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**PROPERTIES OF MOLECULAR SOLIDS AND FLUIDS AT
HIGH PRESSURE AND TEMPERATURE**

Final Report

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Richard D. Etters

**Colorado State University
Fort Collins, Colorado 80523**

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ABSTRACT

The main thrust of this work was directed to the task of determining the thermodynamic behavior of condensed solids and fluids containing simple molecules. Properties calculated include specific heats, equations of state, compressibilities, sound velocities, virial coefficients, viscosities, and thermal expansion. In addition, details of the structural, orientational, and magnetic phase transitions were determined. Dynamical quantities calculated include the lattice, libron, and vibron mode frequencies at various pressures and temperatures.

Also, we developed new techniques required to meet our objectives. One was a method for accurately calculating the Gibbs free energy of various phases. Another is the multiple-histogram Monte Carlo which can dramatically reduce computing time and can provide a continuous map of thermodynamic averages over a range of some thermodynamical variable.

EVALUATION OF PROGRESS

The following articles represent the work during the period of grant DE-FG02-86ER45238. They have been published in various international journals.

1. B. Silvi, V. Chandrasekharan, M. Chergui, and R. D. Etters, "Frequency Shifts of Vibrational and Rotational States of Dilute H_2 , D_2 , and HD Impurities in Solid Ar Under Pressure," *Phys. Rev. B* **33**, 2749 (1986).
2. R. D. Etters, B. Silvi, V. Chandrasekharan, and M. Chergui, "Vibrational and Rotational Frequency Shifts of Dilute H_2 , D_2 , and HD Impurities in Solid Ar, Kr, and Xe Under Pressure," *Int. J. Quant. Chem.* **19**, 675 (1986).
3. V. Chandrasekharan, B. Silvi, M. Chergui, and R. D. Etters, "Crystal Field Induced Frequency Shifts of the Vibrational and Rotational States of H_2 , D_2 , and HD Impurities Under Pressure in Solid Kr and Xe Matrices," *J. Phys. Chem.* **91**, 1623 (1986).
4. D. Kirin and R. D. Etters, "Calculated Static and Dynamic Properties of Solid α - F_2 ," *J. Chem. Phys.* **84**, 3439 (1986).
5. R. D. Etters and D. Kirin, "High Pressure Behavior of Solid F_2 at Low Temperatures," *J. Phys. Chem.* **90**, 4670 (1986).

6. R. E. Etters, V. Chandrasekharan, E. Uzan, and K. Kobashi, "High Pressure Static and Dynamic Properties of the R $\bar{3}$ C Phase of Solid Nitrogen, " Phys. Rev. B 33, 8615 (1986).
7. R. D. Etters, J. Belak, and R. LeSar, "Thermodynamic Character of the Vibron Frequencies and Equation of State in Dense, High Temperature, Fluid N $_2$," Phys. Rev. B 34, 4221 (1986).
8. V. Chandrasekharan, E. Uzan, and R. D. Etters, "Intermolecular Potentials and Solid N $_2$," Dynamics of Molecular Crystals, edited by J. Luscombe, Elsevier, p. 41 (1987).
9. J. Belak, R. D. Etters, and R. LeSar, "Thermodynamic Properties and Equation of State of Dense, Fluid Nitrogen," J. Chem. Phys. 89, 1625 (1988).
10. J. Belak, R. D. Etters, and R. LeSar, "Calculated Thermodynamic Properties and Phase Transitions of Solid N $_2$ at Temperatures $0 \leq T \leq 300$ K and Pressures $0 \leq P \leq 100$ GPa," J. Chem. Phys. 92, 5430 (1990).
11. R. LeSar and R. D. Etters, "Character of the Alpha-Beta Phase Transition in Solid Oxygen," Phys. Rev. b 37, 5364 (1988).
12. B. Kuchta and R. D. Etters, "Prediction of a High Pressure Phase Transition and Other Properties of Solid CO $_2$ at Low Temperatures," Phys. Rev. B 38, 6265 (1988).
13. R. D. Etters and B. Kuchta, "Static and Dynamic Properties of Solid CO $_2$ at Various Temperatures and Pressures," J. Chem. Phys. 90, 4537 (1989).
14. B. Kuchta and R. D. Etters, "Generalized Free Energy Method Used to Calculate the High Pressure-High Temperature Phase Transition in Solid CO $_2$," Phys. Rev. B 47, 14691 (1993).
15. R. D. Etters and B. Kuchta, "New Methods for Calculating Phase Transitions in Simple Molecular Crystals: Application to N $_2$ O and CO $_2$," accepted Plenum Press (1994).
16. B. Kuchta and R. D. Etters, "Calculated Properties of Solid N $_2$ O at Various Temperatures and Pressures," J. Chem. Phys. 95, 5399 (1991).
17. B. Kuchta and R. D. Etters, "A Method for Calculating Solid-Solid Phase Transitions at High Temperatures: Application to N $_2$ O," Phys. Rev. B 45, 5072 (1992).
18. B. Kuchta, R. D. Etters, and R. LeSar, "The Influence of Molecular Shapes on the Relative Stability of Solid Phases: Application to N $_2$ O," J. Chem. Phys. 97, 5662 (1992).
19. B. Kuchta, T. Luty, and R. D. Etters, "On the Nature of the Orientational Transition in Crystalline A-TCNB," J. Chem. Phys. 93, 5935 (1990).
20. B. Kuchta and R. D. Etters, "Calculated High Pressure Properties of Solids Composed of Non-Centrosymmetric Molecules, Frontiers of High Pressure Research, edited by D. Hochheimer and R. D. Etters, Plenum Press, New York, Vol. 286, 171 (1992).

21. Frontiers of High Pressure Research, edited by D. Hochheimer and R. D. Etters, Plenum Press, New York, NATO ASI Series, Vol. 286, March (1992).
22. R. D. Etters, "Structures and Phase Transitions of Simple Molecular Solids, Simple Molecule at Very High Density", edited by A. Polian, P. Loubeyre, and N. Boccarda, Plenum Press, New York, p. 109 (1989).
23. R. D. Etters and B. Kuchta, "Calculation Methods for Predicting Phase Transitions in Simple Molecular Solids," *Low Temp. Phys.* **19**, 373 (1993).

Behavior of H₂, D₂ and HD Impurities in Solid Rare Gases (Articles 1–3)

In this work the vibrational, rotational, and vibrational-rotational spectra of dilute H₂, D₂ and HD molecules, matrix isolated in solid Ar, Kr, and Xe, was calculated at pressures $0 \leq P \leq 57$ GPa. Also calculated were the impurity local mode frequencies and the distortion of the host lattice for 16 shells around the impurity. The modes are red shifted at zero pressure but become strongly blue shifted at high pressure. There is little experimental information at high pressures, but at low pressures our results showed an incorrect identification of several levels in some experimental work.

Solid Fluorine (Articles 4, 5)

Ground state calculations showed that the C2/c structure was the stable state, as deduced from experiment. The lattice parameters, orientations, molar volume, sublimation energy, second virial coefficients, and the zone center phonon and libron frequencies, were determined. The results were very sensitive to the value used for the quadrupole moment Θ , that was poorly known. We found that for $\Theta > 0.7 \times 10^{-26}$ esu the equilibrium structure was the cubic Pa3 phase, and for $\Theta < 0.4 \times 10^{-26}$ esu the structure was R $\bar{3}m$. Although the x-ray data are not of high quality, these symmetries are not possible. We found that $\Theta \approx 0.65 \times 10^{-26}$ esu best predicts the known properties of solid F₂. Recent *ab initio* calculations have determined that Θ is exactly as we deduced. Another work was devoted to calculating properties over the pressure range $0 \leq P \leq 10$ GPa. Determined were the equilibrium structures, the equation of state, and the lattice and vibron frequencies,

versus pressure. The comparison with the limited experiment was excellent. No phase transition was not observed for pressures $P < 10$ GPa.

Solid and Fluid N_2 (Articles 6–10)

The properties of fluid N_2 were calculated for temperatures 300–3000 K and pressures $0.2 \leq P \leq 30$ GPa. Over this range the volumes, enthalpies, vibron frequencies, thermal expansivity, compressibility, specific heat, Grüneisen parameter, speed of sound, and bond lengths were calculated. The results agreed well with experiment, including shock data, where comparisons are possible. In agreement with experimental studies of fluid metals, we find that the velocity of sound varies linearly with density, along isotherms and the Hugoniot. We find that $\rho\gamma_g$, the density times the Grüneisen parameter, varies considerably with density and temperature. This is important because many model and phenomenological equations of state assume that this product is a constant. This is the most extensive work attempted on fluid N_2 .

An exhaustive study of solid N_2 was conducted over the range $0 \leq T \leq 300$ K and $0 \leq P \leq 100$ GPa. the phases $\alpha(Pa3)$, $\beta(P6_3/mmc)$, $\delta(Pm3n)$, and $\epsilon(R\bar{3}c)$, were examined, including the transitions between them. Calculated were the equations of state at 0 K and 300 K, the lattice mode frequencies for the β and δ phases at 300 K, the vibron mode frequencies versus T and P in the α , β , γ , δ , ϵ phases, thermal expansion coefficients, phase transition pressures and temperatures, second virial coefficients, and various orientational order parameters. This is the most global study of solid N_2 yet attempted. Of the numerous findings, two strike me. First, we found that the orientational disorder in the β phases is quite different than previously deduced. Secondly, we found that by either cooling or increasing pressure from the disordered δ phase, resulted into an orientationally ordered phase with low symmetry than the Pm3n structure. Suffice to say that this work was very fruitful.

Solid Oxygen (Article 11)

It was found that the ground state is an antiferromagnetic monoclinic $C2/m$ structure, as is known experimentally. At $T \approx 18$ K we observe a transition into a rhombohedral $R\bar{3}m$ structure, as is known. Simultaneously, a magnetic transition occurs into a quasihelical state with short-ranged correlations. Clearly, this is a frustrated antiferromagnetic system. This is the first determination of the β phase magnetism.

Solid CO_2 (Articles 12–14)

This system has long been difficult both experimentally and theoretically. Until recently the only known solid phase was the cubic $Pa3$ structure. Then, Raman studies indicated that a transition exists at high pressure, into an unknown structure. Our studies on solid CO_2 were over the range $0 \leq T \leq 300$ K and $0 < P \leq 18$ GPa. Calculated were the equations of state, second virial coefficients, libron frequencies, vibron frequencies versus temperature and pressure, and the thermal expansion. In addition, a phase transition from $Pa3$ to $Cmca$ was predicted at 4.3 GPa at low temperature and at 4.43 GPa at 300 K. This transition is characterized by a large hysteresis, which is caused by a large orientational potential barrier between the two phases. Special techniques were developed to calculate the transition pressure at 300 K.

Solid N_2O (Articles 15–18)

N_2O is very much like CO_2 except that it has no center of symmetry. Until recently the only known phase of the solid was either $Pa3$ or $P2_13$. Recent Raman spectra has shown evidence of a phase transition at about 5 GPa at 300 K and between $6 \leq P \leq 10$ GPa at 20 K. As with CO_2 , the transition exhibits a large hysteresis. Calculations at $T = 0$ K showed a transition at $P \approx 4.75$ GPa into a $Cmca$ structure. Using a new development, we were able to calculate the Gibbs free energy at 300 K and determine that the same transition occurs at 4.9 GPa. Thus dP/dT is nearly zero along the

transition line. In conjunction with LANL researchers, x-ray experiments have confirmed the $Cmca$ symmetry of the high pressure structure. Calculations on the low pressure cubic structure confirmed that the average symmetry is $Pa3$ provided that the end-to-end order of the molecules is random.

Organic Solids (Article 19)

Crystalline A-TCNB is interesting orientationally because the nearly static TCNB complexes are orientationally quiescent and the A molecules respond to an orientational double well potential provided by the TNCB. As a consequence the orientational character depends mostly upon a single degree of freedom. Properties calculated include the orientational structures, internal energy, specific heat, and the phase transition temperature. Order parameters that probe the microscopic nature of the transition show features of both an order-disorder and displacive character, much as observed by experiment.

Miscellaneous Results (Articles 20-23)

These works were mostly devoted to generalizations deduced from our and others work, and to important techniques developed for this grant work.

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