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ELASTIC CONSTANTS OF 2H-MoS_2 and 2H-$NbSe_2$ EXTRACTED FROM MEASURED DISPERSION CURVES AND LINEAR COMPRESSIBILITIES

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Abstract—Recent neutron data on the dispersion curves and X-ray measurements of the linear compressibilities of the 2H polytypes of MoS_2 and $NbSe_2$ have been used to obtain approximate values of the five independent elastic constants of these materials. In the case of $NbSe_2$ sufficient information is available to over-determine the elastic constants and the results are self consistent within estimated uncertainties, although the uncertainties are especially large for c_{33} and c_{11}. Additional related considerations such as Debye temperatures and model calculations of c_{33} and c_{44} are also made. It is found that there is significant and unexplained disagreement between the value of the low temperature specific heat Debye temperature of $NbSe_2$ and the value determined on the basis of the elastic constants, but that the model predictions of c_{33} and c_{44} are in satisfactory agreement with the values extracted from the neutron data for both MoS_2 and $NbSe_2$.

1. INTRODUCTION

The elastic constants of the layered metal chalcogenides have not been measured by ultrasonic techniques at present presumably due to the difficulty of performing such measurements on the available crystals. The purpose of this paper is to use the results of existing neutron[1–3] and X-ray[4–6] scattering measurements to obtain approximate values of the elastic constants for the 2H polytypes[7] of MoS_2 and $NbSe_2$. (In the remainder of this paper we will omit the 2H prefix.) This is done through the determination of the initial slopes of acoustic mode dispersion curves and through a knowledge of the linear compressibilities, k_a and k_c. In addition, in the case of $NbSe_2$, two apparently conflicting measurements of k_a and k_c have been made[4, 5] and this work helps resolve this discrepancy. Because of the relatively large widths of the neutron groups, due to the small crystals available, it is not possible to claim accuracies better than about 20 or 25% for any of the elastic constants obtained in this manner. However, the consistency of the data points corresponding to different wave vectors suggests that the accuracy for certain elastic constants may, in fact, be substantially better than 20%; a similar finding was made[8] in the case of pyrolitic graphite for which large single crystals are also unavailable and for which neutron data were used to extract elastic constants.

In order to check our results: (i) It is verified that the appropriate elastic stability criteria are satisfied; (ii) The elastic constant Debye temperature, θ^{el}, at room temperature is determined. This quantity ought to be within about 10% of the Debye temperature as determined from specific heat data at low temperatures, θ_0^c, assuming a "reasonable" temperature dependence of the elastic constants. Values of θ_0^c have been given for $NbSe_2$[9], so comparison with experiment is possible for that material; (iii) Predictions of c_{33} and c_{44} based on a bond stretching force model[6] are obtained. Although the model involves several approximations, the only feature of the model on which the results for c_{33} and c_{44} can be seen to depend, except for small corrections, is the assumption that only adjacent layers interact. Of course, this independence of c_{33} and c_{44} on the details of the model follows from the relative weakness of the interlayer forces in these materials; (iv) The value of the compliance modulus, s_{11}, of $NbSe_2$ is obtained and compared with Barmatz *et al.*'s[10] experimental determination of that quantity. Unfortunately the absolute magnitude of s_{11} was experimentally determined to within only 20–50% accuracy although the temperature dependence of s_{11} was determined accurately[10]. We note that Ref. [10] chiefly concerns the low temperature structural transition in $NbSe_2$.

2. DESCRIPTION OF NEUTRON DATA AND PROCEDURE

From recent neutron data of Moncton[1] the elastic constants c_{11}, c_{44}, $c_{11}-c_{12}$ and c_{33} of $NbSe_2$ can be directly determined. However, large uncertainties must be associated with the values of c_{33} and c_{11} due to both uncertainties in the extent of the regions of linear behavior of the dispersion curves (since the neutron data do not extend to zero wave numbers) and relatively large halfwidths of neutron groups associated with longitudinal acoustic mode scattering. In general Moncton's data are consistent with the required isotropy (in the basal plane) of the acoustic velocities for hexagonal systems and yield consistent values of c_{44} between determinations based on transverse modes propagating parallel (Σ_3 modes) and perpendicular to the basal plane. The transverse branch in the [100] direction, which yields $c_{11}-c_{12}$, appears to show little dispersion so we also have confidence in our value of $c_{11}-c_{12}$. Furthermore where comparison is possible, these data are consistent with those of Wakabayashi *et al.*[2] and with Raman measurements[11].

In the case of MoS_2 the above mentioned consistency of the results for c_{44} is also excellent as determined from neutron data of Wakabayashi *et al.*[3]. Furthermore,

sufficient neutron data[3] are available to obtain c_{11} and c_{33}, although $c_{11}-c_{12}$ cannot be determined directly from these data alone.

From a knowledge of the linear compressibilities, k_a and k_c, and the expressions

$$c_{13}=(1-c_{33}k_c)/2k_a,$$
$$c_{12}=(1-c_{13}k_c-c_{11}k_a)/k_a \tag{1}$$

it is clear that the five elastic constants for both MoS_2 and $NbSe_2$ can be determined. Combining the two equations of (1) yields

$$c_{13}=\frac{1}{2k_a}-\frac{c_{33}\alpha}{2}=\frac{c_{11}+c_{12}}{2-\alpha}-\frac{c_{33}\alpha}{2-\alpha}, \tag{2}$$

where $\alpha \equiv k_c/k_a$. We see that the latter equality of (2) provides a check on the self consistency of the available data for $NbSe_2$.

3. RESULTS

(A) $NbSe_2$

The neutron data[1] yield $c_{11}\approx 10.8$–17.5, $c_{33}\approx 4.3$–6.0, $c_{11}-c_{12}\approx 9.2$ and $c_{44}\approx 1.9$ in 10^{11} dynes/cm^2, where a density value of 6.48 gm/cm^3 was used. Because of the large uncertainties in c_{11} and c_{33} it is of interest to plot (see Fig. 1) both sides of the second equality of eqn (2) as a function of c_{33} for two extreme values of c_{11}. The compressibilities used in the plot are those of Jones *et al.*[4] based on their low pressure X-ray measurements. This plot also illustrates the relatively small uncertainties in c_{33} and c_{13} deriving from the uncertainties in the linear compressibilities, although only the uncertainty in k_a has been taken into consideration. From the appropriate intersections in this plot it is evident that $c_{11}=10.6$, $(c_{11}+c_{12})=12.0$ corresponds to $c_{33}=4.6$ and $c_{13}=3.1$ and that $c_{11}=17.1$, $(c_{11}+c_{12})=25.0$ corresponds to $c_{33}=6.2$ and $c_{13}=-0.2$ in units of 10^{11} dynes/cm^2. Note that both values of c_{33} are roughly consistent with the neutron data. It can also be seen that both sets of values satisfy the elastic stability criteria[12],

$$c_{11}c_{33}>c_{13}^2,$$
$$c_{33}(c_{11}+c_{12})>2c_{13}^2. \tag{3}$$

The linear compressibilities quoted by Flack[5] on the basis of measurements of the lattice parameters at 0 and 48 kb are much smaller than those of Jones *et al.*[4] and can easily be shown to be incompatible with the neutron data. This is not surprising since the compressibility of $NbSe_2$ may decrease substantially over a 48 kb range[13].

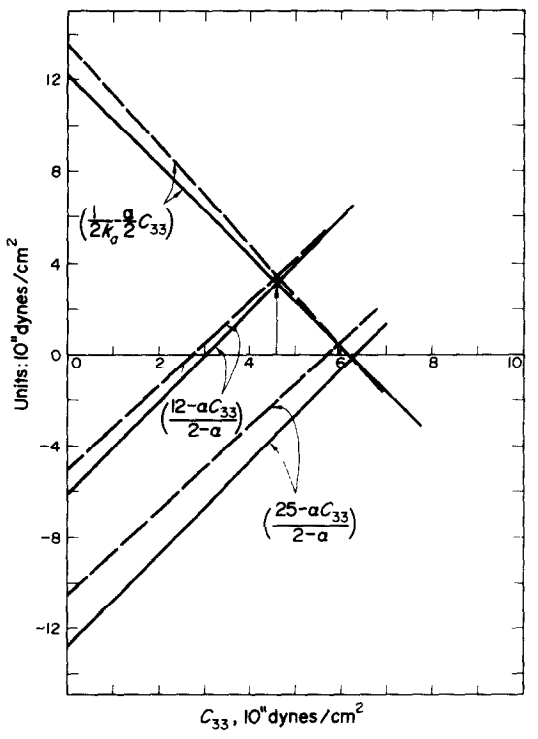

Fig. 1. Graphical solutions of eqn (2) of the text. The solid lines correspond to $k_a=0.041\times10^{-11}$ cm^2/dyne and $k_c=0.162\times10^{-11}$ cm^2/dyne of Jones *et al.* (Ref. [4]). The dashed lines correspond to the same k_c but to $k_a=0.037\times10^{-11}$ cm^2/dyne which is within the ±10% (Ref. [4]) uncertainty in k_a. The effect of the uncertainties of ±3% (Ref. [4]) in k_c is not shown. The arrows indicate the appropriate intersections.

Values of the compliance moduli as well as θ^{el} are given in Table 1. The quantity θ^{el} was computed by numerically performing the appropriate integration to a high precision, so the quoted values are free of computational approximations. The quantities s_{44} and $s_{11}-s_{12}$, given by $1/c_{44}$ and $1/(c_{11}-c_{12})$, respectively, are independent of the choice of $c_{11}+c_{12}$ as indicated in the table. The error quoted for the experimental value of s_{11} in the table corresponds to Barmatz *et al.*'s[10] uncertainty in that quantity. Clearly the set of values of the elastic constants most closely in agreement with the measurement of s_{11} is that corresponding to the larger value of c_{11}.

Table 1. Elastic compliances (in units of 10^{-11} cm^2/dyne) and Debye temperature of $NbSe_2$

Quantity	This Analysis	Exp
s_{11}	.074[a], .118[b]	.056 ± .028[c]
s_{13}	.001[a], -.086[b]	- - - -
s_{33}	.161[a], .334[b]	- - - -
s_{44}	.53	- - - -
$s_{11}-s_{12}$	.108	- - - -
θ (°K)	273[a], 242[b]	210[d], 220 ± 1[e]

[a,b]Based on the set of elastic constants corresponding to $c_{11}+c_{12}=25$ and 12×10^{11} dyne—cm^2, respectively (see text).
[c]Ref. [10].
[d]Van Maaren and Harland[9].
[e]Based on the quoted coefficient of the T^3 term in the specific heat of Harper *et al.*[9]. The data of Harter *et al.* are in excellent agreement with those of Bevolo and Shanks[9], but the latter workers have apparently used an erroneous conversion formula for obtaining Θ_0^c since their quoted values of Θ_0^c appear to be too small.

The disagreement between the calculated and measured Debye temperatures shown in the table is of particular interest. On the basis of the usual temperature dependence of elastic constants and, in fact, of the measured temperature dependence of the Young's modulus for $NbSe_2$[10], it is generally expected that $\theta^{el}(298°K) < \theta_0^c$ whereas the results in the table indicate that $\theta^{el}(298°K) > \theta_0^c$. We believe that this discrepancy is not within the uncertainties of our analysis.

(B) MoS_2

The results for the elastic constants and corresponding Debye temperature of MoS_2 are given in Table 2. As indicated in Section 2, c_{11}, c_{33} and c_{44} were determined directly from the available neutron data[3], assuming a density of 4.99 gm/cm^3, whereas c_{12} and c_{13} were determined with the use of the linear compressibilities[6] and eqns (1). It can be seen that these c_{ij}'s satisfy the stability criteria (expression 3). Wakabayashi *et al.*[3] have also obtained a short range force model which describes their neutron data. Their model yields the predictions $c_{11} - c_{12} = 15 \times 10^{11}$ dynes/cm^2, as extracted by us from their calculated dispersion curves, and $\theta^{el}(298°K) = 308°K$. These values are to be compared with our deduced results, $c_{11} - c_{12} \approx 29 \times 10^{11}$ dynes/cm^2 and $\theta^{el}(298°K) = 335°K$.

Table 2. Elastic constants (in units of 10^{11} dyne/cm^2) and calculated Debye temperature of MoS_2

c_{11}	c_{33}	c_{44}	c_{12}	c_{13}	$\theta^{el}(°K)$
23.8	5.2	1.9	-5.4	2.3	335

4. MODEL PREDICTIONS FOR c_{33} AND c_{44}

It has been stressed by Wieting[14] that the zone center optical data may be described by a linear chain model since the basal planes are displaced rigidly for such modes. Clearly this description is also valid for modes with propagation directions along the c axis since any distortion within a plane would involve a component of the wave vector parallel to the plane. Hence c_{33} and c_{44}, which determine the longitudinal and transverse acoustic velocities for c-axis propagation, may be written in terms of interplanar force constants. Using the method of homogeneous deformation and a short range interplanar force model we obtain

$$c_{33} = \frac{c^2}{4}\frac{\Phi_b^c}{V}\left(1 - \frac{\Phi_b^c}{\Phi_w^c + 2\Phi^c + 2\Phi_b^c}\right)$$
$$c_{44} = \frac{c^2}{4}\frac{\Phi_b^s}{V}\left(1 - \frac{\Phi_b^s}{\Phi_w^s + 2\Phi_b^s}\right) \quad (4)$$

where V is the volume per molecule, or half the unit cell volume, and c is the axial lattice constant. The Φ^c's and Φ^s's are respectively compressional and shear interplanar force constants normalized by the number of atoms within each plane or equivalently the number of molecules within each layer; the subscript, b, refers to neighboring chalcogenide (Ch) planes of adjacent layers; the subscript, w, refers to neighboring metal (M) and Ch planes and ; the absence of a subscript refers to intralayer Ch planes. Only compressional intralayer Ch–Ch force constants are included because of the simplifications of the interatomic force model considered[6]. Values of the interplanar force constants derived essentially[15] on the basis of the model of Ref. [6] are shown in Table 3. Also

Table 3. Model calculations of inter-planar force constants, c_{33}, and c_{44} for MoS_2 and $NbSe_2$*

		MoS_2	$NbSe_2$
	ϕ_b^c	0.76(0.74)	0.92(0.91)
Interplanar	ϕ_w^c	21.7	13.9
Force	ϕ^c	4.18	4.72
Constants	ϕ_b^s	0.271(0.268)	0.334(0.326)
	ϕ_w^s	16.4	9.7
Elastic	c_{33}	5.2(5.2)	5.4(5.5)
Constants	c_{44}	1.89(1.90)	1.95(1.98)

Units: Interplanar force constants in 10^4 dynes/cm/planar atom; Elastic constants in 10^{11} dynes/cm^2.
*Values in parenthesis are rigid layer values (see text).

shown in that table are the calculated values of c_{33} and c_{44} (which compare well with values determined from the neutron data in Section 3) and values based on the rigid layer approximation (*rla*) shown in the table. In the latter approximation, the second terms of (4) are neglected and Φ_b^c and Φ_b^s are directly proportional to the squares of the zone center compressional and shear rigid layer mode frequencies. Since the effects in c_{33} and c_{44} due to the non-rigidity of the layers is small, it is clear that the accuracy of our results for these quantities is determined by the reliability of the assumption that the interatomic forces do not extend beyond adjacent layers, which is difficult to assess, and by the accuracy of the input data, i.e. the "rigid layer" mode frequencies. Since the "rigid layer" shear mode frequency was taken from Raman data which has an estimated accuracy of about 1%, the value of c_{44} is accurate to within 2%, assuming the validity of the model. Similarly the value of c_{33}, which is necessarily based on neutron data, is accurate to within about 10%.

5. DISCUSSION

We have found that for MoS_2 and $NbSe_2$, the available neutron data[1–3], when combined with measured linear compressibilities[4, 6] yield all the second order elastic constants of these materials and that the resulting values satisfy the elastic stability criteria. Furthermore for $NbSe_2$ the calculated compliance modulus, s_{11}, is in agreement with independent measurements of Barmatz *et al.*[10] to within combined uncertainties which are substantial.

In addition our extracted values of c_{44} and c_{33} are in agreement, to within experimental uncertainties, with a

determination based on a simple short range force model. (Wakabayashi *et al.*[2, 3] have previously found that a short range force model can describe the dispersion curves for *c*-axis propagation in these systems.) The agreement for c_{44} is especially gratifying because of the importance of c_{44} in determining the value of θ^{el} for layered materials with weak interlayer forces[16]. We have found that values of θ^{el} for $NbSe_2$ based on two extreme pairs of values of the elastic constants, c_{33} and c_{11}, are both substantially higher than the quoted values of θ_0^c. One possible explanation of this discrepancy is that $\theta^c(T)$ dips down sharply from its $T = 0$ value, so that a minimum in $\theta^c(T)$ occurs in the 7–10°K region, i.e. where the specific heats of pure $NbSe_2$ samples have been analyzed for the T^3 contribution[9]. Contrary to this behavior of θ^c model calculations[3] for MoS_2 yield a monotonically increasing function. However, a comparison of measured dispersion curves and zone center mode frequencies (between MoS_2 and $NbSe_2$) leads to the conclusion that, in the case of $NbSe_2$, θ^c may decrease with increasing temperature at low temperatures. Another possibility is that c_{44} anomalously increases with increasing temperature. Unfortunately the measurements of Barmatz *et al.* which yield accurate results for the temperature dependence of s_{11} are not very helpful in this regard since s_{11} is independent of c_{44}. We have also considered the possibility that the electronic specific heat does not have the assumed linear behavior in T over the 7–10°K region, but an enormous deviation from linearity would be required to explain the discrepancy.

Finally, it is mentioned that in a recent analysis[17] of the uniaxial stress and hydrostatic pressure dependences of the superconducting transition temperature, T_c, for $NbSe_2$, T_c was shown to depend mainly upon the "a" spacing provided it was assumed that $s_{13} \approx 0$. (However, no account was taken of the consequences of the substantial experimental uncertainties on this conclusion.) Our work does not rule out the possibility of a negligible value of s_{13}, as seen in Table 1.

Note added in proof. Recent low temperature specific heat measurements (Schwall R. E., Stewart G. R. and Geballe T. H., *J. Low Temp. Phys.* **22**, 557 (1976)), taken in large magnetic fields yield $\Theta_0^c = 222$°K for $2H$–$NbSe_2$ and remove the possibility mentioned in the text, that $\Theta^c(T)$ has a marked minimum in the 7–10°K region.

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16. This is evident from the smallness of c_{44} and the fact that c_{44} determines the slopes of both transverse branches for propagation along the *c*-axis as well as one of the transverse branches for propagation in the basal plane. See also Komatsu K., *J. Phys. Soc. Japan* **10**, 346 (1955) and Bowman J. C. and Krumhansl J. A., *J. Phys. Chem. Solids* **6**, 381 (1958).
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