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THE DEPENDENCE OF THE COHESIVE AND SURFACE ENERGIES OF CaF_2 ON THE REPULSIVE PARAMETERS AND COMPRESSIBILITY DATA

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ABSTRACT

The theoretical cohesive and surface energies of CaF_2 are calculated for a range of discrete values of the compressibility using relationships based on the Born and Mayer model of an ionic crystal. The sensitivity of the calculated values of the energies and of the repulsive parameters to small changes in the compressibility is reported and discussed.

INTRODUCTION

This paper reports the results of calculations of the theoretical cohesive and surface energies of CaF_2 for a range of values taken for the compressibility of the material. The discrete values assigned to the compressibility were selected in increments below and above the value of the compressibility of CaF_2 as reported by Bridgman (3). For each value of the compressibility the repulsive parameters, b and p , were determined and used in the calculations of the cohesive and surface energies. All of the other material constants and structure constants were held fixed in the calculations of the theoretical energies.

The theoretical cohesive energy was determined using relationships based on the Born and Mayer (2) model of an ionic crystal. The calculations require the summation of the terms representing the electrostatic energy, the first and second van der Waals energies, the repulsive energy, and the zero point energy. Surface energy is defined as the energy that is required to separate a crystal into two parts along a cleavage plane. For CaF_2 cleavage occurs on the (111) plane and the surface energy of the crystal can be expressed as the sum of the electrostatic energy, the dispersion energies, and the repulsive energy. For a detailed discussion and derivation of the equations for each of the energy terms the reader is referred to the work of Benson and Dempsey (1). The values of the material and structure constants used in calculating the cohesive and surface energies in this work are the same as those previously reported by Frounfelker (6).

DISCUSSION

Using the Born-Haber (4) relationship and thermochemical data the experimental value of the cohesive energy of CaF_2 has been determined by Sherman (11) as -617.2 kcal/mole and by Harries and Morris (9) as -617.0 kcal/mole. The theoretical cohesive energy of CaF_2 has been calculated by Benson and Dempsey (1), Harries and Morris (9), and Frounfelker (6), who

obtained values of -627.4 , -610.0 , and -625.0 kcal/mole respectively. The lower energy calculated by Harries and Morris is due, in part, to holding the repulsive parameter, p , fixed at 0.3333. The theoretical energy may be larger than the experimental energy due to a departure from the ideal bonding assumed in the Born and Mayer model. In general, however, the agreement between the theoretical and experimental values of the cohesive energy of CaF_2 is relatively good.

In contrast, a comparison of the experimental and theoretical values of the surface energy of CaF_2 indicates a wide variation in the reported energies. Using a method developed by Obreimov (10) and modified by Gilman (8), the experimental value of the surface energy of CaF_2 has been reported by Gilman as 450 ergs/cm² for cleavage on the (111) plane at -196°C . The theoretical value of the surface energy of CaF_2 has been reported by Benson and Dempsey (1) as 542.6 ergs/cm² and by Frounfelker (7) as 527.9 ergs/cm². The discrepancy between the theoretical values of the surface energy may be attributed to the strong dependence of the repulsive energy on the value taken for the compressibility. A small change in the compressibility causes a substantial variation in the calculated values of the repulsive parameters and results in a significant change in the calculated values of the surface energy. A computer program, previously written by Frounfelker (5), was used to compute the values of the repulsive parameters accurate to four decimal places.

RESULTS

The results of the calculations of the repulsive parameters for six values of the compressibility varying from 1.00 to 1.50 dyne⁻¹ cm² in increments of 0.1 are given in Table I. Both of the repulsive parameters increase with an increase in the value taken for the compressibility. The individual energy terms required to calculate the total theoretical cohesive energy were determined for each set of values of the repulsive parameters. The results are summarized in Table II where U_E is the electrostatic energy, U_{D_0} and U_{D_1} are the van der Waals energies, U_R is the repulsive energy, U_z is the zero point energy, and U_T is the total cohesive energy. The cohesive energy is not strongly dependent on the value taken for the compressibility because the

TABLE I
 VALUES OF THE PARAMETERS

$10^{12} \beta$ (dyne ⁻¹ cm. ²)	$10^{12} b$ (erg. mole ⁻¹)	p (angstroms)
1.00	1.0807	0.2541
1.10	1.1028	0.2729
1.20	1.1235	0.2910
1.30	1.1428	0.3085
1.40	1.1605	0.3252
1.50	1.1768	0.3413

TABLE II
 VALUES OF THE COHESIVE ENERGY TERMS

$10^{12} \beta$ (dyne ⁻¹ cm. ²)	1.00	1.10	1.20	1.30	1.40	1.50
U_E (kcal. mole ⁻¹)	-710.35	-710.35	-710.35	-710.35	-710.35	-710.35
U_{D_0} (kcal. mole ⁻¹)	-17.54	-17.54	-17.54	-17.54	-17.54	-17.54
U_{D_1} (kcal. mole ⁻¹)	-3.43	-3.43	-3.43	-3.43	-3.43	-3.43
U_R (kcal. mole ⁻¹)	88.93	95.30	101.36	107.12	112.60	117.82
U_z (kcal. mole ⁻¹)	3.19	3.19	3.19	3.19	3.19	3.19
U_T (kcal. mole ⁻¹)	-639.20	-632.83	-626.77	-621.01	-615.53	-610.31

repulsive energy is relatively small compared to the electrostatic energy and the variation in the repulsive energy is not significant for small changes in compressibility. The values calculated for the surface energy are shown in Table III where σ_E is the electrostatic energy, σ_{D_0} and σ_{D_1} are the dispersion energies, σ_R is the repulsive energy, and σ_T is the total surface energy. In particular, it should be noted that the contribution of the repulsive energy to the total surface energy is relatively large and the repulsive energy changes significantly with a change in compressibility. Hence, the surface energy of CaF_2 is strongly dependent on the value taken for the compressibility and the calculated values of the repulsive parameters.

TABLE III
 VALUES OF THE SURFACE ENERGY TERMS

$10^{12} \beta$ (dyne ⁻¹ cm. ²)	1.00	1.10	1.20	1.30	1.40	1.50
σ_E (erg. cm. ⁻²)	1093.54	1093.54	1093.54	1093.54	1093.54	1093.54
σ_{D_0} (erg. cm. ⁻²)	176.71	176.71	176.71	176.71	176.71	176.71
σ_{D_1} (erg. cm. ⁻²)	26.86	26.86	26.86	26.86	26.86	26.86
σ_R (erg. cm. ⁻²)	-647.91	-701.69	-754.09	-805.10	-854.72	-902.94
σ_T (erg. cm. ⁻²)	640.20	595.42	543.02	492.01	442.39	394.17

SUMMARY

The values of the repulsive parameters, b and p , the theoretical cohesive energy, and the theoretical surface energy were calculated for a range of values of the compressibility of CaF_2 . The results of the theoretical cohesive energy calculations are in relatively good agreement with experimental results and the cohesive energy is not relatively sensitive to small changes in the compressibility. In contrast, the theoretical surface energy is significantly larger than the experimental value reported by Gilman and the surface energy is strongly dependent on the value taken for the compressibility and on the calculated values of the repulsive parameters. Considerable care must be taken in selecting the material constants that affect the repulsive parameters and in the computer programming technique that is used to evaluate the repulsive parameters and the energies were programmed in the Fortran language and the results were obtained in the D. W. Mattson Computer Center at Tennessee Technological University.

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News of Tennessee Science

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The new, four-year capital expansion program approved for the Medical Units will include a new Basic Medical Sciences Complex (Biochemistry, Physiology, Pharmacology), a new library, Dentistry Building renovation and equipment, a Pathology Building addition, and a new Maintenance Center.

Dr. Albert R. Haskell, Executive Assistant to the Chancellor, received the Tom C. Sharp Sr. 'Pharmacist of the Year Award' at the June meeting of the Tennessee Pharmaceutical Association.

Dr. Richard P. White, Associate Professor of Pharmacology and recently-named member of the Collegium

Internationale Neuro-Psychopharmacologicum, is spending six months at the University of Birmingham Medical School in England investigating the effects certain drugs elicit when applied to neurons.

Dr. Sheldon B. Korones has been appointed Associate Professor of Pediatrics and Director of Newborn Nurseries for the City of Memphis Hospitals.

Dr. James W. Fisher, Professor of Pharmacology, has recently returned from Corrientes, Argentina, where he aided in the organization of a Department of Pharmacology at the Northeast University Medical School.

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