

Pressure effect on the charge-density-wave formation in $2H\text{-NbSe}_2$ and correlation between structural instabilities and superconductivity in unstable solids

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(Received 12 April 1976)

The hydrostatic pressure dependence of the charge-density-wave onset temperature T_0 in $2H\text{-NbSe}_2$ was measured up to 20 kbar. dT_0/dP was found to be $-(3.3 \pm 0.2) \times 10^{-4} \text{ K bar}^{-1}$. An examination of existing high-pressure data concerning structural instabilities and superconductivity in both layered and isotropic compounds is made.

$2H\text{-NbSe}_2$ is a trigonal prismatic coordinated layer compound. On cooling, it undergoes a structural transition¹ at the onset temperature $T_0 = 32 \text{ K}$ of a incommensurate charge-density-wave (CDW) state² and becomes superconducting below $\sim 7.2 \text{ K}$.³ The superconducting transition temperature T_0 of $2H\text{-NbSe}_2$ increases rapidly and nonlinearly with pressure up to $\sim 35 \text{ kbar}$, but slowly and linearly beyond $\sim 35 \text{ kbar}$.⁴ This pressure-enhanced superconductivity has been ascribed to the possible suppression of the structural transition by pressure⁵ or to the band broadening due to pressure-promoted interlayer coupling⁴ (it seems possible that the two are related). Our direct pressure measurements on T_0 show that T_0 decreases with pressure. However, recent results on $2H\text{-TaSe}_2$ show that pressure increases T_0 ,⁶ and also T_c .⁷

Measurements have been made of the pressure dependences of T_0 and T_c of $2H\text{-NbSe}_2$ in the fluid mixture of 1:1 *n*-pentane and isoamyl alcohol, using a self-clamp technique. A sample with a resistance ratio of 30 along the layer between 300 and 8 K was cut from a single crystal grown by iodine chemical vapor transport technique. T_0 is defined as the temperature where the resistance vs temperature curve exhibits a point of inflection. T_0 so defined is slightly lower than that previously obtained⁸ at $P = 1 \text{ bar}$, but gives less uncertainty in determining T_0 at higher pressure. T_c was measured both resistively and inductively. Results are shown in Fig. 1, with the number indicating the sequential order of the experimental runs. The vertical bar for T_0 represents the uncertainty in locating T_0 and that for T_c the transition width. T_0 decreases linearly with pressure up to 20 kbar at a rate of $-(3.3 \pm 0.2) \times 10^{-4} \text{ K bar}^{-1}$. T_c increases with pressure but with a negative

curvature. Both T_c and dT_c/dp apparently depend on the measuring technique used, possibly due to the anisotropic nature of the compounds. At atmospheric pressure, $dT_c/dp = +(5.2 \pm 0.1) \times 10^{-5} \text{ K bar}^{-1}$, and $+(4.5 \pm 0.1) \times 10^{-5} \text{ K bar}^{-1}$ from resistance and induction measurements, respectively. This latter value is in good agreement with previous observations.⁴

At a second-order transition temperature T_0 , the uniaxial stress effect on T_0 is related to the Young's modulus along the i th direction E_i in the following way⁹

$$\left(\frac{dT_0}{d\sigma_i}\right)^2 = -\left(\frac{\Delta E_i}{E_i^2}\right) \frac{T_0}{\Delta C_p},$$

where ΔE_i and ΔC_p are the discontinuities of E_i and the specific heat at the transition. Based on results of the elastic¹⁰ and specific-heat measure-

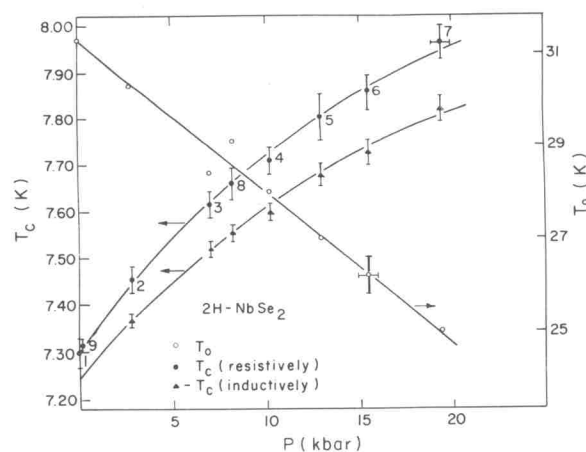


FIG. 1. Pressure dependences of T_0 and T_c of $2H\text{-NbSe}_2$.

ments,⁸ $|dT_0/d\sigma_a| = (6 \pm 2) \times 10^{-4}$ Kbar⁻¹ for 2H-NbSe₂ parallel to the layer. Using this value, we deduced the interlayer stress effect $dT_0/d\sigma_c$ to be $-(15 \pm 4) \times 10^{-4}$ or $+(9 \pm 4) \times 10^{-4}$ Kbar⁻¹, depending on whether $dT_0/d\sigma_a$ is positive or negative. The corresponding strain derivative of T_0 is -5×10^2 or $+4 \times 10^2$ K for the "+" or "-" sign of $dT_0/d\sigma_a$, based on the estimates of the elastic stiffness constants obtained from neutron and elastic modulus measurements.¹¹ The interlayer separation thus has a large effect on the CDW formation. The linearly extrapolated critical pressure for the suppression of T_0 to below T_c is larger than 35 kbar. However, the drastic change of dT_c/dP at ~ 35 kbar can still be related to the suppression of CDW to below T_c , because of the usual nonlinear behavior of T_0 near the critical pressure.¹²

Recently T_0 of 2H-TaSe₂ was observed to increase under hydrostatic pressure up to 19 kbar.⁶ The CDW in 2H-TaSe₂ becomes commensurate in a first order transition at $T_d \approx 90$ K, with a small increase in the CDW amplitude. dT_d/dP is negative,⁶ and the critical pressure for the complete suppression of the commensurate state is ~ 17 kbar.⁶ dT_c/dP was determined up to 21 kbar to be positive for the superconducting transition of only a small fraction of the sample. The full transition could not be seen, because the experiment could not be conducted at a lower temperature.⁷ However this positive value is consistent with the general trend in dT_c/dP across the 2H-TaS_{2-x}Se_x system.⁷ Therefore the positive dT_c/dP in 2H-TaSe₂ does not seem to be completely accounted for by a possible reduction of the CDW amplitude with pressure due to decreasing T_d .

The effects of pressure on the CDW temperatures T_0 and T_d , and on T_c are known for a num-

ber of layer compounds. In general, the three types of phase transitions at T_0 , T_d , and T_c are not all observed in the same layer compound, except in the case of 2H-TaSe₂. However, the results in Table I reveal that the pressure coefficients of the three transitions in different compounds at $P=1$ bar fall into three distinct regions and follow the sequence $|dT_d/dP| > |dT_0/dP| > |dT_c/dP|$, with about an order of magnitude difference between each. This demonstrates that the influence of pressure on a phase transition depends more on the type of transition involved than on the chemical constituents or the polytype of the layer compound. The larger effect of pressure on T_d than on T_0 suggests that the incommensurate-commensurate transition at T_d depends more critically on the band structure of the compound than the normal-incommensurate transition at T_0 .

It is interesting to compare the pressure data on layer compounds with those obtained on unstable isotropic superconductors, as shown in Table II. This is especially true of β -W high- T_c compounds, which show structural instabilities, since it has been suggested that these may be due to CDW instability^{13,14} (although not yet proven). The magnitude of the pressure dependence of the structural transition temperature T_M in these compounds is similar to that of T_0 in the layer compounds (see Table I). Since T_0 or T_M is always higher than T_c , the relative changes, $|d\ln T_0/dP|$ or $|d\ln T_M/dP|$ and $|d\ln T_c/dP|$ thus become roughly comparable to each other. This is consistent with the propositions^{13,15} that structural changes and superconductivity are just two aspects of the same electronic instability. However, one should also note that, in spite of this resemblance, the CDW formation at T_0 in layer compounds differs from the

TABLE I. Pressure effects on T_c , T_0 , and T_d . For compounds, in which nonlinear pressure behavior exists, the quoted values are for $P=1$ bar.

Compound	T_c (K)	dT_c/dP (10^{-5} Kbar ⁻¹)	T_0 (K)	dT_0/dP (10^{-4} Kbar ⁻¹)	T_d (K)	dT_d/dP (10^{-3} Kbar ⁻¹)
2H-NbSe ₂	7.3	+4.95 ^a	31.3	-3.3 ^b	...	...
2H-TaSe ₂	0.14	+1.3 ^c	122	+3.5 ^d	92.5	-2.7 ^d
2H-TaS ₂	0.49	+9.3 ^c	76	-2.2 ^e	...	...
1T-TaS ₂	...	...	...	...	190	-9 ^f
1T-TaSe ₂	...	...	...	...	473	-4.7 ^g
4Hb-TaS ₂	...	...	...	...	315	-5.5 ^h

^a Reference 4.

^b Present work.

^c Reference 7.

^d Reference 6.

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