this interpretation, the critical field for the ordered phase is probably an order of magnitude less than the expected antiferromagnetic critical field of 7.4 T.

Another curious feature seen in Fig. 3(a) is that the curve T_{AB} corresponding to the transition between the two superfluid phases of liquid ^{3}He seems to intersect the solid transition line about 0.45 T, very near the field at which the solid changes behavior. It is unknown whether this is a coincidence or whether there exists a relationship between the AB transition in liquid ^{3}He and the magnetic phase transition in solid ^{3}He. We believe that the latter possibility is unlikely, although it should be remarked that the measured quantities relate to phenomena occurring at the liquid-solid interface and that the bulk solid is not in thermal equilibrium with the liquid.

We gratefully acknowledge the expert advice and skillful machining of W. E. Steeger. Thanks are extended to P. L. Coleman for maintaining a continuous supply of helium since this run began in mid-September.

---

†Work supported in part by the National Science Foundation and the Research Corporation.

*Present address: Department of Physics, Colorado State University, Fort Collins, Colo. 80523

‡John Simon Guggenheim Memorial Fellow on leave September 1974–June 1975 from Cornell University, Ithaca, N. Y. 14850

[1] S. B. Trickey, W. P. Kirk, and E. D. Adams, Rev. Mod. Phys. 44, 668 (1972).

[2] W. P. Kirk and E. D. Adams, Phys. Rev. Lett. 27, 392 (1971).

[3] J. M. Dundon and J. M. Goodkind, Phys. Rev. Lett. 32, 1343 (1974).

[4] W. P. Halperin, C. N. Archie, F. B. Rusmussen, R. A. Buhrman, and R. C. Richardson, Phys. Rev. Lett. 32, 927 (1974).

[5] Yu. D. Anufriyev, Zh. Eksp. Teor. Fiz., Pis'ma Red. 1, 1 (1965) [JETP Lett. 1, 155 (1965)].

[6] G. C. Straty and E. D. Adams, Rev. Sci. Instrum. 40, 1393 (1969).

[7] W. P. Halperin, private communication. We have used $T_0 = 16.88$ mK and $P_0 = 3.37830$ MPa. Our pressure calibration was adjusted so that the A transition in the liquid for $B = 0$ occurs at $P_A = 3.43420$ MPa.

[8] W. R. Abel, A. C. Anderson, W. C. Black, and J. C. Wheatley, Phys. Rev. 147, 111 (1966).

[9] R. A. Scribner, M. F. Panczyk, and E. D. Adams, J. Low Temp. Phys. 1, 313 (1969); E. R. Grilly, *ibid.* 4, 615 (1971).

[10] D. D. Osheroff, R. C. Richardson, and D. M. Lee, Phys. Rev. Lett. 28, 885 (1972).

[11] A. Landesman, J. Phys. (Paris), Colloq. 31, C3-55 (1970); L. J. de Jongh and A. R. Miedema, Advan. Phys. 33, 1 (1974).

Pauling's Ionicity and Charge-Density Waves in Layered Transition-Metal Dichalcogenides

A. H. Thompson
Corporate Research Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036

(Received 7 November 1974)

The crystal distortions commonly observed in the layered transition-metal dichalcogenides have been attributed to a Fermi-surface instability, i.e., a charge-density wave. I find that the temperatures of these distortions correlate with the ionicity of the metal-chalcogen bond. This results suggests that these distortion temperatures can be specified without knowing the details of the Fermi surface.

The layered transition-metal dichalcogenides and their intercalation complexes have received much attention as a result of their highly anisotropic properties.[1] Quite apart from the anisotropies, the disulfides and diselenides of Ta and Nb are unstable at lower temperatures and undergo crystal distortions. The discovery of magnetic anomalies associated with these distortions was made by Quinn, Simmons, and Banewicz[2] in their studies of $2H$-TaSe$_2$. Lee *et al.*[3] measured the transport and magnetic properties of $2H$-TaSe$_2$ and $2H$-NbSe$_2$. Ehrenfreund *et al.*[4] showed that the magnetic and transport anomalies are not associated with magnetic ordering as originally suggested,[2] but most likely with subtle crystal distortions.

More recently, many new transitions have been discovered (see Table I) and a mechanism for the distortions has been proposed independently by Williams, Parry, and Scruby,[5] and by Wilson, DiSalvo, and Mahajan.[6] These authors cite electron diffraction evidence to support their propos-

TABLE I. Listing of the known distortions in layered dichalcogenides. The transition temperatures are defined from the transport measurements. The notation "est" indicates mixed polytypes (octahedral and trigonal prismatic layers) where the true values of c/a for individual layers are not known.

Continuous distortions				Discontinuous distortions			
Material	c/a	T_c (°K)	Ref.	Material	c/a	T_c (°K)	Ref.
(1) $2H$-TaSe$_2$	1.850 ±0.002	90	3,10	(7) $1T$-TaSe$_2$	1.805 ±0.002	473	1,14
(2) $2H$-TaS$_2$	1.822 ±0.002	56	8,1	(8) $1T$-TaS$_2$	1.755 ±0.003	350	9
(3) $2H$-NbSe$_2$	1.8209 ±0.0004	26	3,11	(9) $1T$-TiSe$_2$	1.697 ±0.001	200 ±10	12
(4) $1T$-VSe$_2$	1.817 ±0.002	55 ± 5	12	(10) $4Hb$-TaS$_2$	1.752 (est)	320	13
(5) $6R$-TaS$_2$	1.805 (est)	15	12	(11) $4Hb$-TaSe$_2$	1.806 (est)	410	15
(6) $4Hb$-TaS$_2$	1.793 (est)	15 ± 3	13	(12) $6R$-TaS$_2$	1.763 (est)	311	12

al that charge-density waves[7] occur in the layered compounds and cause the crystal distortions. The primary support for this model rests on the observation of an incommensurate periodic distortion[5,6] and on evidence that the distortion periodicity is a function of the electron to atom ratio.[6]

I present a systematic study of the distortions in the layered compounds based primarily on electron-transport measurements. I show that the transition temperatures are not a function of metal-site symmetry but closely follow the trends in the ratio of the lattice parameters c/a. The ratio c/a is shown to be a fine-grid indicator of the ionicity.

The known distortions in the layered compounds are summarized in Table I. The continuous and discontinuous grouping qualitatively characterizes the temperature dependence of the transport properties. I will consistently define the distortion temperatures as those associated with the transition between the incommensurate and commensurate (or nearly commensurate) states. Thus I only consider the high-temperature distortions in $1T$-TaS$_2$ and TiSe$_2$ where the crystals distort in two steps.[9,12] I will consider both transitions in the mixed polytypes $4Hb$-TaS$_2$[13] and $6R$-TaS$_2$.[12] In these polytypes there are two distortions in each: a high-temperature transition in octahedral layers and an independent, low-temperature transition in trigonal prismatic layers.[13]

The T_c's for the discontinuous distortions are easy to define, but the T_c's of continuous transitions are not easy to define because the transport properties change gradually. I will take T_c for the continuous group to be the point of maximum slope in the Hall constant versus temperature plot. This definition of T_c has been found to correspond to the incommensurate-commensurate (or nearly commensurate) transition as determined from electron and neutron diffraction studies.[16]

Perhaps the most important newly discovered transition is the one in stoichiometric $1T$-VSe$_2$.[12] This transition is similar to those in $2H$-TaS$_2$,[8] $2H$-TaSe$_2$,[3] and $2H$-NbSe$_2$[3] but VSe$_2$ has octahedral coordination of the chalcogen about the metal[12] while the $2H$ compounds are trigonal prismatic. *Thus, the character of the transition (continuous or discontinuous) is not a function of metal-site symmetry.* Inspection of the c/a's, however, reveals that they are similar for VSe$_2$ and the $2H$ compounds. For the mixed polytypes of TaS$_2$ and TaSe$_2$, c/a also correlates with the transition type provided it is assumed, as suggested by DiSalvo *et al.*[13] that the continuous, low-temperature distortions occur in trigonal prismatic layers while the higher-temperature distortions occur in octahedral layers. I will assume that the thicknesses of the octahedral and trigonal prismatic layers are different. I estimate the layer thicknesses by taking the ratio of the c axes, $c_{\text{octahedral}}/c_{\text{trigonal prismatic}}$, to be a constant. The c-axis ratio is determined from the unmixed $1T$ and $2H$ polytypes and then used to weight the contributions of the octahedral and trigonal prismatic layers to the combined c axis in a mixed polytype.

The correlations between the type of transition and c/a suggests that c/a is an important ruler with which the T_c's should be compared. When this is done for the two groups of transitions, it is found that there is a linear relationship between T_c and c/a. For the discontinuous transitions $T_c = 0$ when c/a is 1.608 while for the continuous transitions $T_c = 0$ when c/a is 1.793. The success of these comparisons implies that all of the T_c's may be related to c/a in a single corre-

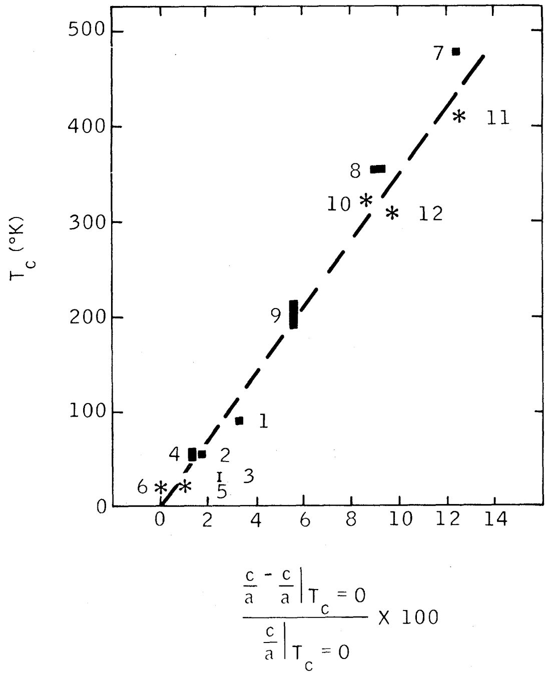

FIG. 1. Transition temperature versus normalized c/a. The numbers on data points designate the materials of Table I. The points marked with an asterisk are estimated c/a values.

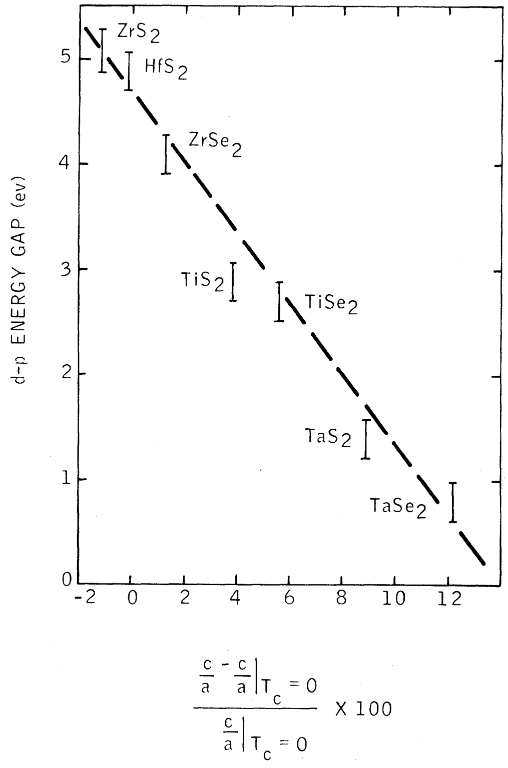

FIG. 2. The d-p energy gap versus the normalized c/a for octahedral, $1T$ materials. The energy gap is arbitrarily defined from the photoemission data of Refs. 20 and 21 as the energy difference between the bottom of the d band and the peak in the density of states in the highest, σ-bonding, p band.

lation. To construct this comparison c/a must be renormalized such that the renormalized c/a at $T_c = 0$ is the same for both groups of data. This is done in Fig. 1.

The data displayed as in Fig. 1 show that octahedral VSe_2 logically fits in with the other continuous distortions. The group-IVB dichalcogenide $TiSe_2$ resides between the extreme groups. The mixed polytypes fall near the correlation for the unmixed polytypes. Other layered dichalcogenides can be compared with Fig. 1 to predict where a distortion should occur. One noteworthy prediction is that none of the polytypes of NbS_2 would be expected to undergo distortions. Some effort has been made to find transitions in this material without success.[16,17]

Our generation of the T_c versus c/a relation actually followed from the supposition that T_c would be related to the ionicity. But there is not yet available enough thermochemical data to derive ionicities or to plot T_c versus the heat of formation directly. Huisman *et al.*[18] suggested that departures from the ideal close packing of chalcogen atoms (reflected in c/a) are caused by the covalent character in the metal-chalcogen bond. An inspection of the trends within the dichalcogenides of groups IVB, VB, and VIB shows that this is indeed the case. The most ionic compounds in group IVB have the smallest c/a's while the most covalent compounds of group VIB have the largest c/a's.

In an earlier discussion of ionicity Gamble[19] showed that the ionicity correlates with the a-axis lattice dimension when the sulfides, selenides, and tellurides are treated independently. This correlation could also be used in the present case. The primary reason for choosing c/a to indicate the ionicity is that it is a normalized parameter that permits the grouping of all the chalcogenides into a single correlation.

An experimental test of the correlation between covalency and c/a is provided by the photoemission studies on these compounds.[20,21] The covalent mixing between the metal d and chalcogen p orbitals is reflected in the splitting between the d-like conduction band and the p-like valence band. This splitting may be estimated from the

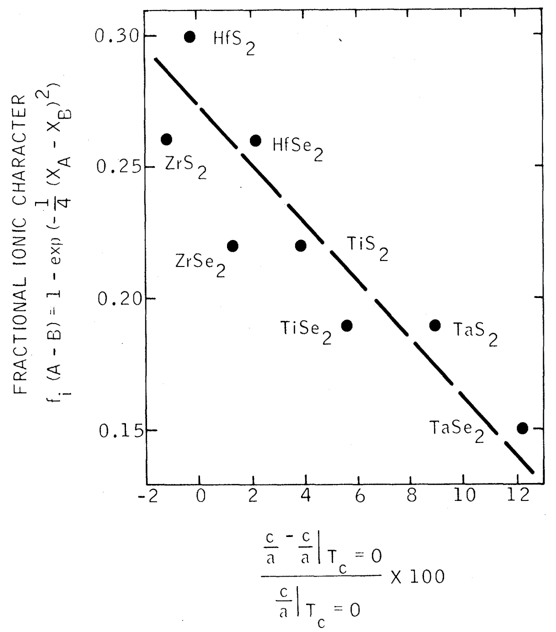

FIG. 3. The fractional ionic character f_i versus the normalized c/a ratio for the octahedral, 1*T* dichalcogenides. The ionicity f_i was defined by Pauling (Ref. 22) and the values plotted here are taken from Ref. 19.

photoemission spectra and compared to the normalized c/a. This is done in Fig. 2 for the octahedral materials for which adequate data are available. The high correlation shown in Fig. 2 supports our conclusion that c/a is a fine-grid indicator of the covalent character of the metal-chalcogen bond. In Fig. 2 the group-IV*B* materials logically fit in with those of group V*B*.

The normalized c/a ratio may also be compared to the fractional ionicity f_i as defined by Pauling.[22] This comparison is made for the materials of Fig. 2 in Fig. 3. The correlation is good considering the coarseness of the Pauling ionicity scale but an improved treatment of ionicity such as suggested by St. John and Block[23] or by Harrison and Ciraci[24] is needed for these compounds.

The correlations presented here have not yet provided a mechanism for the transitions but instead they emphasize that in addition to charge-density waves, a structural instability inherent in the local chemical bond is needed to account for first-order, incommensurate-commensurate transitions. The inclusion of both continuous and discontinuous distortions in the T_c versus c/a correlation suggests that all of the transitions are first order. Recent resistivity data indicate that the continuous distortion in 2*H*-TaS$_2$ has a first-order component.[25] The separate treatment of the continuous and discontinuous groups is probably required by the substantially higher vibrational entropy associated with structures in the discontinuous group. A comprehensive analysis of the transition thermodynamics is needed for further insight into distortion mechanisms but it is clear from available data[9,12-15] that the transition entropies are a function of both temperature and structure.

I conclude that neither the continuous-discontinuous character nor T_c is a function of crystal symmetry. I find that isolating the group-IV*B* from -V*B* materials or the sulfides from the selenides is not necessary. I conclude that the T_c's are strongly correlated with c/a and the ionicities. From this correlation, I can predict the distortion temperatures for a large number of layered dichalcogenides without any knowledge of the details of the band structure.

The author thanks F. R. Gamble, B. M. Hoffman, H. M. McConnell, J. R. Schrieffer, and B. G. Silbernagel for helpful discussions and suggestions. He thanks P. M. Williams, F. J. DiSalvo, and J. A. Wilson for use of data prior to publication.

---

[1] F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. DiSalvo, and T. H. Geballe, Science 174, 493 (1971).

[2] R. K. Quinn, R. Simmons, and J. Banewicz, J. Phys. Chem. 70, 230 (1966).

[3] H. N. S. Lee, M. Garcia, H. McKinzie, and A. Wold, J. Solid State Chem. 1, 190 (1970).

[4] E. Ehrenfreund, A. C. Gossard, F. R. Gamble, and T. H. Geballe, J. Appl. Phys. 42, 1491 (1971).

[5] P. M. Williams, G. S. Parry, and C. B. Scruby, Phil. Mag. 29, 695 (1974).

[6] J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Phys. Rev. Lett. 32, 882 (1974).

[7] A. W. Overhauser, Phys. Rev. 167, 691 (1968).

[8] A. H. Thompson, F. R. Gamble, and R. F. Koehler, Jr., Phys. Rev. B 5, 2811 (1972).

[9] A. H. Thompson, F. R. Gamble, and J. F. Revelli, Solid State Commun. 9, 981 (1971).

[10] E. Bjerkelund and A. Kjekshus, Acta Chem. Scand. 21, 513 (1967).

[11] R. E. Jones, Jr., H. R. Shanks, D. K. Finnemore, and B. Morosin, Phys. Rev. B 6, 835 (1972).

[12] A. H. Thompson and B. G. Silbernagel, to be published.

[13] F. J. DiSalvo, B. G. Bagley, J. M. Voorhoeve, and J. V. Waszczak, J. Phys. Chem. Solids 34, 1357 (1973).

[14] F. J. DiSalvo, R. G. Maines, J. V. Waszczak, and R. E. Schwall, Solid State Commun. 14, 497 (1974).

[15] R. Huisman and F. Jellinek, J. Less-Common Metals 17, 111 (1969).

[16] F. J. DiSalvo, private communication.

[17] P. M. Williams, private communication.

[18] R. Huisman, R. DeJonge, C. Haas, and F. Jellinek, J. Solid State Chem. 3, 56 (1971).

[19] F. R. Gamble, J. Solid State Chem. 9, 358 (1974).

[20] P. M. Williams and F. R. Shepherd, J. Phys. C: Proc. Phys. Soc., London 6, L36 (1973); F. R. Shepherd and P. M. Williams, to be published.

[21] G. K. Wertheim, F. J. DiSalvo, and D. N. E. Buchanan, Solid State Commun. 13, 1225 (1973).

[22] L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, N.Y., 1960), 3rd ed.

[23] J. St. John and A. Block, Phys. Rev. Lett. 33, 1095 (1974).

[24] W. A. Harrison and S. Ciraci, Phys. Rev. B 10, 1516 (1974).

[25] J. P. Tidman, O. Singh, A. E. Curzon, and R. F. Frindt, Phys. Mag. 30, 1191 (1974).

Nuclear Spin-Lattice Relaxation and Local Susceptibilities in Tetrathiafulvalene Tetracyanoquinodimethane*

E. F. Rybaczewski,[†] A. F. Garito, and A. J. Heeger
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174

and

E. Ehrenfreund[‡]
Department of Physics, Technion-Israel Institute of Technology, Haifa, Israel

(Received 29 October 1974; revised manuscript received 27 January 1975)

We present the temperature dependence of the proton spin-lattice relaxation rates (T_1^{-1}) for pure tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) and its deuterated analogs TTF(D_4)-TCNQ and TTF-TCNQ(D_4). In the metallic region, the relaxation is Korringa-like, characteristic of metals without strong electron-electron Coulomb correlations.

We have measured the proton spin-lattice relaxation rates (T_1^{-1}) in the one-dimensional organic metal tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ)[1-7] and its deuterated analogs TTF(D_4)-TCNQ and TTF-TCNQ(D_4) from 4.2 to 300 K. Since the protons are directly coupled to the electronic system through the hyperfine interaction, selective deuteration of the proton sites on either the TTF or the TCNQ chains allows the use of NMR to probe the local electronic susceptibility.

TTF-TCNQ crystallizes in regular segregated chains[8] of TTF donors containing holes and of TCNQ acceptors containing an equal number of electrons. If precisely one electron were transferred in the salt, both the anion and cation chains would be half-filled with a Fermi wave number $k_\mathrm{F} = \pi/2a$. However, there is evidence from analysis of x-ray measurements of molecular bond lengths[8] and from photoemission studies[9] that the charge transfer is incomplete, leading to different band occupations on each chain. The relatively large negative thermopower[7] is consistent with incomplete charge transfer. Because of the different Fermi wave numbers and the intrinsically different intramolecular interactions, the TTF and TCNQ chains are not expected to be the same. Hence, nuclear-relaxation studies on the individual molecular chains are important.

High-purity TTF-TCNQ and its deuterated analogs were prepared by methods described earlier.[5] TTF and TCNQ were deuterated following the procedures of Yamagishi *et al.*[10] Mass spectral analyses showed greater than 99% deuteration for TCNQ(D_4) and 93% for TTF(D_4), with each level of deuteration being maintained during the formation of the corresponding TTF-TCNQ salt. High-resolution infrared measurements of the relative intensities of C-H and C-D molecular stretch modes in TTF(D_4) and TCNQ(D_4) confirmed the percentage of deuteration in each case, and high-resolution NMR measurements of TCNQ(D_4) and TTF(D_4) solutions were consistent with these results.

The proton spin-lattice relaxation times (T_1) were measured at 10 and 38 MHz using a 90°-comb-τ-90°-pulse sequence to within an accuracy of ±15%. The nuclear-spin magnetization re-