Effect of Nonstoichiometry on the Periodic Lattice Distortion in Vanadium Diselenide[1]

LYNN F. SCHNEEMEYER,[2] ANGELICA STACY, and M. J. SIENKO*

Precise measurements of the static magnetic susceptibility have been carried out over a range of temperatures (1.8–300 K) on a series of compounds of formula $V_{1+x}Se_2$ (0 < x < 0.20). The onset temperature of the charge-density-wave transition decreases slightly while the magnitude of the susceptibility drop rapidly decreases with increasing deviation from ideal stoichiometry. Enhancement of the Curie tail and decrease of the crystallographic c/a ratio are attributed to excess vanadium in the van der Waals gap.

Introduction

Vanadium diselenide is a metallic compound having the cadmium iodide layer structure (space group $P\bar{3}m1$) which, below a characteristic onset temperature, undergoes a periodic lattice distortion (PLD) coupled with a charge density wave (CDW).[3] The onset of the distortion, which at first is incommensurate with the periodicity of the underlying lattice, occurs at 117 K,[4] but there is another transition at 75 K[4] where the CDW and associated PLD lock in and become commensurate with the undistorted lattice. The combined distortion CDW–PLD shows up as a superlattice in electron diffraction and X-ray diffraction photographs.[5]

Vanadium diselenide is notable for commonly showing departure from 1:2 vanadium-to-selenium stoichiometry.[6] Generally, there is an excess of vanadium which is believed to reside in the van der Waals gap between the successive Se–V–Se sandwiches that make up this layer compound. The aim of this investigation was to examine the effect of this departure from stoichiometry on the CDW–PLD transitions. Since magnetic susceptibility is particularly sensitive for detecting the CDW transition in VSe_2,[7] it was the property examined. The program comprised synthesis of $V_{1+x}Se_2$ over a range of stoichiometry, analytical and X-ray characterization of the products, and measurement of the magnetic susceptibility over a range of temperatures in the cryogenic region.

Experimental Section

Materials. All samples were prepared from high-purity reagents in order to minimize magnetic impurities. Starting materials were 99.98% V from Materials Research Corp. and 99.999% Se from Ventron Division, Alfa Products. Appropriate quantities of the elements were placed in fused silica tubes which were then evacuated to 10^{-5} torr and sealed. Tubes were prepared by cleaning with aqua regia and degassing at 1000 °C for 1 h.

Sample tubes, inside Kanthal coils, were placed in the portion of box or tube furnaces where the temperature profile is nearly flat. Samples were heated to 300 °C for 3 days. The temperature was then raised to 800 °C and held there for 1 week. After 1 week at 800 °C, samples were cooled to room temperature, shaken thoroughly, then reheated at 800 °C for 3 days, and annealed at 650 °C for 1 week. Samples were quenched into water from 650 °C. Small traces of free selenium on the order of a few milligrams were condensed on the walls of all the sample tubes.

Four additional samples with $0 \leq x \leq 0.04$ plus one sample containing a slight excess of selenium were prepared as described above. However, these samples were heated for a second week at 800 °C and then quenched into water from that temperature. Again, traces of selenium condensed onto the walls of the sample tubes. The quantity

Table I. Analytical Data for Some $V_{1+x}Se_2$ Materials

sample	nominal compn	determined compn
V1	$V_{1.005}Se_2$	$V_{0.98 \pm 0.02}Se_2$
V3	$V_{1.02}Se_2$	$V_{1.03 \pm 0.02}Se_2$
V4	$V_{1.04}Se_2$	$V_{1.06 \pm 0.02}Se_2$
V7	$V_{1.10}Se_2$	$V_{1.07 \pm 0.02}Se_2$

of free Se was about the same for all samples (with the exception of the sample prepared with excess selenium) and was still on the order of a few milligrams. However, the amounts were greater than amounts observed in samples quenched from 650 °C.

As a calibration specimen, one sample was prepared to be as stoichiometric as possible. Its reaction and annealing temperatures were 400 °C, and it was prepared under an excess of selenium calculated to give 1 atm overpressure, with the assumption of $Se_2(g)$. The sample was first heated for 22 days at 400 °C and then ground and reheated for another 9 days at 400 °C. Unlike the 600 °C quenched material, which appeared crystalline, the 400 °C material was a fine gray powder that looked and smeared like MoS_2. The c parameter of the 400 °C material (6.132 Å) was slightly higher than that of the 600 °C material (6.106 Å), suggesting less interstitial vanadium between the layers. This is believed to be the most stoichiometric VSe_2 of the lot, as its Curie tail was apparent only below 20 K.

Analysis. Samples were analyzed for vanadium content by the Analytical Facility of the Materials Science Center of Cornell University using both neutron activation analysis and atomic absorption spectrometry. While values determined by atomic absorption spectrometry had better precision, the results are relatively insensitive to the level of vanadium excess. Results determined by atomic absorption spectrometry are given in Table I.

All samples were characterized by powder X-ray diffraction. A sample with nominal composition $V_{1.20}Se_2$ showed extra lines in its X-ray pattern, indicating that the phase limit for hexagonal $V_{1+x}Se_2$ occurs for x < 0.20.

Powder X-ray Diffraction. Powder diffraction patterns were recorded on film by using a 114.6-mm Debye–Scherrer camera and nickel-filtered copper Kα radiation. Powder samples were sealed in Pyrex capillaries. As it was found that grinding greatly broadened back-reflection lines, samples were sieved through a No. 100 mesh wire.

X-ray lines were measured to 0.03 cm and intensities estimated visually. Distances and diffraction angles were calculated by the Straumanis method, correcting for film shrinkage and uncertainty in the camera radius. All lattice parameters were determined by Cohen's least-squares method for hexagonal systems.

Figure 1 shows the variation of lattice parameters with composition. The compositions used in these figures are nominal compositions. Actual compositions are approximately 0.5% more metal rich. Both the a and the c parameters show smooth variations. The variations are such that the c/a ratio decreases nearly linearly for 0 < x < 0.12.

Magnetic Susceptibility Measurements. Susceptibilities were measured by the Faraday method using the procedure and apparatus described elsewhere.[8] Approximately 10-mg samples were weighed in Spectrosil silica buckets by using a Cahn RG electrobalance. The field gradient was calibrated with $HgCo(SCN)_4$. Susceptibilities were generally found to be field independent; values reported are an average

(1) This research was sponsored by the Air Force Office of Scientific Research under Grant No. 74-2583 and was supported in part by the National Science Foundation and the Materials Science Center at Cornell University.
(2) Marion Talbot Fellow of the American Association of University Women.
(3) Wilson, J. A.; DiSalvo, F. J.; Mahajan, S. *Adv. Phys.* **1975**, *24*, 117.
(4) Schneemeyer, L. F.; Sienko, M. J. *J. Less-Common Met.* **1978**, *62*, 343.
(5) Williams, P. M. In "Physics and Chemistry of Materials with Layered Structures"; Levy, F. Ed.; D. Reidel: Boston, 1976; Vol. 2, p 64.
(6) Hoschek, E.; Klemm, W. *Z. Anorg. Allg. Chem.* **1939**, *242*, 49.
(7) Bayard, M.; Sienko, M. J. *J. Solid State Chem.* **1976**, *19*, 325.

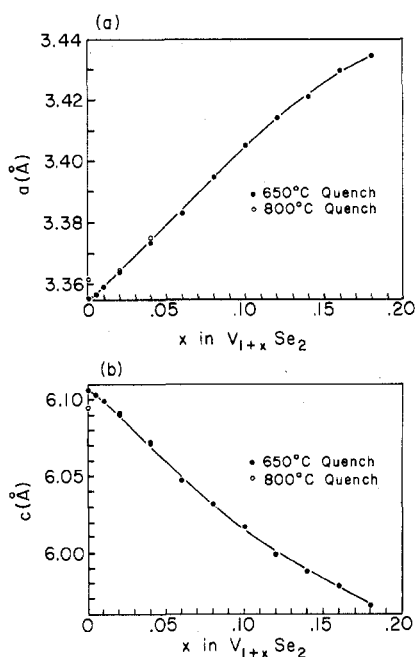(8) Young, J. E., Jr. Ph.D Thesis, Cornell University, 1971.

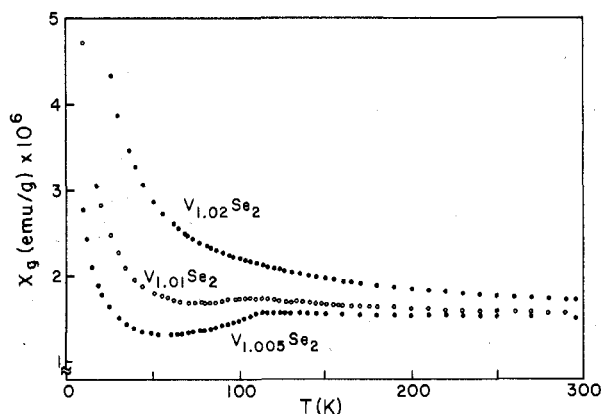**Figure 1.** Lattice parameters in the system $V_{1+x}Se_2$: (a) a parameter vs. x; (b) c parameter vs. x.

Figure 2. Gram-susceptibilities vs. temperature for several non-stoichiometric vanadium diselenides.

Figure 3. Gram-susceptibilities vs. temperature for several non-stoichiometric diselenides.

Figure 4. Kink anomaly in the gram-susceptibility vs. temperature of $V_{1.01}Se_2$.

Table II. Onset (T_o) and Lock-In (T_D) Temperatures of VSe_2

investigator	T_o, K	T_D, K	ref
Bayard, Sienko	110	100	11
Thompson, Silbernagel	120	~75	10
Williams	120	~70	5
van Bruggen, Haas	100	80	12
DiSalvo, Waszczak	112	~80	13
Schneemeyer, Sienko	117	75	4

of those measured at the three highest applied fields. Measurements were carried out over the range 1.8–300 K. Temperatures were controlled to 0.1 K or better with an Oxford Instruments digital temperature controller fitted for use with a gold +0.07% iron vs. chromel P thermocouple with a liquid-nitrogen reference. The temperature region 1.8–100 K was monitored by a CryoCal calibrated germanium resistance thermometer; 100–300 K, by a copper-constantan thermocouple.

All susceptibilities reported include a correction for the diamagnetism of the quartz bucket. The bucket was found to have a small Curie-like paramagnetic component which became important below about 40 K. An uncertainty of about 2 or 3% can be attributed to the results.

Figures 2 and 3 show the temperature dependence of the observed gram-susceptibilities for a series of $V_{1+x}Se_2$ materials where x again represents nominal composition. Most noticeable is the increase in the Curie tail with increasing vanadium excess. Also, the slope discontinuity moves to lower temperatures as x increases, occurring at ~115 K for $V_{1.005}Se_2$ and decreasing to ~105 K in $V_{1.01}Se_2$. A detail of the kink anomaly of the $V_{1.01}Se_2$ sample is shown in Figure 4. As can be seen in this figure, assignment of T_{onset} becomes somewhat ambiguous as the nonstoichiometry is increased.

Discussion

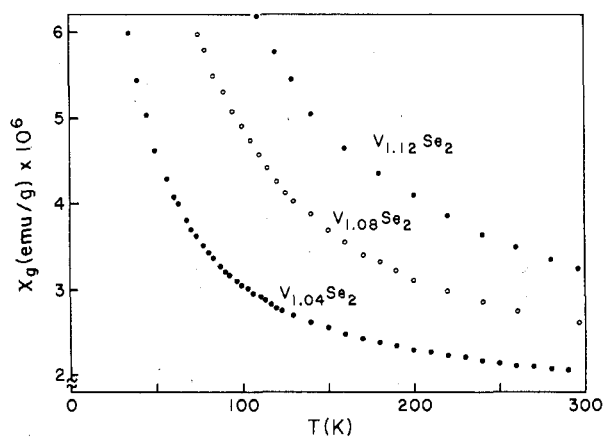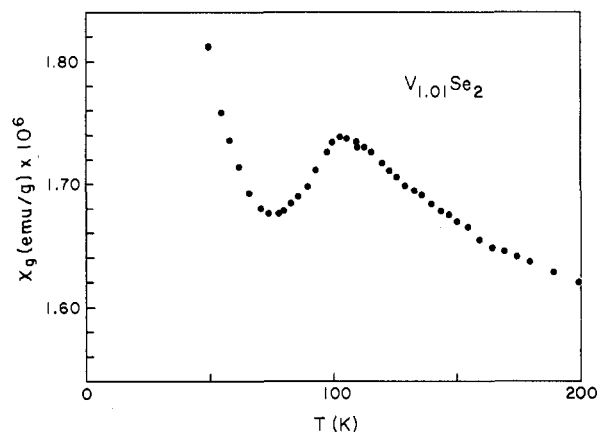The precise temperature of the onset of the incommensurate CDW in vanadium diselenide has been the subject of some

controversy. Temperatures given for the onset to the incommensurate CDW state range from 100 to 140 K while reported lock-in temperatures range from 70 to 106 K. A summary of these results is given in Table II.

The first report of a CDW state in VSe_2 by Thompson and Silbernagel[9,10] contained little detail and no conclusions could be drawn from their data. Bayard and Sienko[11] reported an onset temperature of 105–110 K for a sample prepared at 750 °C with no excess selenium. The temperature was estimated from the appearance of a slope discontinuity in the magnetic susceptibility. In an investigation of VSe_2 single crystals prepared by selenium transport in an 870 °C → 780 °C gradient (pressure ~3.5 atm with the assumption of Se_2 molecules in the vapor), van Bruggen and Haas[12] found an onset temperature of ~100 K. They reported an analysis of the material which showed the actual composition of their

(9) Thompson, A. H. *Phys. Rev. Lett.* **1975**, *34*, 520.
(10) Thompson, A. H.; Silbernagel, B. G. *Bull. Am. Phys. Soc.* **1976**, [2] *21*, 260.
(11) Bayard, M.; Sienko, M. J. *J. Phys. (Orsay, Fr.)* **1976**, *37*, 169.
(12) van Bruggen, C. F.; Haas, C. *Solid State Commun.* **1976**, *20*, 251.

Table III. Room-Temperature Susceptibilities, Temperature-Independent Susceptibility Components, and Curie-Weiss Constants of $V_{1+x}Se_2$ Samples

material[a]	$10^6 \chi_{RT}$, emu/g	$10^6 \chi_{TI}$, emu/g	$10^4 C$, cm³ deg/g	Θ, K	μ,[b] μ_B	T_o, K
VSe₂, 400 °C quenched	1.42	0.74	0.0094	−1.4		119
VSe₂, 600 °C quenched	1.63	0.85	0.039	0.0		117
$V_{1.005}Se_2$	1.51	1.03	0.14	+1.2	2.2	~115
$V_{1.01}Se_2$	1.56	1.10	0.35	+0.2	2.4	~105
$V_{1.02}Se_2$	1.72	1.60	0.71	+0.6	2.4	
$V_{1.04}Se_2$	2.04	2.63	1.2	+1.4	2.3	
$V_{1.08}Se_2$	2.60	1.49	3.3	+1.6	2.7	
$V_{1.12}Se_2$	3.23	1.60	4.9	+2.2	2.7	

[a] $V_{1+x}Se_2$ samples quenched from 650 °C with no excess selenium; VSe₂ samples annealed with 1 atm overpressure of selenium. [b] Calculated from $\mu = 2.83(C_M/x)^{1/2}$.
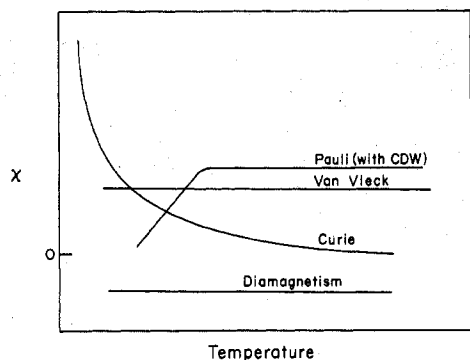

Figure 5. Components contributing to the observed susceptibility in a sample showing CDW formation.

Figure 6. $\chi_{Pauli-CDW}$ vs. temperature, showing the susceptibility change due to onset of the CDW, in $V_{1.01}Se_2$.

samples to be $V_{1.015}Se_2$. For samples prepared at 650 °C under 1 atm Se₂ pressure, believed to be very close to ideal stoichiometry, DiSalvo and Waszczak[13] gave an onset temperature of 112 K. More recently, Thompson and Silbernagel,[14] reporting on VSe₂ crystals for which preparation conditions were not specified, indicated for the susceptibility a small drop (of unknown origins) near 140 K, the onset of a large change near 120 K, and a discontinuity near 75 K.

From these data it appears that there is a correlation between reaction temperature and CDW onset temperature. As samples are made less stoichiometric by preparation at higher temperatures, the onset temperature, estimated from the appearance of the kink anomaly in the magnetic susceptibility, decreases. There is, however, a problem in assigning exactly where the kink anomaly begins.

The raw susceptibility as measured by the Faraday method is the sum of several components:

$$\chi = \chi_{core} + \chi_{LP} + \chi_{Pauli} + \chi_{VV} + \chi_{Curie}$$

χ_{core} is a diamagnetic part due to core electrons, χ_{LP} is a second diamagnetic part due to Landau–Peierls diamagnetism of itinerant electrons, χ_{Pauli} is the Pauli paramagnetism of the electron gas, χ_{VV} is the Van Vleck high-frequency paramagnetism, and χ_{Curie} is the Curie paramagnetism of localized magnetic moments. In first order, all these terms except the last are expected to be temperature independent. They are related ideally as shown in Figure 5. The Pauli susceptibility, which is proportional to the density of states at the Fermi level, is normally temperature independent but will be drastically reduced by onset of the charge density wave, since the CDW leads to destruction of some of the conduction band states. Hence, a kink anomaly is observed in the susceptibility. Unfortunately, there may also be changes in χ_{LP} and χ_{VV} associated with the destruction of conduction band states, so
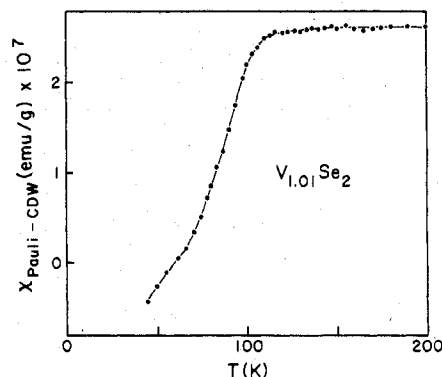
the individual contributions cannot be cleanly separated as shown. Still, by using the low-temperature data it should be possible to separate out the Curie contribution, provided there is no strong interaction between the localized moments. Writing the low-temperature susceptibility as the sum of a temperature-independent (χ_{TI}) and a temperature-dependent term $[C/(T - \Theta)]$, we have computer fitted the low-temperature data to obtain the results shown in Table III. The exceedingly small values of the Weiss constant Θ indicate negligible interaction between the localized moments giving rise to the Curie tail.

When the gram Curie constants of the Curie tail are plotted as a function of x, the variation is found to be linear. Since the molar constant C_M is given by $(N\mu^2)/3k$, we can calculate from it the magnetic moment per excess vanadium atom. These moments, as shown in Table III, come out to be ~2.5 μ_B, similar to that found in V_5Se_8.[15] This suggests that the interlayer vanadium is in the form of V^{3+} (d^2) ions.

Once the Curie–Weiss part and the low-temperature term χ_{TI} have been established, we can look at the temperature dependence of the Pauli susceptibility as modified by onset of the CDW. Writing

$$\chi_{Pauli-CDW} = \chi_{obsd} - \chi_{TI} - C/(T - \Theta)$$

we have for $\chi_{Pauli-CDW}$ the behavior shown in Figure 6. For a sample with nominal composition $V_{1.01}Se_2$, $\chi_{Pauli-CDW}$ is nearly constant at high temperatures, begins to fall off slightly near 140 K, and then falls off sharply near 100 K. Small discontinuities near 75 K are presumably associated with the transition to the commensurate CDW state. Thompson and Silbernagel[15] suggest the slight falloff at ~140 K is due to precursor effects and assign $T_o = 120$ K to all $V_{1+x}Se_2$ samples. Although we agree qualitatively with Silbernagel and Thompson, we also find that the kink discontinuity associated

(13) DiSalvo, F. J.; Waszczak, J. V. *J. Phys. (Orsay, Fr.)* **1976**, *37*, 157.
(14) Thompson, A. H.; Silbernagel, B. C. *Phys. Rev. B: Condens. Matter* **1979**, *19*, 3420.

(15) Thompson, A. H.; Silbernagel, B. G. *J. Appl. Phys.* **1978**, *49*, 1477.

with T_{onset} sets in at *slightly lower* temperature with increasing deviation from ideal nonstoichiometry.

Nonstoichiometry also causes a rapid reduction in the magnitude of the CDW anomalies. The drop-off in $\chi_{Pauli-CDW}$ in the 0.5%-excess sample is nearly twice as great as in the 1%-excess sample. Thus, since the magnitude of the effect reflects the change in the density of states at the Fermi level, increased deviation from ideal stoichiometry leads to a decrease in the number of Fermi surface states destroyed. The cause of the effect is not well understood. It may be that donation of electrons to the conduction band by interlayer vanadium acts to remove inherent Jahn–Teller type distortion in VSe_2 layers. This appears to be the case on intercalation of lithium to form $LiVSe_2$, where the lattice expands by only 0.25 Å in spite of the Li introduced between the layers.[16] Alternatively,

band filling may move the Fermi surface off a peak in the density of states and make CDW effects increasingly unfavorable with increased deviation from ideal stoichiometry.

Compared to other layer compounds, stoichiometric VSe_2 has an anomalously large c/a ratio.[9] As seen in Figure 1, the c parameter decreases and the a parameter increases with increasing deviation from stoichiometry. The former comes from the action of interlayer vanadium atoms to pin the layers together; the latter, from increased Coulombic repulsion due to electrons donated into the layer by excess vanadium atoms in the gap.

Registry No. VSe_2, 12299-51-3.

---

(16) Beal, A. B.; Liang, W. Y. *J. Phys. C* **1973**, *6*, L482.

Contribution from the Department of Chemistry,
The University of Texas at Austin, Austin, Texas 78712

Ground States of Molecules. 54.[1] MNDO Study of Carboranes

MICHAEL J. S. DEWAR* and MICHAEL L. McKEE

MNDO calculations are reported for all the known carboranes up to and including $(B,C)_{12}$ which have not been treated in an earlier paper of this series. If appropriate symmetry constraints are applied, the calculated geometries are in good agreement with experiment. In some cases, however, the symmetrical structures are not local minima on the MNDO potential surface. Other calculated properties also agree well with the available data.

Introduction

The boron hydrides and carboranes represent an area of chemistry of unusual theoretical interest in view of the prevalence of multicenter bonds. While the basic principles governing bonding in such "electron deficient" molecules were established many years ago by Longuet-Higgins,[2] this is clearly a field where quantitative calculations of molecular structure and chemical reactivity would be of great interest and value. Numerous calculations have of course been reported, but virtually none so far has been of value in this connection, for the following reasons.

The first is purely technical. If we are concerned with interpreting or predicting the structures of molecules, we must calculate their geometries properly, by minimizing their energies with respect to all the relevant geometrical parameters and without making *any* assumptions. We must also make sure that the stationary points we find do in fact correspond to local minima and not to saddlepoints (i.e., transition states). This is particularly necessary in cases of molecules with potential symmetry because it is very easy to mistake for a minimum a symmetrical structure which in fact is the transition state for the interconversion of two unsymmetrical mirror-image isomers. This situation arises frequently in the boron hydrides and carboranes where symmetrical "nonclassical" structures are related in this way to pairs of "classical" isomers. It is important to establish whether the latter are stable species, interconverted via a "nonclassical" transition state, or unstable species, only the "nonclassical" structure representing a local minimum. At present the only reliable procedure for this purpose is one introduced by McIver and Komornicki,[3] i.e., calculating and diagonalizing the

Hessian (force constant) matrix. At a minimum, the eigenvalues of the Hessian are all positive, apart from six zero values corresponding to translation and rotation), while at a transition state one, and only one, is negative. The presence of six vanishing eigenvalues also serves as a useful criterion of convergence to the stationary point. The need for these precautions has been demonstrated very clearly by our own calculations for the boron hydrides.[4]

Similar considerations apply even more forcefully to studies of chemical reactions where it is necessary to establish not only that a given stationary point is of the right type (i.e., a saddlepoint) but also that it is a transition state for the reaction under consideration and not for some different process. One must establish that there are downhill paths from it to both reactants and products. Here again our own experience has shown these precautions to be absolutely essential.[5]

No calculations which met these conditions have as yet been reported for any carborane.

Second, one must naturally use a procedure which can reasonably be expected to give sufficiently accurate results. *No* theoretical treatment currently applicable to polyatomic molecules gives values for the total energies of molecules that are accurate enough for chemical purposes.[6] Nevertheless

---

(1) Dewar, M. J. S.; Rzepa, H. S. *Inorg. Chem.* **1979**, *18*, 602.
(2) Longuet-Higgins, H. C. *J. Chim. Phys. Chim. Biol.* **1949**, *46*, 268.
(3) McIver, J. W., Jr.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625. Komornicki, A.; McIver, J. W., Jr. *Ibid.* **1973**, *95*, 4512.

(4) Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1978**, *17*, 1569.
(5) See, e.g.: Dewar, M. J. S.; Ford, G. P.; Rzepa, H. S. *J. Chem. Soc., Chem. Commun.* **1977**, 728.
(6) The errors in molecular energies calculated by the Hartree–Fock procedure (i.e., those given in the limit by RH treatments if sufficiently large basis sets are used) are comparable with their heats of atomization, e.g., ca. 1000 kcal/mol for benzene. This error, due to neglect of electron correlation, can be reduced by CI to an extent depending on the size of the basis set. With the largest basis sets that have been used for polyatomic molecules (double ζ + polarization), ca. 80% of the correlation energy can be recovered. The higher percentages often quoted in the literature refer to *recoverable* correlation energy, not to total correlation energy. An error equal to 20% of the heat of atomization of a molecule is very large by chemical standards (e.g., 200 kcal/mol for benzene).