationship between the directions of the polarized light and the magnetic field is shown in Fig. 1.

III. RESULTS AND DISCUSSION

Figure 2 shows the absorption spectrum of a single-layer NbS_2 suspension for $B=0$ and 23 kG for $\mathbf{E}\parallel\mathbf{B}$ and $\mathbf{E}\perp\mathbf{B}$. When $B=23$ kG, a large difference is seen for the interband absorption peak height at 2.7 eV for $\mathbf{E}\parallel\mathbf{B}$ and $\mathbf{E}\perp\mathbf{B}$. The main peak height for $\mathbf{E}\perp\mathbf{B}$ is about 9 times that for $\mathbf{E}\parallel\mathbf{B}$, while the main peak height for $B=0$ is exactly in between. Figure 3 shows the relation of the absorption peak height (I_0/I at $\lambda=460$ nm) versus magnetic field for both $\mathbf{E}\parallel\mathbf{B}$ and $\mathbf{E}\perp\mathbf{B}$. It is clear that the observed optical effects are due to a particle orientation. The response time of particle rotation was observed to be about a second. The alignment of the particles is compromised by the thermal fluctuation of the particles in water; however, the tendency for the absorption curves to saturate clearly indicates that there is significant alignment of the NbS_2 single layers at 23 kG.

The absorption anisotropy of a suspension of optically anisotropic platelets has been treated by Li *et al.*[12] For absorption constants $\alpha_\perp$ and $\alpha_\parallel$ (for $E_\perp$ and $E_\parallel$ to the plane of the platelet) one has for $\mathbf{E}\parallel\mathbf{B}$:

$$-dI_{\parallel\mathbf{B}}=(\alpha_\perp\cos^2\theta+\alpha_\parallel\sin^2\theta)I\frac{\rho(\theta)d\Omega}{\int\rho(\theta)d\Omega}dt\ , \qquad (1)$$

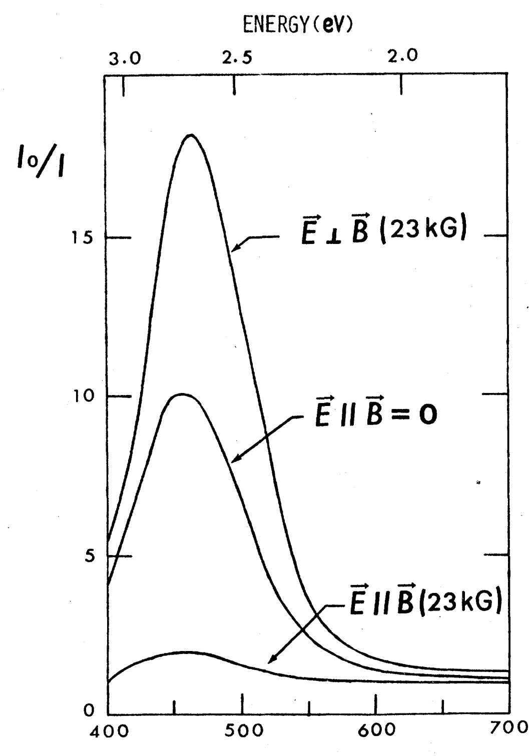

FIG. 2. Optical absorption of an NbS_2 single-layer suspension in a 23 kG magnetic field for $\mathbf{E}\parallel\mathbf{B}$ and $\mathbf{E}\perp\mathbf{B}$, compared with that in zero field.

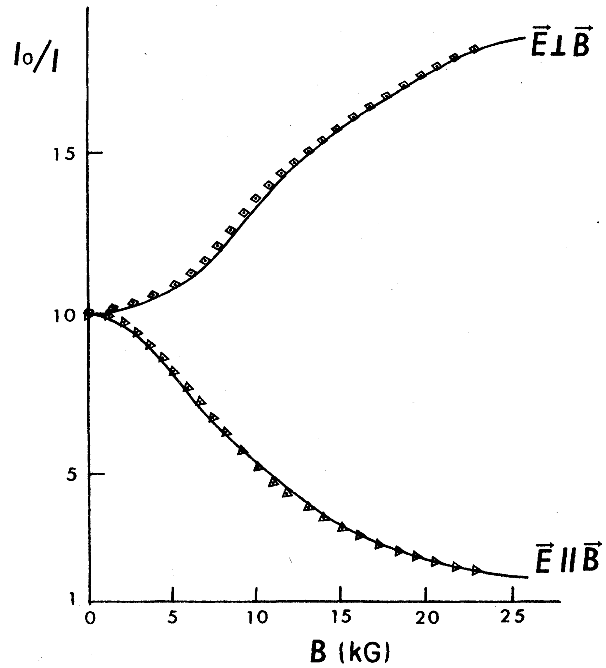

FIG. 3. Single NbS_2 layer absorption peak height (I_0/I at $\lambda=460$ nm) vs magnetic field for both $\mathbf{E}\parallel\mathbf{B}$ and $\mathbf{E}\perp\mathbf{B}$ polarized incident light. Points: experimental data. Solid lines: a computer fitting by Li *et al.* (Ref. 12).

where I is the intensity, θ the angle between the platelet normal and $\mathbf{B}$, t the platelet thickness, and $\rho(\theta)$ the probability that the platelet normal is in the solid angle $d\Omega$. $\rho(\theta)$ depends on B and the sample magnetic anisotropy and is given by

$$\rho(\theta)\propto\exp\left(\frac{VB^2}{\mu_0 k_B T}\right)[\chi_\parallel+(\chi_\perp-\chi_\parallel)\cos^2\theta]\ , \qquad (2)$$

where $\chi_\parallel$ and $\chi_\perp$ are the magnetic susceptibilities parallel and perpendicular to the layers and V is the platelet volume.

Integration of Eq. (1) over Ω and t gives

$$\frac{I_0}{I_{\parallel\mathbf{B}}}=\exp[\alpha_\parallel-(\alpha_\parallel-\alpha_\perp)\langle\cos^2\theta\rangle]t\ , \qquad (3)$$

$$\langle\cos^2\theta\rangle=\frac{\int\cos^2\theta\rho(\theta)d\Omega}{\int\rho(\theta)d\Omega}\ , \qquad (4)$$

where I_0 is the incident intensity.

A similar expression can be obtained for $\mathbf{E}\perp\mathbf{B}$:

$$\frac{I_0}{I_{\perp\mathbf{B}}}=\exp\left(\frac{\alpha_\perp+\alpha_\parallel}{2}+\frac{\alpha_\parallel-\alpha_\perp}{2}\langle\cos^2\theta\rangle\right)t\ . \qquad (5)$$

This treatment ignores refraction, reflection, and demagnetization effects of the single layers. It can be shown from Eqs. (3) and (5) that

$$\ln(I_{\parallel B}/I_{\parallel B=0})/\ln(I_{\perp B=0}/I_{\perp B})=2$$

and this can be used as a test of the theory. From Fig. 2 we obtain a value of 2.7 at the peak absorption, in reasonable agreement with theory, considering the assumptions made.

A computer fit using Eqs. (3), (4), and (5) has been made[12] and the result is shown in Fig. 3. This fit leads to a magnetic anisotropy $(\chi_{\perp} = \chi_{\parallel}) = 25\times 10^{-6}$ (CGS units) for single-layer NbS_2, where a layer thickness of 0.6 nm and a typical lateral dimension of 200 nm were used (a calculation[12] using a distribution of lateral sizes including the range 50–300 nm gives essentially the same result). This value of $(\chi_{\perp} - \chi_{\parallel})$ is about 4 times larger than the experimental value 6.2×10^{-6} for bulk $2H$-TaS_2.[9] Bulk values for $2H$-NbS_2 are not available but we expect that they are close to that for $2H$-TaS_2. Thus the anisotropy of single-layer NbS_2 appears to be a few times larger than that for comparable bulk layered compounds.

Recent calculations by Li *et al.*[12] of the band structure for single-layer NbS_2 have been carried out using a tight-binding model with zero interlayer interaction, and the magnetic susceptibility of single-layer NbS_2 has been calculated. The results of this calculation give a $\chi_{\parallel}$ that is relatively unchanged from the expected bulk value and an increase in $\chi_{\perp}$ of a factor of about 3 over the expected bulk value. This increase is consistent with the increase in the magnetic anisotropy required to account for the observed alignment of the single-layer NbS_2 suspensions in a magnetic field. The enhancement in magnetization comes mainly from the band narrowing and increase in density of states at the Fermi level for single-layers. It is of interest to note that calculations for isolated Ni monolayers also indicate an enhancement of magnetization.[13,14]

Since the layers of NbS_2 are nearly aligned perpendicular to **B** at high fields, it is reasonable to say that the main peak height for $\mathbf{E}\parallel$layers $(\mathbf{E}\parallel\mathbf{L})$ is about 9 times that for $\mathbf{E}\perp$layers $(\mathbf{E}\perp\mathbf{L})$ according to Fig. 2. To express the absorption peak in terms of the absorption coefficient α, we can assume that α is the same for the case of $\mathbf{E}\parallel\mathbf{L},\mathbf{k}\parallel\mathbf{L}$ and for that of $\mathbf{E}\parallel\mathbf{L}$, $\mathbf{k}\perp\mathbf{L}$ and assume in our experiment the "effective thickness" of the sample is the same for both $\mathbf{E}\parallel\mathbf{L},\mathbf{k}\parallel\mathbf{L}$ and $\mathbf{E}\perp\mathbf{L},\mathbf{k}\parallel\mathbf{L}$ (this ignores "refraction" by the single layers). Using a value of $\alpha_{\parallel}$ of 6.5×10^5 cm^{-1} at the main absorption peak for NbS_2 for $\mathbf{E}\parallel\mathbf{L},\mathbf{k}\perp\mathbf{L}$,[15] and neglecting reflection and scattering effects, which we do not expect to be significant for very high values of the absorption constant, we can estimate that the sample effective thickness is about 45 nm. This gives an $\alpha_{\perp}$ of about 1.6×10^5 cm^{-1} for $\mathbf{E}\perp\mathbf{L}$ at the main peak. That is, $\alpha_{\parallel}/\alpha_{\perp}$ is about 4 at 2.7 eV. Calculations have been carried out recently by Li *et al.*[12] on the optical absorption of single-layer NbS_2 taking into account polarization effects where both joint density of states and oscillator strengths are calculated (including oscillator strengths is essential to give agreement with experiment). They consider (below 5 eV) only transitions from the occupied "p/d" valence band to the half-filled "dz^2" conduction band[15] and obtain a value for $\alpha_{\parallel}/\alpha_{\perp}$ of about 3 at 2.7 eV, in reasonable agreement with our results. No such calculations have been carried out to date on the optical anisotropy of bulk NbS_2 or other layered compounds.

It is of interest to compare our measurements on single-layer NbS_2 with the anisotropic reflectivity from the edge of crystals of $2H$-$NbSe_2$ and $3R$-NbS_2.[8] We note that for $2H$-$NbSe_2$ there is a weakened reflectivity peak at 2.5 eV for $\mathbf{E}\perp\mathbf{L}$ relative to $\mathbf{E}\parallel\mathbf{L}$, and for $3R$-NbS_2 a strongly suppressed reflectivity peak is observed for $\mathbf{E}\perp\mathbf{L}$. The strong suppression of the transition for $\mathbf{E}\perp\mathbf{L}$ for both the $3R$-NbS_2 and the single-layer NbS_2 results gives support to the view[7] that the $3R$ structure with an *ABCABC* stacking for the Nb atoms is more "two dimensional" than the $2H$ structure with its in-line Nb stacking.

IV. CONCLUSION

The alignment of NbS_2 single layers in suspension in a magnetic field has been observed using the anisotropy in the optical absorption of an interband transition at 2.7 eV. The results indicate that the magnetic susceptibility perpendicular to the layers is enhanced over the bulk value, in reasonble agreement with recent theory on single-layer NbS_2. The weak absorption at 2.7 eV observed for **E** perpendicular to the layers is consistent with recent theory on the optical anisotropy of single-layer NbS_2.

We also note that the alignment of small crystal platelets (not necessarily single layers) in suspension in a magnetic field can be applied to optical anisotropy studies of many other layered materials.

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