recast forms of the energy roots (3) into the Van Vleck equation (4) and the mean susceptibility calculated from $\chi = (\chi_{\parallel} + 2\chi_{\perp})/3$. At temperatures where kT is greater than D, the expression for the parallel component of the susceptibility reduces to

$$\chi_{\parallel} = N\beta^2 g_{\parallel}^2(5 - 9D/kT)/4kT \qquad (6)$$

At 4.2°K, where $kT = 2.9\ \text{cm}^{-1}$ and with the above value of D, $\chi_{\parallel}$ is estimated from eq 6 to be reduced by a factor of only 0.06 from the susceptibility predicted from the spin-only formula. Thus, since the magnitude of the perpendicular component is comparable to that of the parallel component of the susceptibility, the departure of the experimental data from the calculated susceptibility of an isolated hexaamminechromium(III) ion, as is indicated by the Weiss constant, must arise from intermolecular magnetic interactions. Since θ is positive, these magnetic interactions are antiferromagnetic.

With the assumption that the structural details for hexaamminechromium(III) pentachlorocadmate(II) are similar to those of the analogous copper compound, we may now consider the question of the magnetic interactions between ions in these cubic lattices. First we know that there is a weak antiferromagnetic interaction between the $CuCl_5^{3-}$ ions in $[Co(NH_3)_6][CuCl_5]$, and it has been suggested[4] that these intermolecular interactions are transmitted through the orbitals of the axial ligands since the unpaired electron is located in the d_{z^2} orbital. These chloride–chloride intermolecular distances are 4.11 Å. This is to be compared with the closest nitrogen–nitrogen intermolecular distance which is 4.057 Å in $[Cr(NH_3)_6][CuCl_5]$. However, in the chromium case, the unpaired electrons are in the t_{2g} orbitals, and the molecular features which are necessary for the discussion of the magnetic interactions are available from the structural data. In the crystal structure, a given hexaaminechromium(III) ion has 12 nearest $Cr(NH_3)_6^{3+}$ ions (Cr–Cr internuclear separations of 7.9 Å) located at the end of vectors which have their origin at the chromium ion and which pass near the 12 edges of the trigonally distorted octahedron. Also, ammine ligands of neighboring complex cations are directed toward the points of closest contact. Due to this orientation the magnetic wave functions, which are not expected to have an appreciable amplitude at such distances from the chromium(III) ion, may not overlap effectively, and consequently the resulting interaction is rather weak. Presumably, interactions between hexaamminechromium(III) ions which may be transmitted through intervening pentachlorocadmate anions are negligible in comparison to the interactions between nearest neighbors since there are no known precedents for such transmissions.

Acknowledgments.—This research was supported by the Materials Research Center of the University of North Carolina through Contract SD-100 with the Advanced Research Projects Agency and by the National Science Foundation (Grants GP-7400 and GY-7311). We are grateful for this continuing support. We wish to thank Dr. D. J. Hodgson for helpful discussions and Dr. Juan F. Villa for experimental assistance.

CONTRIBUTION FROM THE JAMES FRANCK INSTITUTE AND
DEPARTMENTS OF CHEMISTRY AND GEOPHYSICAL SCIENCES,
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The Enthalpy of Ilmenite–Perovskite Transformation in Cadmium Titanate

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Received October 23, 1970

The compounds $CdTiO_3$[1] and $CdSnO_3$[2] are unusual among solids of the stoichiometry ABO_3 in that each exists in both ilmenite and perovskite forms at atmospheric pressure. Liebertz and Rooymans[3] have shown that the transformation is reversible, with the ilmenite occurring at low temperature and pressure and the perovskite at high temperature and pressure. A knowledge of the thermodynamic parameters for this transition would offer quantitative insight into the energy relations, at least in one specific case, among two very important and widespread structure types. Since some difficulty was encountered in reversing the transformation under hydrothermal conditions at lower temperatures[3] and since thermodynamic properties calculated by the application of the Clausius–Clapeyron relation to the phase boundary are often subject to rather large uncertainties, a direct determination of the enthalpy of this transformation is desirable. This communication reports the results of a study of the enthalpy of the ilmenite–perovskite transformation in $CdTiO_3$ and of the enthalpy of formation of $CdTiO_3$ from the oxides, by high-temperature solution calorimetry at 692 ± 2°, using molten $3Na_2O \cdot 4MoO_3$ as solvent.

Experimental Section

Sample Preparation.—The starting materials were Baker Analyzed reagent CdO and TiO_2 (anatase) dried to constant weight at 200°. A mixture of the appropriate stoichiometry was weighed, ground under acetone, and annealed in a platinum crucible at about 850° for a total of 24 hr, with three intermediate grindings. The X-ray pattern of this product, a white powder, showed it to be single-phase α-$CdTiO_3$, the ilmenite form. Complete conversion of a portion of this sample to the perovskite form was achieved by heating at about 1150° for a total of 36 hr, with four intermediate grindings. This material was initially pale yellow but slowly turned a very light brown upon standing in air. It was shown not to invert back to the α form upon heating overnight near 700°, thus ensuring the possibility of making meaningful solution calorimetric experiments at that temperature.

Calorimetry.—The calorimeter, sample assembly, and technique have already been described.[4,5] The molten oxide mixture $3Na_2O \cdot 4MoO_3$ has been shown to be a satisfactory calorimetric solvent for both CdO and TiO_2, as well as for a number of Cd^{2+}- and Ti^{4+}-containing spinels.[5] Accordingly, this solvent, prepared as before,[5] was used in the present work. Samples of 40–150 mg of solute were dissolved in 10–12 g of melt. No difficulty was observed in the solution of the low-temperature α form, but samples of the β form initially tended to leave an undissolved residue detectable at the end of the calorimetric experiment. This problem was overcome by the use of quite small (40–50 mg)

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(1) E. Posnjak and T. W. Barth, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **88**, 271 (1934).

(2) I. Morgenstern-Badarau, P. Poix, and A. Michel, *C. R. Acad. Sci.*, **258**, 3036 (1964).

(3) J. Liebertz and C. J. M. Rooymans, *Z. Phys. Chem.* (*Frankfurt am Main*), **44**, 242 (1965).

(4) O. J. Kleppa, *Proc. Brit. Ceram. Soc.*, **8**, 31 (1967).

(5) A. Navrotsky and O. J. Kleppa, *J. Inorg. Nucl. Chem.*, **30**, 479 (1968).

samples of material which had been sifted to pass a 250-mesh screen.

Results and Discussion

The results of twelve successful solution experiments on α-$CdTiO_3$ and seven on β-$CdTiO_3$ are shown in Table I. From these data, we may calculate $\Delta H°_{965}$ = 3.58 ± 0.18 kcal/mol for the reaction

TABLE I

ENTHALPIES OF SOLUTION OF THE CADMIUM METATITANATES IN $3Na_2O \cdot 4MoO_3$ at 692 ± 2°

Amt of solute, mg	Cal, obsd	ΔH^{m}_{soln}, kcal/mol	Amt of solute, mg	Cal, obsd	ΔH^{m}_{soln}, kcal/mol
α-$CdTiO_3$ (Ilmenite Form)					
50.18	−0.132	−0.547	95.47	−0.253	−0.551
53.51	−0.153	−0.597	110.86	−0.455	−0.854
90.53	−0.262	−0.602	110.74	−0.242	−0.501
88.22	−0.234	−0.553	83.55	−0.259	−0.646
90.75	−0.217	−0.497	41.61	−0.127	−0.634
79.74	−0.198	−0.518	159.31	−0.409	−0.535
				Av	−0.586 ± 0.097[a]
β-$CdTiO_3$ (Perovskite Form)					
45.68	−0.875	−3.991	41.08	−0.816	−4.138
50.41	−1.012	−4.182	51.02	−1.083	−4.421
44.83	−0.861	−3.998	45.31	−0.920	−4.230
54.01	−1.094	−4.221			
				Av	−4.169 ± 0.148[a]

[a] Error estimate is standard deviation.

$$CdTiO_3\ (\alpha,\ \text{ilmenite}) = CdTiO_3\ (\beta,\ \text{perovskite}) \qquad (1)$$

By applying the Clausius–Clapeyron reaction to the higher temperature portion of their hydrothermal phase diagram and on the basis of the known molar volumes of the two phases at room temperature and atmospheric pressure, Liebertz and Rooymans[3] estimated the entropy change for reaction 1 to be 3.4 cal/(deg mol). Their data suggest an equilibrium transformation temperature of about 830° at 1 atm. Since under those conditions the Gibbs free energy of the transition is zero, one may deduce that

$$\Delta H_1° = T_{\text{equil}}\Delta S_1 \cong 1103 \times 3.4 = 3.74\ \text{kcal/mol} \qquad (2)$$

Our calorimetric value is in good agreement with this.

It is of interest to note that, for this transformation, ΔS and ΔV have opposite signs, and the denser polymorph appears as the high-temperature form in the phase diagram. It would appear, then, that, despite the smaller total molar volume of the perovskite form, its vibrational (lattice) entropy, at least at temperatures near the transformation, is substantially greater than that of the ilmenite, since there is virtually no possibility of substitutional disorder and a configurational entropy term. Qualitatively, this can be rationalized if one visualizes the Cd^{2+} ion to be somewhat too small for the 12-fold site it occupies in the perovskite structure and therefore to "rattle" within this interstice. This less rigid binding of Cd^{2+} would give rise both to an increased entropy and to a less favorable energy, as is observed. Although the ionic radii of Cd^{2+} and Ca^{2+} are generally given very similar values (Pauling: Cd^{2+}, 0.97 Å; Ca^{2+}, 0.99 Å; Goldschmidt: Cd^{2+}, 1.03 Å; Ca^{2+}, 1.06 Å),[6] there is considerable evidence that, in solids, Cd^{2+} behaves as though it were significantly smaller than Ca^{2+}. Thus, the lattice parameters of CdO and CaO are 4.6953 and 4.8105 Å, respectively.[7] CdO forms ternary spinels with Fe_2O_3, Mn_2O_3, Ga_2O_3, Cr_2O_3, and some other oxides,[8] whereas substitution by Ca^{2+} in the spinel structure is rather limited. $CdCl_2$ crystallizes in a layer structure similar to that of other transition metal chlorides and of $MgCl_2$, whereas $CaCl_2$ crystallizes in a distorted rutile structure.[6] The observed dimorphic behavior of $CdTiO_3$ (and $CdSnO_3$), while $CaTiO_3$ exists only as a perovskite, is a further manifestation of this effect. The larger polarizability and tendency toward covalent bonding due to the filled 4d shell of Cd^{2+} is probably at least partially responsible for this behavior.

Using the enthalpies of solution of CdO and of TiO_2 (rutile) in $3Na_2O \cdot 4MoO_3$ measured previously by Navrotsky and Kleppa[5] under essentially identical calorimetric conditions (−9.59 ± 0.07 and +2.38 ± 0.09 kcal/mol, respectively), one can calculate the enthalpy of formation of $CdTiO_3$ from its constituent oxides, as in

$$CdO\ (\text{rock salt}) + TiO_2\ (\text{rutile}) = CdTiO_3\ (\alpha,\ \text{ilmenite}) \qquad (3)$$

$$\Delta H°_{965} = -6.62 \pm 0.12\ \text{kcal/mol}$$

To our knowledge, no values for either the enthalpy or the free energy of this reaction have been reported. One may compare this enthalpy value with values for the free energies of formation from the oxides of the ilmenite titanates of the smaller divalent ions ($MgTiO_3$, $\Delta G°_{1000} = -5.7$ kcal/mol;[9] $FeTiO_3$, $\Delta G°_{1273} = -4.7$ kcal/mol;[10] $CoTiO_3$, $\Delta G°_{1373} = -3.6$ kcal/mol;[11] $NiTiO_3$, $\Delta G°_{1273} = -2.5$ kcal/mol[10]), on the one hand, and with the tabulated thermodynamic data for perovskite, $CaTiO_3$, on the other hand ($\Delta G°_{1000} = -20.5$ kcal/mol, $\Delta H°_{1000} = -20.9$ kcal/mol[9]). It is clear that $CdTiO_3$ belongs to the first group and has only a moderate (5–10 kcal) stability relative to the oxides. Indeed the pattern of stability of the metatitanates of Mg, Fe, Co, Ni, and Cd appears not unlike that previously observed for spinels,[5] tungstates,[12] and orthosilicates[13] containing these ions. Further calorimetric study of these ilmenites, of $CdSnO_3$, and of selected oxides with the perovskite structure would be of interest.

Acknowledgments.—This work has been supported by the Army Research Office, Durham, N. C., and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. The work has also benefited from the general support of Materials Sciences at The University of Chicago provided by ARPA. A. N. wishes to thank the University Grants Committee, Arizona State University, for a summer fellowship.

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(6) R. C. Evans, "Crystal Chemistry," Cambridge University Press, Cambridge, England, 1964.

(7) ASTM Powder Data File.

(8) G. Blasse, *Philips Res. Rep., Suppl.*, **No. 3** (1964).

(9) R. A. Robie and D. R. Waldbaum, *U. S. Geol. Surv. Bull.*, **No. 1259** (1968).

(10) R. W. Taylor and H. Schmalzried, *J. Phys. Chem.*, **68**, 2444 (1964).

(11) B. Brezny and A. Muan, *J. Inorg. Nucl. Chem.*, **31**, 649 (1969).

(12) A. Navrotsky and O. J. Kleppa, *Inorg. Chem.*, **8**, 756 (1969).

(13) A. Navrotsky, *J. Inorg. Nucl. Chem.*, in press.