Elasticity measurements in the layered dichalcogenides TaSe$_2$ and NbSe$_2$

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We have measured the Young's modulus and internal friction in the two-dimensional layered dichalcogenides 2H-TaSe$_2$ and 2H-NbSe$_2$ using a vibrating reed technique. Weak elastic anomalies are observed at the incommensurate charge-density-wave transitions in TaSe$_2$ and NbSe$_2$ at 121 and 30 K, respectively. Heating and cooling measurements through these transitions show hysteretic effects of less than 0.3 K, which may be attributed to experimental uncertainties. At the commensurate charge-density-wave transition near 90 K in TaSe$_2$, the Young's modulus and internal friction exhibit extrema, which are an order of magnitude larger than the anomalies at the incommensurate transition. Furthermore, there are large hysteretic effects (~5 K), which verify the first-order nature of this transition. At all the charge-density-wave transitions, the internal friction maximum occurs at a lower temperature than the modulus minimum. At the NbSe$_2$ superconducting transition, $T_c = 7.2$ K, the Young's modulus undergoes a smeared-out discontinuity of ~6 ppm and a change in slope. We observe no other anomalies (e.g., a commensurate transition in NbSe$_2$) down to 1.3 K. Estimates of the uniaxial stress dependence and expansivity anomaly at these transitions are also given.

I. INTRODUCTION

The layered dichalcogenides have received considerable attention in recent years as a result of their two-dimensional anisotropic properties$^{1-5}$ and associated electronic instabilities.$^3$ Recent electron-diffraction studies of these materials$^4$ reveal the existence of superlattice structures which are attributed to the formation of charge-density waves (CDW's). Experiments indicate that there are three symmetry-related CDW's in the basal plane of these hexagonal crystals. The metal coordination within a layer may be octahedral or trigonal prismatic, and the layers may be stacked in a variety of ways, leading to a number of polytypes$^5$ (1T, 2H, 4Hb, ...). Most of these polytypes are now known to be unstable toward CDW formation.$^5$

In this paper, we present elastic measurements in the 2H polytype (trigonal prismatic coordination) of the layered dichalcogenides TaSe$_2$ and NbSe$_2$. Young's modulus and internal-friction measurements in the frequency range 0.5-5 kHz were carried out from 1.3 to 300 K using a vibrating-reed technique.$^6$ Detailed measurements were taken at the commensurate and incommensurate transitions induced by the CDW's. The commensurate transition in TaSe$_2$ shows elastic hysteresis effects over a 5-K interval which clearly demonstrates the first-order character of the transformation as predicted by theoretical models.$^7$ On the other hand, the incommensurate transition in TaSe$_2$ exhibits small hysteresis effects, which may be associated with experimental uncertainties. The lack of (observable) hysteresis as well as the shape of the modulus anomaly strongly suggest (but cannot prove) that these transitions are predominantly second order. We also report resistivity measurements which confirm the hysteresis findings of the elastic measurements.

II. CHARGE-DENSITY WAVES

The CDW's may be thought of as periodic variations of the conduction electron density which produce a lattice distortion of the same period.$^9$ The wave vector of the periodic distortion $q_0$ is determined by a particular spanning wave vector of the Fermi surface. At high temperatures, the structure of these layered compounds is undistorted; however, as the temperature is lowered below an onset temperature $T_o$, the CDW's form and are detectable as sharp satellite spots in electron-diffraction patterns.$^4$ Generally, the periodicity of the CDW distortion is not a simple multiple of a lattice spacing just below $T_o$, and, therefore, this is designated the incommensurate charge-density-wave (ICDW) transformation. At some lower temperature $T_s < T_o$, the periodicity of the CDW may become locked in to a small multiple of a lattice spacing leading to a commensurate charge-density-wave (CCDW) transition. Whether a CDW becomes locked in to the lattice periodicity has been shown to depend on sample composition$^{11}$ and pressure.$^{12}$

In the case of 2H-TaSe$_2$, anomalous behavior in the electrical resistivity$^{13,4}$ and magnetic susceptibility$^{14,13,4}$ near 120 K were explained$^4$ in terms of CDW formation. It was assumed,$^4$ however, that the CDW's initially formed commensurate with the lattice, i.e., $T_s = T_o$. Preliminary elastic measurements$^{15}$ revealed, in addition to a weak anomaly near 120 K, a large modulus minimum.

12
and internal friction maximum near 90 K which suggested a second phase transition. In contrast, previous resistivity and magnetic susceptibility measurements showed only smooth and slowly varying behavior near 90 K. Subsequently, high-precision neutron scattering measurements showed that the CDW's in 2H-TaSe₃ are actually a few percent out of commensurability at the onset temperature (T₀ = 122.3 K), and the elastic anomalies near 90 K are associated with the lock-in or commensurate transition. The neutron study also showed that the CDW's in 2H-NbSe₂ (T₀ = 33.5 K) is again only a few percent out of commensurability, but the CDW's remain incommensurate down to at least 5 K.

III. Technique

Measurements of the Young's modulus and internal friction were carried out using a vibrating-reed technique which is described in detail elsewhere. The single-crystal samples, grown by the iodine chemical vapor transport technique, were prepared in the form of thin reeds, approximately 7-12 mm long, 1-2 mm wide, and 0.05-0.15 mm thick. The 2H polype type of TaSe₃ and NbSe₂ are hexagonal, and the samples were oriented with the layers (basal plane) in the plane of the reed. One end of each specimen was soldered with indium to a copper block as shown in Fig. 1. The reeds were excited into flexural vibrations with an electrostatic transducer situated on one side of the free end. An identical receiver transducer detected the amplitude of vibration through the modulation of the receiver capacitance.

The flexural resonant frequencies fₙ for a clamped-free rectangular reed are given by

\[ f_n = \frac{(\kappa/2\pi) (k_n/\ell)^{1/2} v_B}{2}, \]

where the radius of gyration \( \kappa = \ell/(12)^{1/2} \) and \( \ell \) and \( \ell \) are the thickness and length, respectively. The \( k_n \)'s are constants 1.875, 4.694, ..., corresponding to the overtones \( n = 1, 2, \ldots \). The Young's modulus velocity is \( v_B = (E/\rho)^{1/2} \), where \( E \) is the Young's modulus along the reed axis and \( \rho \) is the density. Thus the measured modulus corresponds to that of the basal plane of these hexagonal crystals. We have carried out measurements for the two lowest resonances in the frequency range 0.5-5 kHz.

In these dichalcogenide materials, adjacent layers are loosely coupled to one another by Van der Waals forces, and the interlayer spacing is usually much larger than the atomic spacing within a layer. For an ideal elastically two-dimensional material (i.e., having no elastic coupling between layers) Eq. (1) is no longer valid, and the reed frequency would, in fact, be zero. However, for 2H-TaSe₃ and 2H-NbSe₂, the moduli measured by this method are reasonably high (8x10¹¹-1.8x10¹² dyn/cm²), and we have therefore assumed all corrections to Eq. (1) to be negligible.

Many of the samples were not of ideal rectangular geometry and led to large uncertainties [(20-50)%] in the absolute magnitude of the modulus. However, measurements of the modulus temperature dependence have a relative accuracy better than 0.2%. For this reason, all modulus measurements were presented in the dimensionless form \( \Delta E/E_0 = E(T)/E_0(T_0) - 1 \), where \( T_0 \) is a reference temperature usually associated with a particular transition or room temperature.

A detailed description of the low-temperature apparatus was reported previously. The temperature of the specimen was monitored with an Au-Fe versus chromel thermocouple, situated in the copper block holding the sample. The thermocouple and a heater, also in the copper block, were used to regulate the sample temperature to better than 0.02 K. Equilibrium and drift measurements were carried out at pressures between 10⁻³ and 10⁻⁶ Torr, depending on the magnitude of the internal friction. Heating and cooling drift rates ranged between 0.1 and 0.3 K/min. For the fundamental resonance at any of the transitions investigated, we found reproducibility in the transition temperature and modulus minimum to be ~0.3 K and 0.1%, respectively.

The flexural resonances were investigated using

FIG. 1. Schematic of the electronics. PAR 124 is phase-locked to the antisymmetric component of the flexural resonance. Continuous record of the resonant frequency and received signal amplitude was obtained as the sample temperature changed.