Specific Heat Anomaly of Ferroelectric Cadmium Niobate at the Curie Temperature*

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The anomalous specific heat of ferroelectric $Cd_2Nb_2O_7$ has been measured in the region of its Curie temperature, $T_c = 193°K$, using a vacuum adiabatic calorimeter. The values of the transition energy and the transition entropy change are 18 ± 2 cal/mole and 0.09 ± 0.01 cal/°K-mole, respectively. A comparison between the experimental values of the transition entropy change, the spontaneous polarization, and the Curie constant is made.

INTRODUCTION

COOK and Jaffe[1] recently reported $Cd_2Nb_2O_7$ to be ferroelectric below 170°K. Subsequent dielectric measurements by other investigators[2,3] on ceramic samples of this compound, exhibiting Curie temperatures between 182°K and 188°K, have revealed the existence of a second phase transition at 85°K. Cadmium niobate, in addition to having similar chemical properties, contains metal octahedra, MO_6, characteristic of previously studied oxide ferroelectrics such as $BaTiO_3$. However, it differs from the latter in that its structure above the Curie point is face-centered cubic of the pyrochlore type.[4] An x-ray study of single crystals has shown that $Cd_2Nb_2O_7$ transforms to a tetragonal structure below the Curie point.[5]

Specific heat measurements have played an important role in the study of ferroelectrics, since a knowledge of the anomalous behavior of the specific heat enables one to calculate the change in energy, ΔE, and the change in entropy, ΔS, associated with the transition. These values, in turn, form an integral part of the experimental data needed in theoretical treatments of the phenomenon of ferroelectricity. In KH_2PO_4, for example, Stephenson's experimental value[6] for ΔS has given strong support to the Slater theory,[7] which is based on a statistical mechanical arrangement of the hydrogen bonds. In $BaTiO_3$, the experimental values of ΔE at the three transitions are in qualitative agreement with the values derived from the thermodynamic treatment of Devonshire.[8] Finally, as discussed later, ΔS is closely related to the spontaneous polarization and the Curie constant.[9]

APPARATUS AND METHOD

The specific heat measurements were made using a vacuum adiabatic calorimeter of the classical Nernst type. Numerous references concerning the essential details of construction and the method of measurement have been given in the literature.[10] Essentially, this apparatus allows one to add a measured amount of heat electrically to the sample, which is thermally insulated in an evacuated adiabatic shield system, and to observe the temperature rise produced. The specific heat of the sample is then computed from the equation

$$C_p = \left[\frac{VIt}{J(T_2 - T_1)} - C_0 \right] \frac{M}{m},$$

where V and I are the average voltage and current supplied for a time t, J is the mechanical equivalent of heat, T_1 and T_2 are the initial and final temperatures of the sample respectively, and C_0 is the heat capacity of the sample container. Multiplication by the ratio of the molecular weight M to the weight of the sample m gives C_p in cal/°K-mole. In practice the amount of heat added is small, so that the value of C_p may be taken as the value of the specific heat of the sample at the temperature $(T_1+T_2)/2$. A series of such heating periods yields a plot of C_p against T. In the present study, the temperatures were measured by observing, with a Leeds and Northrup type K-2 potentiometer, the thermal emf developed by a single copper-constantan thermocouple.

The operation of the apparatus was checked by measuring the anomalous specific heats of KH_2PO_4 and $BaTiO_3$, the latter at its lowest transition. For KH_2PO_4 a maximum in the specific heat curve occurred at 123.5°K, and the value of the transition energy, $\Delta E = \int \Delta C_p dT$, was 87 ± 6 cal/mole. The corresponding entropy change, $\Delta S = \int (\Delta C_p/T)dT$, was 0.72 ± 0.05 cal/°K-mole. These results are in excellent agreement with those reported by Stephenson.[6] For $BaTiO_3$ the maximum value of the specific heat appeared at 210.5°K, and the integrated values of ΔE and ΔS were 11 ± 2 cal/mole and 0.05 ± 0.01 cal/°K-mole

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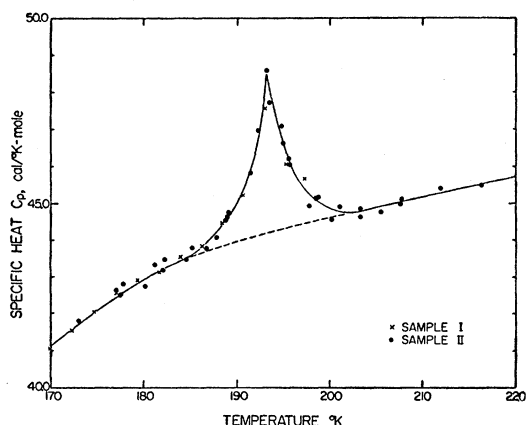[9] E. T. Jaynes, *Ferroelectricity* (Princeton University Press, Princeton, 1953).

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FIG. 1. Specific heat of $Cd_2Nb_2O_7$.

respectively, in good agreement with the values obtained by other investigators.[11-13]

PREPARATION OF MATERIAL

Two separate ceramic samples of $Cd_2Nb_2O_7$ were prepared by pre-firing milled mixtures of $CdCO_3$ and Nb_2O_5 at 1150°C, remilling and firing at 1250°C. The lattice constants, determined from powder photographs, were $a = 10.371$ A for both sample I and sample II. These values are consistent with the values of a obtained from other specimens prepared in this laboratory.[5] Dielectric measurements revealed peak values of the dielectric constant at 191.4°K and 191.8°K for samples I and II, respectively.

It will be noted that the transition temperatures, T_c, of these samples are higher than any reported thus far. Hulm[3] has pointed out that the Curie temperature of $Cd_2Nb_2O_7$ depends on the temperature at which the specimen is fired. A higher firing temperature results in the lowering of the Curie point; unequal rates of evaporation of $CdCO_3$ presumably lead to slight variations in the stoichiometric formula.

RESULTS

The experimental specific heat data for $Cd_2Nb_2O_7$ between 170°K and 220°K were obtained from measurements performed on two calorimeter loadings (66.2 g of sample I and 69.7 g of sample II). Heating periods of 4, 5, 8, and 10 minutes were used, employing a heating rate of 0.36 watt. This heating rate produced an average temperature rise of 0.44°K per minute. The values of C_p are plotted as a function of temperature in Fig. 1. The values obtained from sample I are indicated by crosses (×), and those obtained from sample II by circles (○). The points lie on a smooth curve to

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TABLE I. A comparison of the calculated and experimental values of the spontaneous polarization for Rochelle salt, KH_2PO_4, $BaTiO_3$, and $Cd_2Nb_2O_7$.

Material	$\Delta S, \dfrac{cal}{°K\text{-mole}}$	C, °K	ρ/M, cc^{-1}	$P_{calc}, \dfrac{\mu coul}{cm^2}$	$P_{exp}, \dfrac{\mu coul}{cm^2}$
Rochelle salt	<0.007	180	1.8/282	<0.27	0.25
KH_2PO_4	0.72	260	2.3/136	5.4	5
$BaTiO_3$	0.12	12 700	6.1/233	24.0	20
$Cd_2Nb_2O_7$	0.09	5600	6.2/523	7.5	10

within 0.5%, and the agreement of the points determined from the two samples is within the accuracy of the apparatus. The transition temperature, determined by the maximum value of C_p, is at 193.2°K, in good agreement with T_c determined from the dielectric measurements. Assuming that the normal specific heat can be taken as the broken curve shown in the figure, the value of the transition energy is 18 ± 2 cal/mole, and the associated entropy change is 0.09 ± 0.01 cal/°K-mole.

DISCUSSION

The transition entropy change, the maximum value of the spontaneous polarization P attained at low temperatures, and the Curie constant C (defined below) have been related theoretically by the equation $P^2 = 2C\Delta S$. This relation was derived by Jaynes[9] from the postulates of the Devonshire theory for $BaTiO_3$.[8] The derivation depends on the particular form of the free energy, which for zero stress may be expanded in even powers of the polarization. Moreover, it is assumed (a) that this free energy function is valid above and below the Curie temperature; (b) that the coefficients of the terms of order P^4 and higher are temperature independent and small compared with the coefficient of P^2; and (c) that the reciprocal susceptibility χ^{-1}, which is the coefficient of P^2, is a linear function of temperature: i.e., $\chi^{-1} = (T - T_c)/C$, where C is the Curie constant. Although general validity of this equation has not been established, it describes quite well the relation between ΔS, P, and C for Rochelle salt, KH_2PO_4, and $BaTiO_3$.

The equation may be rewritten in the form $P^2 = 9.3\rho C\Delta S/M$, where ρ is the density in g/cc and M is the molecular weight in g. This gives P in $\mu coul/cm^2$ when ΔS is given in cal/°K-mole. For $Cd_2Nb_2O_7$, $M = 523$ g, and $\rho = 6.2$ g/cc as calculated from the lattice constant. Taking $\Delta S = 0.09$ cal/°K-mole and $C = 5600$°K, which is the average of all the values of C reported thus far, we obtain $P \sim 7.5$ $\mu coul/cm^2$. The experimental value of the spontaneous polarization has been reported as $P = 10$ $\mu coul/cm^2$.[5] For the sake of comparison, the experimental and calculated values of P for Rochelle salt, KH_2PO_4, $BaTiO_3$, and $Cd_2Nb_2O_7$ are listed in Table I.

The agreement between the experimental value of P and the value calculated from the experimental values

of ΔS and C has twofold significance. First, it indicates the essential correctness of all three of the experimental values. Second, it provides an additional example, in what may well become a new subclass of ferroelectrics, of the applicability of the equation $P^2 = 2C\Delta S$. In the light of the general agreement of this equation in previously studied ferroelectrics, it appears that a single free-energy function theory may be capable of explaining ferroelectricity in general.

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Influence of Alternating Electric Fields on the Light Emission of Some Phosphors

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The influence of an alternating electric field on the fluorescence and phosphorescence of various ZnS and ZnS:CdS phosphors was investigated. The light pulses and the average brightness of the luminescence were measured simultaneously. The wave pattern during fluorescence consists of two different pulses per cycle. The two pulses differ in their respective amplitudes, time dependence, and shape. The pulses corresponding to positive polarity of the illuminated electrode show a similar behavior for all phosphors. The second pulse differs for the various phosphors. Voltage dependence of the amplitudes and light sums per cycle were found to be different for the two pulses. These two pulses must be due to two different processes and suggest surface effects.

INTRODUCTION

THE effects of alternating electric field on the luminescence of powdered nonelectroluminescent phosphors have been investigated by a number of authors. As early as 1920, Gudden and Pohl[1] found that on application of electric fields some of their photoconducting phosphors emitted momentary light flashes. Destriau and his co-workers[2-5] have made extensive investigations of the various influences of the electric field on the luminescence of some types of ZnS phosphors. They have studied in particular the changes in the average brightness of luminescence as a function of the voltage and temperature both during excitation and phosphorescence.

Olson[6] has investigated the quenching of the phosphorescence caused by the ac field as a function of the frequency for one particular phosphor (ZnS:CdS:Cu). Matossi and Nudelman[7] have studied the quenching during excitation as a function of the frequency for another particular phosphor (ZnS:Cu). Matossi[8] has attempted to explain the effects observed during excitation by extending the theory of Randall and Wilkins[9] on luminescence in phosphors. By including assumptions that the electric field causes emptying of traps as well as draining off of electrons by field-induced nonradiative transitions, he seems to account for the momentary illumination, subsequent quenching, and superposition of a ripple of frequency twice that of the applied voltage. It will be shown in this paper that there are a number of important effects which make it doubtful whether this theory in its present form can be applied to the phosphors we have investigated.

There has recently been a considerable amount of experimental and theoretical work on electroluminescent phosphors.[10] It should be emphasized, however, that explanations which may be valid in cases of electroluminescence do not necessarily account for the various effects of electric fields during fluorescence and phosphorescence. The hope of practical applications of electroluminescence has induced many workers to concentrate mainly on this phase of research. An understanding of the influence of electric fields on the usual nonelectroluminescent phosphor is more general in nature and may shed light on electroluminescence as well.

This series of experiments was undertaken in the hope of finding unifying features in the wealth of experimental data on the influence of ac fields on powdered phosphors. This paper is concerned with phosphors of the type ZnS and ZnS:CdS with Cu and Ag activators. In a later publication, we intend to report results on the effects of ac fields on doubly activated infrared-stimulated phosphors.

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