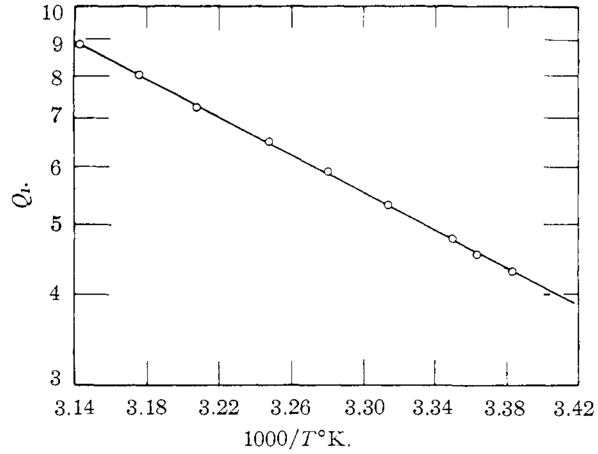

Fig. 3.—The temperature dependence of Q_1.

± 0.1°. Milburn and Vosburgh[4] had reported molar extinction coefficients for the three ferric species at 340 mμ: $\epsilon_{Fe^{+++}}$ = 2.84, $\epsilon_{FeOH^{++}}$ = 925 and $\epsilon_{Fe_2(OH)_2^{+4}}$ = 3000. A check was made by calculating the optical density of the three solutions and comparing the results with those obtained experimentally. The results are

Solution	$\Sigma(H^+)$	D_{exp} (2.00 cm. cell)	D_{calcd}
1	0.250	0.068	0.0682
2	.0528	.276	.280
3	.0308	.512	.512

Using the calculated concentrations of Fe^{++-}, $FeOH^{++}$ and $Fe_2(OH)_2{}^{+4}$, and the measured optical density values for the three solutions, the molar extinction coefficients shown in columns 2, 3 and 4 in Table IV were obtained.

To obtain the molar extinction coefficients for $FeCl^{++}$ a solution identical to the high acid solution (0.250 M H^+) used above was prepared with the addition of 0.0555 M NaCl. Under these conditions, higher chloride complexes (*e.g.*, $FeCl_2{}^+$) are relatively unimportant. Using Rabinowitch and Stockmayer's[2] approximate value for Q_2, it is seen that the concentration of $FeCl_2{}^+$ is less than 5% of the concentration of $FeCl^{++}$. Neglecting the presence of $FeCl_2{}^+$, the measured optical density values and the calculated values of Q_H, Q_D, Q_1, $\epsilon_{Fe^{+3}}$, $\epsilon_{FeOH^{+2}}$, $\epsilon_{Fe_2(OH_2)^{+4}}$ gave the $\epsilon_{FeCl^{++}}$ values shown in column 5 of Table IV.

Although this method of obtaining the molar extinction coefficients is not highly precise, it does give a consistent set of values which may be used to check optical densities of experimental solutions. The individual values may well be in error by 10%.

TABLE IV

APPROXIMATE MOLAR EXTINCTION COEFFICIENTS USED FOR CHECKING CONCENTRATIONS

λ, mμ	$\epsilon_{Fe^{+3}}$[a]	$\epsilon_{FeOH^{+2}}$	$\epsilon_{Fe_2(OH)_2^{+4}}$	$\epsilon_{FeCl^{+2}}$[b]
390	0.61	81	1.48×10^2	2.38×10^2
380	0.63	129	4.3×10^2	4.28×10^2
370	1.00	194	1.03×10^3	7.02×10^2
360	1.59	346	1.75×10^3	1.06×10^3
350	1.97	545	2.72×10^3	1.44×10^3

[a] Milburn and Vosburgh[4] give 0.90 and 1.20 at 360 and 350 mμ, respectively. [b] Approximate values read from a graph of Olerup's data reproduced in ref. 13 are 200, 450, 750, 1000 and 1300, respectively, for the wave lengths listed.

The comparison of the values in Table IV with those reported by other workers indicates satisfactory agreement within experimental limits of error. These molar extinction coefficients were checked several times in later experiments by making known solutions and comparing experimental and calculated optical densities, with the agreement usually being within 2%.

Measurement of ΔH_1 (see equation 1).—A ferric chloride solution was prepared containing 0.01222 M $Fe(ClO_4)_3$, 0.0111 M NaCl and 1.298 M $HClO_4$, giving an ionic strength of 1.382. Equilibrium quotients for hydrolysis and dimerization of Fe(III) were calculated from the ionic strength dependence equations of Milburn and Vosburgh.[4] Using these values of $Q_H = 1.53 \times 10^{-3}$ and $Q_D = 886$ and the molar extinction coefficients previously discussed, Q_1 could be determined as a function of temperature by optical density measurements. The wave length used was 370 mμ where the total optical density due to Fe^{+++}, $FeOH^{++}$ and $Fe_2(OH)_2{}^{+4}$ is less than 4% of the total optical density. Furthermore, the amount of ferric hydrolyzed and complexed was very small (about 6%) and corrections on (Fe^{+++}) became almost negligible. It was assumed that the molar extinction coefficients did not change with temperature or with ionic strength.

The measurements were made on a Beckman Model DU spectrophotometer with a thermostated cell holder, using quartz cells. The temperature in the cell was held constant to ±0.1° over a temperature range from 22 to 45°. The temperatures were measured to ±0.02° with a thermistor placed inside the cell. Figure 3 shows a plot of log Q_1 *versus* 1000/T°K. The data fall on a straight line, the slope of which gives ΔH_1 = 6.0 ± 0.1 kcal./mole.

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BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE IBM WATSON LABORATORY AT COLUMBIA UNIVERSITY AND THE IBM POUGHKEEPSIE RESEARCH LABORATORY]

Variation of the Latent Heat of the Cubic–Tetragonal Transformation in the System $KNbO_3$–$KTaO_3$

BY JOHN J. HALL AND SOL TRIEBWASSER

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Measurements of the latent heat of transition of ceramic samples of $KTa_xNb_{(1-x)}O_3$ from the tetragonal to the cubic phase are reported for values of the parameter x ranging from 0 to 0.18. The latent heat is observed to decrease rapidly as x is increased from zero. The method of sample preparation, apparatus and experimental procedures are described briefly. On the basis of certain simplifying assumptions, the spontaneous polarization at the ferroelectric Curie point is calculated, using the phenomenological theory proposed by Devonshire.

Introduction

The system $KNbO_3$–$KTaO_3$ forms a continuous range of solid solutions in which the temperature of transformation from the cubic (paraelectric) phase to the tetragonal (ferroelectric) phase varies from about 680°K. for pure $KNbO_3$ to 13°K. for pure $KTaO_3$. The phase diagram of the system (which we shall write $KTa_xNb_{(1-x)}O_3$) has been studied previously[1] and the ferroelectric behavior described.[2] The purpose of the present work is to de-

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(1) A. Reisman, S. Triebwasser and F. Holtzberg, THIS JOURNAL, **77**, 4228 (1955); A. Reisman and E. Banks, *ibid.*, **80**, 1877 (1958).

(2) S. Triebwasser and F. Holtzberg, *Phys. Rev.*, **98**, 1201 (1955).

termine the effect of the variation of the mole fraction N on the latent heat at the cubic–tetragonal transition, and the correlation of this latent heat to the spontaneous polarization using the phenomenological theory proposed by Devonshire.[3]

Experimental

Sample Preparation.—The samples were prepared from reagent grades of K_2CO_3, Nb_2O_5 and Ta_2O_5. The mixed powders were milled, heated at 850° for 18 hours, quenched and ground. This process was twice repeated, with the firing temperature raised to 1000° to ensure completion of the reaction. The resultant solid solutions (x = 0, 0.06, 0.12 and 0.18) were then mixed with a 1:9 weight mixture polyvinyl alcohol–water, in the proportion of one cc. of liquid to each 5 g. of powder. After overnight drying, the compounds were pressed into $^1/_2''$ cylinders approximately $^1/_2''$ in length with a hydraulic ram at a pressure of 16,000 pounds. These were fired for $^1/_2$ hour at 975°, resulting in mechanically strong ceramics with about 80% theoretical density.

Three cylinders of each composition were drilled along their axes and slipped over and cemented to a sample heater made of Kanthal resistance wire wound upon a $^1/_{16}''$ diameter Alundum tube. The four samples thus prepared were sprayed with a reflective silver coating and oven dried. Two small holes were drilled in the sides of each sample and lined with quartz cups to receive thermocouple junctions. In effect, the samples served as their own calorimeters.

Apparatus.—The sample under test was mounted in an evacuated adiabatic shield, consisting of a thin-walled copper tube, one inch in diameter and twelve inches long, close-wound with Nichrome V heater ribbon so that 80% of the shield area was covered. Copper plugs, upon which small heaters were wound, close the top and bottom of the shield and serve to correct for end heat losses. Fine Alundum tubes suspend the sample from the top heater plug and also carry the sample heater leads. The adiabatic shield is supported by an Inconel tube and surrounded by an Inconel radiation shield, which in turn is mounted inside a water-cooled vacuum jacket. In practice, the system was pumped for 24 hours with the shield maintained at an elevated temperature to exhaust residual gases from the sample chamber as the pumping path was rather poor.

To maintain the adiabatic shield precisely at the sample temperature, the differential voltage between a thermocouple attached to the shield wall and a matched sample thermocouple was fed into a Brown chopper amplifier. The amplified direct current differential voltage was used to control the bias on the grids of four 6AS7G current passing tubes whose common cathode load was the shield heater. To increase the current capacity of the circuit, the tubes were by-passed with a variable resistor, the latter also providing a convenient means for controlling the effective gain of the system. The top heater was controlled by a similar arrangement, while the bottom heater was connected in parallel with the shield heater through a variable resistor. Power to the sample was provided from a storage battery through a dropping resistor.

Procedure.—In operation, the shield temperature was maintained within 0.01° of the sample temperature. Stability of the system was such that, with no power input to the sample, drift rates of less than $^1/_4$° per hour were always obtained, compared with typical heating rates of $^1/_4$ to 1° per minute. The measured response time of the shield to a change in sample power input was about 20 seconds and dynamic equilibrium was obtained in less than one minute. During a run, which usually covered a temperature span of 100°, constant power was fed to the sample to produce the desired heating rate. The sample temperature was continuously recorded on a Leeds and Northrup X-T recorder, so that the specific heat as a function of temperature could be calculated from the known sample weight, the power input and the heating rate as determined from the recorder chart, minor corrections being made for the heat capacity of the sample heater and the conductive silver coating. The mechanical equivalent of heat was taken to be 4.1840 abs. joules/cal.

Results

The specific heat curves obtained for the various values of the parameter x in the neighborhood of the cubic–tetragonal transformation are shown in Figs. 1 and 2. The latent heat L was determined in each case by integration of the anomalous component of the specific heat above the background; the results are presented in Table I. The uncertainties given are estimated from the scatter obtained over a series of runs. In all cases, the specific heat anomaly was observed to increase in magnitude during the first few runs, perhaps due to the alleviation of local strains within the sample after several passages through the transition.[4]

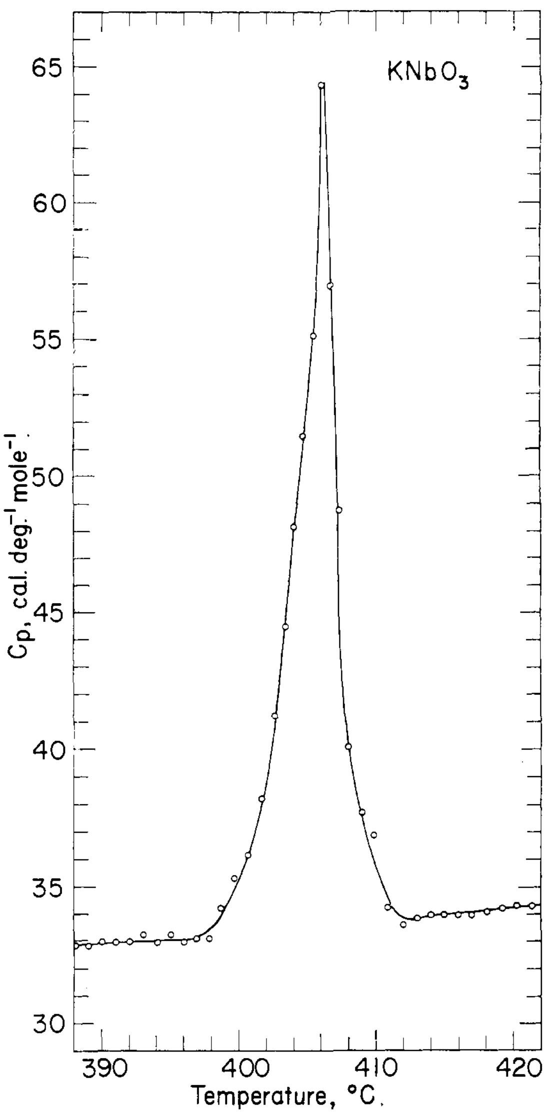

Fig. 1.

TABLE I

VALUES OF L, T_{cf}, AND P_c FOR VARIOUS VALUES OF x

x	L, cal./mole	T_{cf}, °K.	A 10^5 °K.$^{-1}$	P_c, μcoulombs/cm.^{2}
0	110 ± 10	679	2.6	27
0.06	46 ± 4	656	2.7	17.7
.12	10 ± 2	623	2.85	7.9
.18	4.0 ± 2	591	3.05	5.1

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[3] A. F. Devonshire, *Phil. Mag.*, **40**, 1040 (1949); **42**, 1065 (1951).

[4] A. Reisman, F. Holtzberg and E. Banks (THIS JOURNAL, **80**, 37 (1958)) observed similar behavior in their study of $Na_2O \cdot Nb_2O_5$.

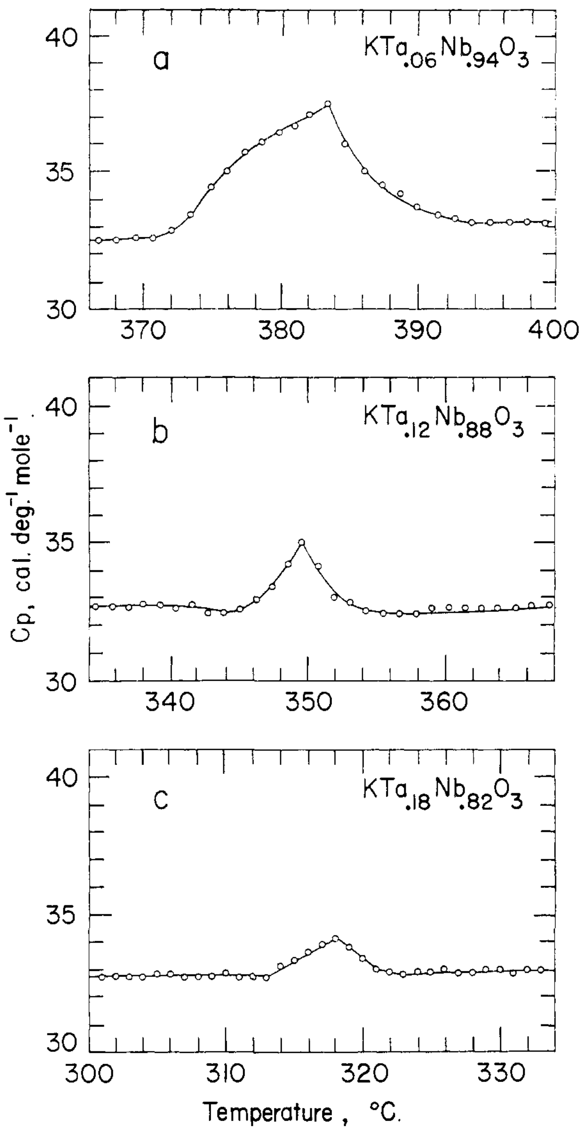

Fig. 2.

In addition to the measurements on ceramic samples, a limited series of measurements was made upon a small single crystal of pure $KNbO_3$, yielding a latent heat $L = 115 \pm 15$ cal./mole, in substantial agreement with the result obtained above. The large mechanical strains set up in the transition caused the sample to crack severely and eventually to crumble, forcing the single crystal experiments to be discontinued. In both samples of $KNbO_3$, however, the value obtained for L was substantially lower than those reported by Shirane, *et al.*[5] and Triebwasser and Halpern,[6] 190 ± 15 cal./mole and 134.5 ± 5 cal./mole, respectively.

Discussion

Thermodynamic data on ferroelectrics have been correlated by the phenomenological theory proposed by Devonshire.[3] In his treatment the free energy is expressed as a power series in the polarization of the form

$$F(P,T) = A(T - T_{cp})P^2 + BP^4 + CP^6 + F_0(T) \quad (1)$$

where P is the polarization, T the temperature, T_{cp} the paraelectric Curie temperature, A, B and C constants and $F_0(T)$ the polarization independent part of the free energy. Since the entropy S is given by $-(\partial F/\partial T)_P$, the change in entropy associated with the onset of spontaneous polarization is given by

$$\Delta S = AP_c^2 + \frac{\partial B}{\partial T}P_c^4 + \frac{\partial C}{\partial T}P_c^6 = \frac{L}{T_{cf}} \quad (2)$$

where P_c is the value of the polarization at the ferroelectric Curie point and T_{cf} the ferroelectric Curie temperature. If B and C are assumed to be independent of the temperature, then eq. 2 reduces to the relationship given by Jaynes[7]

$$\Delta S = \frac{L}{T_{cf}} = AP_c^2 \quad (3)$$

From eq. 3 and values of A reported elsewhere,[8] P_c may be calculated for various values of x. Results of these calculations together with the values of A are given in Table I. The value found for pure $KNbO_3$ agrees closely with the value 26 μcoulombs/cm.^{2} previously reported.[6] On the other hand, direct measurements of B in the isomorphous ferroelectric $BaTiO_3$ indicate that the term $(\partial B/\partial T)P_c^4$ in eq. 2 contributes $^1/_3$ again as much as AP_c^2 to the value of ΔS in that material, to which $KNbO_3$ has been shown to be very similar in behavior.[9] Hence there is no reason to believe that the contribution is negligible in $KNbO_3$, so that the values of P_c may be regarded as only approximate.

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NEW YORK, N. Y.

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(5) G. Shirane, H. Danner, A. Pavlovic and R. Pepinsky, *Phys. Rev.*, **93**, 672 (1954).

(6) S. Triebwasser and J. Halpern, *ibid.*, **98**, 1562 (1955).

(7) E. T. Jaynes, "Ferroelectricity," Princeton Univ. Press, Princeton, N. J., 1953.

(8) S. Triebwasser, *Phys. Rev.*, **114**, 63 (1959).

(9) S. Triebwasser, *ibid.*, **101**, 993 (1956).