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Pressure effect on the charge-density-wave formation in $2H$-$NbSe_2$ and correlation between structural instabilities and superconductivity in unstable solids

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The hydrostatic pressure dependence of the charge-density-wave onset temperature T_0 in $2H$-$NbSe_2$ was measured up to 20 kbar. dT_0/dP was found to be $-(3.3\pm0.2)\times10^{-4}$ K bar^{-1}. An examination of existing high-pressure data concerning structural instabilities and superconductivity in both layered and isotropic compounds is made.

$2H$-$NbSe_2$ is a trigonal prismatic coordinated layer compound. On cooling, it undergoes a structural transition[1] at the onset temperature $T_0 = 32$ K of a incommensurate charge-density-wave (CDW) state[2] and becomes superconducting below ~7.2 K.[3] The superconducting transition temperature T_0 of $2H$-$NbSe_2$ increases rapidly and nonlinearly with pressure up to ~35 kbar, but slowly and linearly beyond ~35 kbar.[4] This pressure-enhanced superconductivity has been ascribed to the possible suppression of the structural transition by pressure[5] or to the band broadening due to pressure-promoted interlayer coupling[4] (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 $2H$-$TaSe_2$ 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 $2H$-$NbSe_2$ 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 obtained[8] at $P = 1$ 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 $-(3.3\pm0.2)\times10^{-4}$ Kbar^{-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, $dT_c/dp = +(5.2\pm0.1)\times10^{-5}$ Kbar^{-1}, and $+(4.5\pm0.1)\times10^{-5}$ Kbar^{-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 ith direction E_i in the following way[9]

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

where ΔE_i and ΔC_p are the discontinuities of E_i and the specific heat at the transition. Based on results of the elastic[10] and specific-heat measure-

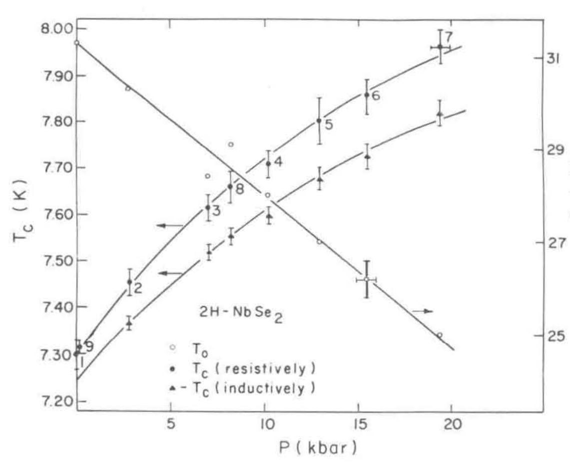

FIG. 1. Pressure dependences of T_0 and T_c of $2H$-$NbSe_2$.

ments,[8] $|dT_0/d\sigma_a| = (6\pm 2)\times 10^{-4}$ Kbar^{-1} for $2H$-$NbSe_2$ 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 $2H$-$TaSe_2$ was observed to increase under hydrostatic pressure up to 19 kbar.[6] The CDW in $2H$-$TaSe_2$ becomes commensurate in a first order transition at $T_d \simeq 90$ 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 $2H$-$TaSe_2$ 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 number 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 $2H$-$TaSe_2$. 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.
[e] R. Delaplace *et al.*, J. Phys. Lett. 36 (1976).
[f] C. W. Chu *et al.* (unpublished).
[g] F. J. DiSalvo *et al.*, Solid State Commun. 14, 497 (1974).
[h] F. J. DiSalvo *et al.*, J. Phys. Chem. Solids 34, 1357 (1973).

TABLE II. Pressure effects on T_c and T_M. For compounds, in which nonlinear pressure behavior exists, the quoted values are for $P=1$ bar. We have also found that, dT_M/dP and dT_c/dP of La_3S_4 and La_3Se_4 have opposite signs. This may be caused by the slight difference in compositions. Details are still under study. The unusually large values of dT_c/dP and dT_M/dP may be associated with the virtual f states of La.

Compound	T_c (K)	dT_c/dP (10^{-5} K bar^{-1})	T_M (K)	dT_M/dP (10^{-4} K bar^{-1})
V_3Si	16.5	+3.65 [a]	21.5	−1.5 [a]
Nb_3Sn	17.8	−1.40 [b]	43.2	+3.3 [b]
$V_{0.54}Ru_{0.46}$	4.92	+0.91 [c]	45	−3.2 [c]
HfV_2	8.9	+6.5 [d]	128	−8 [d]
ZrV_2	7.9	~0 [d]	124	−1 [d]
La_3S_4	8.1	+11 [e]	86	+13 [e]
La_3Se_4	7.6	+7 [e]	65	+38 [e]

[a] C. W. Chu and L. R. Testardi, Phys. Rev. Lett. 32, 766 (1974).
[b] Reference 13.
[c] C. W. Chu *et al.*, Phys. Rev. B 11, 1866 (1975).
[d] T. F. Smith *et al.*, J. Phys. F 3, 2157 (1973).
[e] R. N. Shelton *et al.*, Mater. Res. Bull. 10, 1111 (1975).

structural transition at T_M in $A15$ isotropic compounds in a certain way. For the layer compounds, the macroscopic local conditions have been shown[16,17] to have a smaller effect on T_0 than on T_d. On the other hand, the occurrence of the structural transformation at T_M in an isotropic superconductor[18] depends sensitively on the sample conditions, e.g., impurity and local strain as reflected in the drastic variation of T_M with the resistance ratio (or the mean life time of the d electrons) of the sample.[19,20] In this sense, the structural transition at T_M in the isotropic superconductors seems to be more reminiscent of the T_d transition than the T_0 transition in the layer compounds. It would thus not be too surprising for one to see another transition corresponding to the onset of an incommensurate CDW in $A15$ high-T_c superconductors above T_M.

In conclusion, we have determined the effect of pressure on the formation of the CDW in $2H$-$NbSe_2$. Analysis of the acoustic and the present results indicates that interlayer coupling may have a large effect on the CDW formation in $2H$-$NbSe_2$. Comparison of these results with those on $2H$-$TaSe_2$ suggests that the suppression of T_0 by pressure is not a necessary condition for the enhancement of superconductivity. By examining all available high-pressure data on both layered and isotropic unstable superconductors, we find that $|dT_c/dP|$, $|dT_0/dP|$ or $|dT_M/dP|$, and $|dT_d/dP|$ fall into three distinct orders of magnitude. The similarity of the data for the isotropic and layer compounds with structural instabilities is not inconsistent with the existence of CDW's in both classes of materials, although more information is needed concerning the exact nature of the transition of an isotropic superconductor at T_M. This is in agreement with the proposition that the electron energy spectrum plays a dominant role in the occurrence of the structural instability and superconductivity.

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[1]M. Marezio, P. D. Dernier, A. Menth, and G. W. Hull, J. Solid State Chem. 4, 425 (1972).
[2]D. E. Moncton, J. D. Axe, and F. J. DiSalvo, Phys. Rev. Lett. 34, 734 (1975).
[3]E. Revolinsky, G. A. Spiering, and D. J. Beerntsen, J. Phys. Chem. Solids 26, 1029 (1965).
[4]T. F. Smith, R. N. Shelton, and R. E. Schwall, J. Phys. F 4, 2009 (1974), and references therein.
[5]P. Molinie, D. Jerome, and A. J. Grant, Philos. Mag. 30, 1091 (1974); and J. Friedel, J. Phys. Lett. 36, L279 (1975).
[6]C. W. Chu, L. R. Testardi, F. J. DiSalvo, and D. E. Moncton, Phys. Rev. B (to be published).
[7]T. F. Smith, R. N. Shelton, and R. E. Schwall, J. Phys. F 5, 1713 (1975).
[8]J. M. E. Harper, T. H. Geballe, and F. J. DiSalvo, Phys. Lett. A 54, 27 (1975).
[9]L. R. Testardi, Phys. Rev. B 12, 3849 (1975).
[10]M. Barmatz, L. R. Testardi, F. J. DiSalvo, Phys. Rev. B 12, 4367 (1975).
[11]L. R. Testardi (private communication).
[12]Very recently C. Berthier, P. Molinie, and D. Jerome [Solid State Commun. 18, 1393 (1976)] have measured T_0 of $2H$-$NbSe_2$ up to 36 kbar and observed T_0 decreasing nonlinearly near the critical pressure. These authors suggest that dT_c/dP and dT_0/dP should always have opposite signs.
[13]L. P. Gorkov, Z. Eksp. Teor. Fiz. 65, 1658 (1973) [Sov. Phys.-JETP 38, 830 (1974)], and references therein. Also R. N. Bhatt and W. L. McMillan, Phys. Rev. B 14, 1007 (1976).
[14]T. M. Rice and G. K. Scott, Phys. Rev. Lett. 35, 120 (1975).
[15]C. W. Chu, Phys. Rev. Lett. 33, 1283 (1974); C. W. Chu, S. Huang, T. F. Smith, and E. Corenzwit, Phys. Rev. B 11, 1866 (1975), and references therein.
[16]W. L. McMillan, Phys. Rev. B 12, 1187 (1975).
[17]F. J. DiSalvo, J. A. Wilson, B. B. Bagley, and J. V. Waszczak, Phys. Rev. B 12, 2220 (1975).
[18]For reviews, see L. R. Testardi, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1973), Vol. 10.
[19]S. J. Williamson, C. S. Ting, and H. K. Fung, Phys. Rev. Lett. 32, 9 (1974).
[20]M. P. Sarachik, M. Milewitz, and S. J. Williamson, Bull. Am. Phys. Soc. 21, 230 (1976).