

## Specific heats of lead and cadmium niobates at low temperatures

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Specific-heat data (2–25 K) are reported on the ferroelectrics  $\text{PbNb}_2\text{O}_6$  (orthorhombic),  $\text{Cd}_2\text{Nb}_2\text{O}_7$ , and  $\text{Cd}_{1.6}\text{Pb}_{0.4}\text{Nb}_2\text{O}_7$ , and on the nonferroelectrics  $\text{PbNb}_2\text{O}_6$  (rhombohedral),  $\text{Pb}_2\text{Nb}_2\text{O}_7$ , and  $\text{CdNb}_2\text{O}_6$ . All materials display maxima in  $CT^{-3}$ , and excellent fits to experimental data are obtained with a single Einstein term added to the Debye background. The Einstein frequencies vary from  $9\text{ cm}^{-1}$  for  $\text{PbNb}_2\text{O}_6$  (rhombohedral) to  $76\text{ cm}^{-1}$  for  $\text{CdNb}_2\text{O}_6$ , and the Debye temperatures from 171 K for  $\text{PbNb}_2\text{O}_6$  (rhombohedral) to 408 K for  $\text{CdNb}_2\text{O}_6$ . The ferroelectric form of  $\text{PbNb}_2\text{O}_6$  varies dramatically from the nonferroelectric form: Einstein frequency,  $37.6\text{ cm}^{-1}$ , and Debye temperature 224 K. The 20-mole %-Pb substitution on the Cd site in  $\text{Cd}_2\text{Nb}_2\text{O}_7$  lowers both the Einstein frequency and Debye temperature: 53 to  $43\text{ cm}^{-1}$  and 393 to 315 K, respectively. For all materials except  $\text{CdNb}_2\text{O}_6$ , the Debye contribution is smaller than the Einstein contribution. Below 4 K, the ferroelectric niobates and  $\text{CdNb}_2\text{O}_6$  have a Schottky contribution with an energy separation  $\sim 50\text{ mK}$  (assumed two level). It is suggested that this term is due to the electric-quadrupole moment of Nb in an electric-field gradient. Published data on  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  support this interpretation.

### I. INTRODUCTION

Ferroelectricity occurs in the niobates of lead and cadmium in contrasting and seemingly contradictory ways: Cadmium *pyroniobate*,  $\text{Cd}_2\text{Nb}_2\text{O}_7$ , and lead *metaniobate*,  $\text{PbNb}_2\text{O}_6$ , are ferroelectric whereas  $\text{Pb}_2\text{Nb}_2\text{O}_7$  and  $\text{CdNb}_2\text{O}_6$  are not. Moreover, there is a wide range of solid solubility in the  $(\text{Cd,Pb})_2\text{Nb}_2\text{O}_7$  system, the effect of the Pb substitution being to markedly lower the Curie temperature. The basic structural unit in these materials is the corner-linked  $\text{NbO}_6$  octahedron, and given the chemical similarity of Pb and Cd, it might be expected that the lattice dynamics of these materials would likewise be similar even though they differ markedly in the occurrence of ferroelectricity.

In the case of  $\text{Pb}_2\text{Nb}_2\text{O}_7$ , specific-heat measurements<sup>1</sup> have revealed a large density of low-lying acoustic phonons at  $30\text{ cm}^{-1}$  which dominate the specific heat below  $\sim 25\text{ K}$  (e.g., at  $\sim 10\text{ K}$  the Debye contribution to the specific heat is only  $\sim 40\%$ ). This same phenomenon has been observed in the specific heats of all soft-mode dielectrics (ferroelectrics, anti-ferroelectrics, paraelectrics) measured to date,<sup>1,2</sup> yet  $\text{Pb}_2\text{Nb}_2\text{O}_7$  has definitely been shown<sup>3</sup> not to have an antiferroelectric transition at 14 K as originally believed.<sup>4</sup>

The purpose of this study is to extend these specific-heat measurements to other members of this unusual family of lead and cadmium niobates to see what similarities there are, if any, in their low-lying

vibrational modes. Specifically, measurements are reported on the ferroelectric and nonferroelectric forms of  $\text{PbNb}_2\text{O}_6$ , on  $\text{Cd}_2\text{Nb}_2\text{O}_7$ ,  $\text{Cd}_{1.6}\text{Pb}_{0.4}\text{Nb}_2\text{O}_7$ , and  $\text{CdNb}_2\text{O}_6$ . The previously published data for  $\text{Pb}_2\text{Nb}_2\text{O}_7$  are included for comparison.

The cubic pyrochlore  $\text{Cd}_2\text{Nb}_2\text{O}_7$  transforms to a tetragonally-distorted ferroelectric phase at 185 K, and hysteresis loops have been observed down to 4 K.<sup>5,6</sup> The Pb substitution in  $\text{Cd}_{1.6}\text{Pb}_{0.4}\text{Nb}_2\text{O}_7$  lowers the Curie point to 50 K and increases the lattice constant 0.7%.<sup>6</sup> The nonferroelectric metaniobate  $\text{CdNb}_2\text{O}_6$  has an orthorhombic columbite structure.<sup>7</sup>

The metaniobate  $\text{PbNb}_2\text{O}_6$  is polymorphic: If the ceramic sintering temperature exceeds  $1250^\circ\text{C}$ , the tetragonal form is obtained which transforms to an orthorhombic ferroelectric phase at 843 K.<sup>8</sup> Below  $1250^\circ\text{C}$ , the nonferroelectric rhombohedral form is obtained.<sup>9</sup> The pyroniobate  $\text{Pb}_2\text{Nb}_2\text{O}_7$  crystallizes in a slight rhombohedral distortion of the cubic pyrochlore structure.

### II. EXPERIMENTAL METHOD AND RESULTS

The niobate samples were prepared from reagent-grade powders by conventional ceramic methods. Nylon jars and  $\text{ZrO}_2$  grinding media were used to avoid alumina and iron impurities in ball milling. Ceramic firing schedules were determined which yielded dense bodies with minimal weight loss ( $\leq 1\%$ ), and subsequent x-ray analyses confirmed that the samples had the desired crystal structures.

The specific-heat measurements were made in the low-temperature calorimeter described previously.<sup>1</sup> The temperature rises  $\Delta T/T$  were maintained at 2–3%, and as a percentage of the total heat capacity the addenda varied from 14% for  $\text{CdNb}_2\text{O}_6$  to 2% for  $\text{PbNb}_2\text{O}_6$  (orthorhombic).

The data for the lead niobates are shown in Fig. 1 and for the cadmium niobates in Fig. 2. The data are plotted as  $CT^{-3}$  because a low-lying Einstein mode will give rise to a maximum in  $CT^{-3}$  against the constant Debye background. This maximum occurs at  $T_{\text{max}} \approx \frac{1}{3}\omega$ , where  $\omega$  is the mode frequency in  $\text{cm}^{-1}$ .

The Fig. 1 data show a dramatic difference between the orthorhombic-ferroelectric form of  $\text{PbNb}_2\text{O}_6$  and the rhombohedral-nonferroelectric form (note the scale difference). The specific heats are approximately equivalent down to 15 K, but at the lowest temperatures the rhombohedral form has a specific heat an order of magnitude larger than the orthorhombic form. The position and heights of the  $CT^{-3}$  maxima indicate a large density of low-lying modes in both forms of  $\text{PbNb}_2\text{O}_6$  and a frequency shift from  $\sim 10 \text{ cm}^{-1}$  for the rhombohedral form, to  $\sim 40 \text{ cm}^{-1}$  for the orthorhombic form (see below).

The specific heats of  $\text{Pb}_2\text{Nb}_2\text{O}_7$  and orthorhombic  $\text{PbNb}_2\text{O}_6$  are quite similar despite the difference in ferroelectric behavior. Below about 4 K, the ferroelectric niobate has a steep rise in  $CT^{-3}$  with de-

creasing temperature. A similar rise has been observed in several ferroelectrics and attributed to a  $T^{3/2}$  contribution from domain walls.<sup>1,10</sup>

The Fig. 2 data on the cadmium niobates show steep rises in  $CT^{-3}$  below about 4 K for all three niobates, although  $\text{CdNb}_2\text{O}_6$  is nonferroelectric. There is evidence for a low-lying mode in  $\text{CdNb}_2\text{O}_6$  because of the slight rise in  $CT^{-3}$  above 7 K.

The Pb substitution in  $\text{Cd}_2\text{Nb}_2\text{O}_7$  has two effects: The specific heat increases below 25 K by  $\sim 70\%$  and the low-lying mode frequency decreases from  $\sim 50$  to  $\sim 40 \text{ cm}^{-1}$ .

The experimental evidence for low-lying modes in these niobates shown in Figs. 1 and 2 was pursued by fitting these data to a model which describes the low-lying mode by a single Einstein term added to the Debye background,

$$C(T) = C_D(\Theta_D/T) + 3rRx^2e^x/(e^x - 1)^2, \quad (1)$$

$$x = \hbar\omega/kT$$

Here  $C_D$  and  $\Theta_D$  are the Debye function and Debye temperature (normalized to one atom per lattice site),  $r$  is the strength of the Einstein mode and  $\omega$  is the frequency. This model assumes that only one mode frequency dominates  $CT^{-3}$  in the temperature range of interest, and it was found previously<sup>1,2</sup> that Eq. (1) gives excellent fits to the experimental data

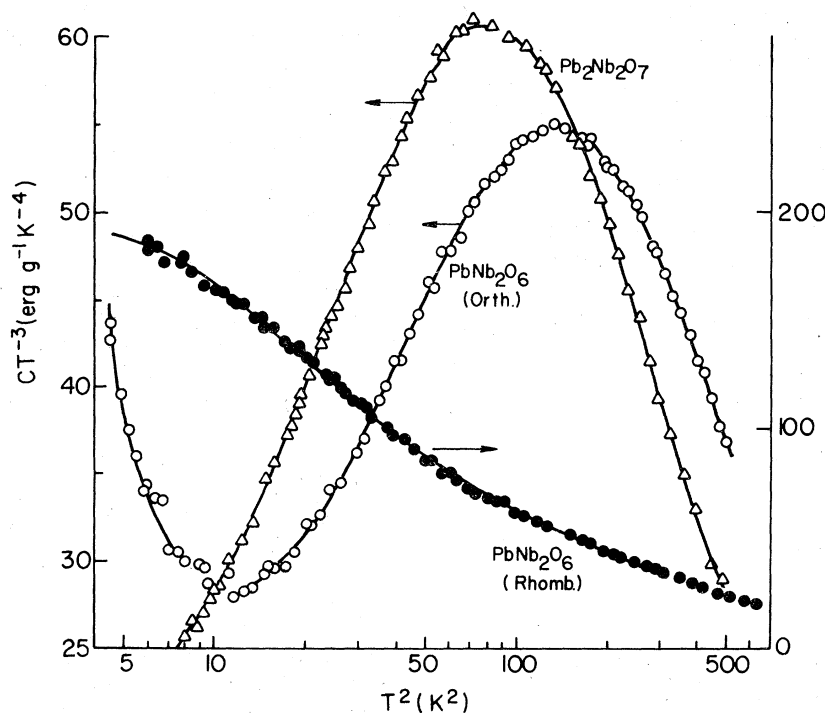


FIG. 1.  $CT^{-3}$  vs  $T^2$  plots for ceramic samples of three lead niobates. The  $\text{PbNb}_2\text{O}_6$  (orthorhombic) metaniobate is the only ferroelectric representative (note scale change for the rhombohedral  $\text{PbNb}_2\text{O}_6$ ). The data for  $\text{Pb}_2\text{Nb}_2\text{O}_7$  are from Ref. 1.

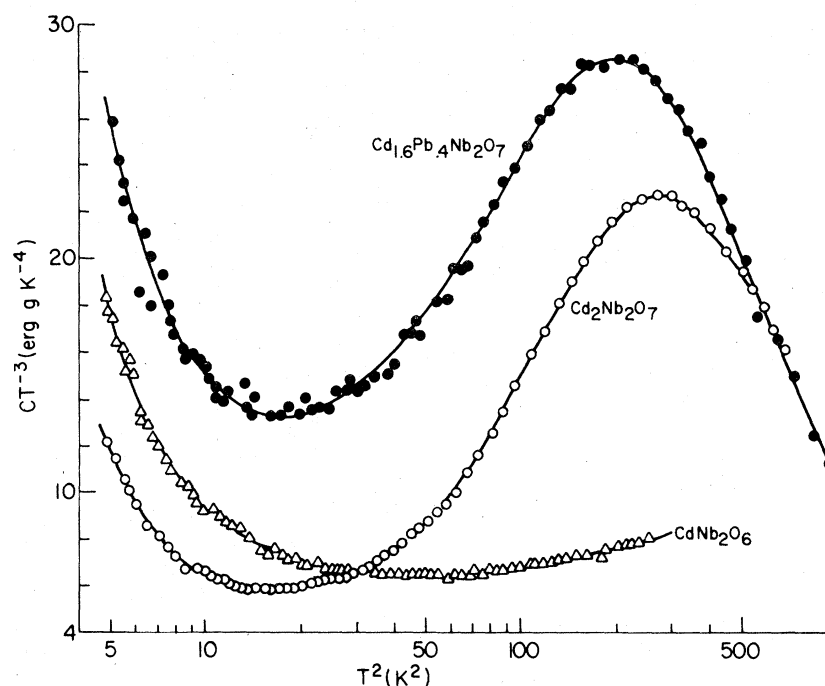


FIG. 2.  $CT^{-3}$  vs  $T^2$  plots for ceramic samples of three cadmium niobates. The pyroniobates are ferroelectric with Curie temperatures of 185 K for  $Cd_2Nb_2O_7$  and 50 K for  $Cd_{1.6}Pb_{0.4}Nb_2O_7$ . The metaniobate  $CdNb_2O_6$  is nonferroelectric.

on all the ferroelectric-type materials measured below 30 K to date.

The results of fitting the Fig. 1 data on the lead niobates to Eq. (1) are shown in Fig. 3, and on the cadmium niobates in Fig. 4. The data on the steep rises in  $CT^{-3}$  at the lowest temperatures were, of course, excluded from these fits. The data in Figs. 3 and 4 are plotted to the low-temperature form of Eq. (1) (i.e.,  $x \gg 1$ ), and the curves shown are the fitted curves. Excellent fits to the experimental data are obtained over several orders of magnitude in  $T^2$  ( $C_{exp} - C_{Debye}$ ). Even the slight rise in  $CT^{-3}$  for  $CdNb_2O_6$  in Fig. 2 yields an excellent Einstein plot in Fig. 4. The fitting parameters for these niobates are given in Table I.<sup>11</sup> Also given in Table I

is the ratio of the number of Einstein modes  $N_E$ , to the Debye modes  $N_D$ , estimated from  $N_E/N_D = r(k\Theta_D/\hbar\omega)^3$ . This ratio is a measure of the extent to which the low-lying mode dominates the specific heat.

Attempts to fit the steep rises in  $CT^{-3}$  below about 4 K in Figs. 1 and 2 according to either a  $T^{3/2}$  term or an Einstein term were unsuccessful. These data do, however, accurately follow a Schottky term,

$$C_{Sch} = Rg_0g_1(g_0 + g_1)^{-2}(\delta/T)^2, \quad T \gg \delta, \quad (2)$$

added to the Debye term, where  $g_0, g_1$  are degeneracies of a two-level system where  $\delta$  is the energy separation measured in absolute degrees. The form

TABLE I. Specific-heat parameters for lead and cadmium niobates.

Material	$\Theta_D$ (K)	$\omega$ (cm <sup>-1</sup> )	$r$	$N_E/N_D$
$Pb_2Nb_2O_7$	222	30.2	0.316	54.2
$PbNb_2O_6$ (Orth.)	224	37.6	0.382	29.7
$PbNb_2O_6$ (Rhomb.)	171	9.35	0.0285	78.7
$Cd_2Nb_2O_7$	393	52.8	0.696	105.0
$Cd_{1.6}Pb_{0.4}Nb_2O_7$	315	42.6	0.347	47.0
$CdNb_2O_6$	408	76.0	0.186	9.6

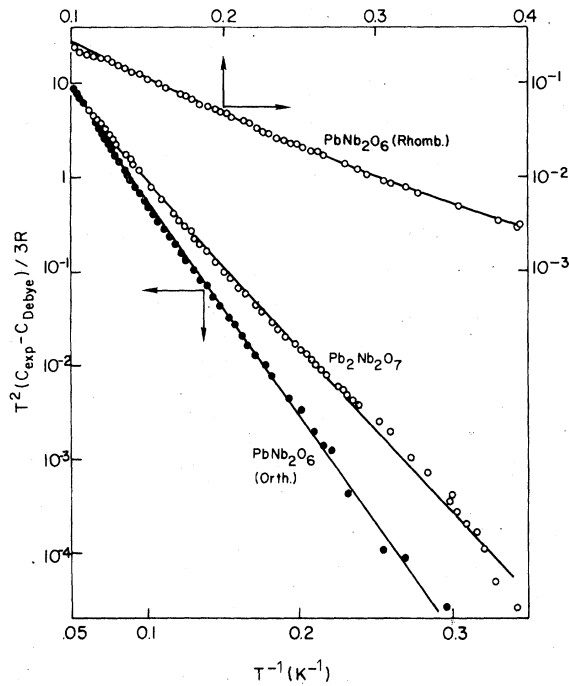


FIG. 3. Results of fitting the lead niobates data to Eq. (1). The Debye temperature was one of the fitting parameters, and the curves were drawn using the fitting parameter data in Table I. The steeply rising  $CT^{-3}$  data below 4 K were not included in these fits.

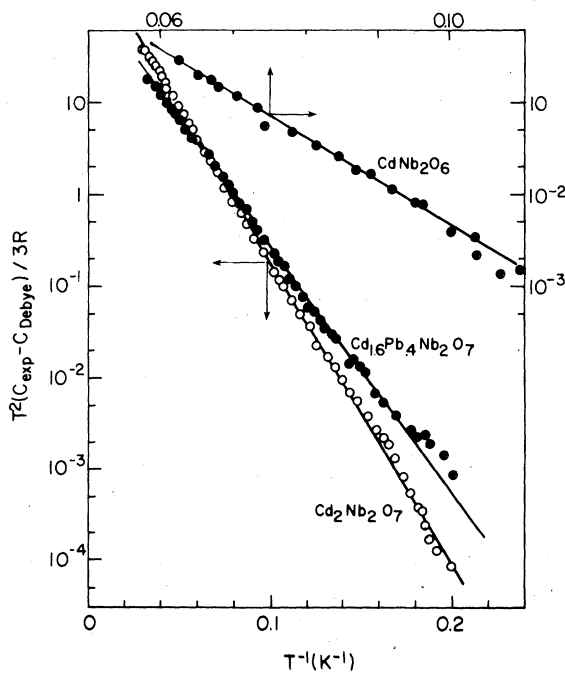


FIG. 4. Same as Fig. 3 for the cadmium niobates.

of Eq. (2) is the high-temperature expansion for the two-level system, although we have no reason to choose a two-level over, say, a three-level system. What is important is the  $T^{-2}$  dependence of the Schottky term, and Fig. 5 shows the data below about 4 K plotted as  $CT^2$  vs  $T^5$ . The curves drawn in Fig. 5 result from least-squares fits; the slopes are related to the Debye temperature and the intercepts are  $T^2 C_{Sch}$  from Eq. (2).

The fitting parameters  $\Theta_D$  and  $\delta$  from the Fig. 5 data are given in Table II, assuming  $g_0 = g_1$  [actually, the energy separation  $\delta$  is not too sensitive to the degeneracies because of the cancellation in Eq. (2)].

The Debye temperatures in Tables I and II agree reasonably well, considering the strongly non-Debye features of the data being fitted. The Debye temperatures obtained from the Schottky fits, Table II, are probably more reliable because the higher-temperature fits, Table I, are based on the assumption of a single Einstein term. Numerical estimates show that the Einstein term makes a negligible contribution in the Schottky region and *vice versa* for these materials. The energy separations  $\delta$  are re-

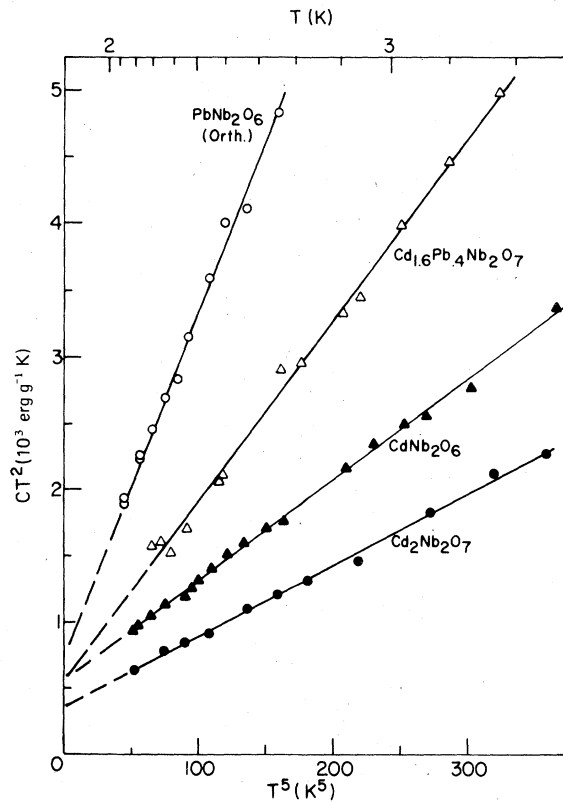


FIG. 5. High-temperature Schottky plots for the materials showing steep rises in  $CT^{-3}$  below about 4 K in Figs. 1 and 2. The curves were drawn using the fitting parameter data in Table II.

TABLE II. Schottky-term parameters below 4 K ( $g_0 = g_1$ ).

Material	$\Theta_D$ (K)	$\delta$ (mK)
$\text{Cd}_2\text{Nb}_2\text{O}_7$	$423.2 \pm 1.4$	$47.0 \pm 0.8$
$\text{Cd}_{1.6}\text{Pb}_{0.4}\text{Nb}_2\text{O}_7$	$303.9 \pm 1.4$	$61.2 \pm 1.9$
$\text{CdNb}_2\text{O}_6$	$388.3 \pm 0.9$	$51.7 \pm 0.4$
$\text{PbNb}_2\text{O}_6$ (Orth.)	$240.4 \pm 1.3$	$67.4 \pm 1.7$

markedly similar for the four niobates with the Pb-containing niobates having the higher  $\delta$  values. However, these fitted energy separations cannot be used to infer reliably the specific heat in the mK range.

### III. DISCUSSION

The marked dissimilarities in the ferroelectric properties of the lead and cadmium niobates extend to their low-temperature specific heats also. For example, the specific heat of  $\text{CdNb}_2\text{O}_6$  is an order of magnitude smaller than the specific heat of the similarly nonferroelectric  $\text{PbNb}_2\text{O}_6$  (rhombohedral) below about 10 K.

With the exception of  $\text{CdNb}_2\text{O}_6$ , these niobates show a striking departure from Debye behavior. That is, dielectrics such as  $\text{NaCl}$  or  $\text{Al}_2\text{O}_3$  have slight minima in the effective Debye temperature at these temperatures, but these effects are very small compared to what occurs in these ferroelectric-type materials where  $N_E/N_D$  is considerably larger than unity, as in Table I. For example, near the maximum in  $CT^{-3}$  the Debye contribution is only 26% for  $\text{Cd}_2\text{Nb}_2\text{O}_7$ .

There is a striking difference in the thermal properties of ferroelectric and nonferroelectric  $\text{PbNb}_2\text{O}_6$ : For the ferroelectric form the Debye temperature is increased 31% (171 to 224 K) and the mode frequency by 302% (9.35 to 37.6  $\text{cm}^{-1}$ ).

The cadmium niobate data in Fig. 2 and Table II show that the effect of the 20-mole%-Pb substitution on the Cd site shifts the mode frequency from 52.8 to 42.6  $\text{cm}^{-1}$ . This is too large an effect to be explained by the reduced mass. It is possible these are the soft-mode frequencies which are temperature-shifted by the difference in transition temperatures (185 and 50 K). The large differences in the Debye temperatures of the cadmium niobates cannot be accounted for in terms of differences in density, molecular weight, or melting point according to the Lindemann relation.<sup>12</sup>

It is likely that the low-lying Einstein modes in these niobates are due to a large density of TA phonons, for the following reasons. First, the mode in  $\text{Pb}_2\text{Nb}_2\text{O}_7$  has been shown<sup>3</sup> to be field-independent up to 27.3 kV/cm, which indicates acoustic rather

than optic modes. The neutron data on  $\text{PbTiO}_3$  indicate a large density of TA phonons in the 50–70  $\text{cm}^{-1}$  range,<sup>13</sup> and finally the Raman data on  $(\text{Pb,Lu})(\text{Zr,Ti})\text{O}_3$  ceramics indicate a band of zone-boundary TA phonons in the range 39–52  $\text{cm}^{-1}$ .<sup>14</sup> These types of scattering data are necessary on these niobate materials, however, before mode assignments can be established, because the specific-heat measurement samples the entire Brillouin zone.

It is possible to speculate on the oscillations responsible for these low-lying modes from the  $r$  values in Table I. A motion of the  $\text{Nb}^{5+}$  ion within the oxygen octahedron would correspond to an optic mode for which  $r \sim 0.2$ . This may be the case of  $\text{CdNb}_2\text{O}_6$ . An acoustic-type oscillation of the  $\text{NbO}_6$  octahedra would correspond to  $r \sim 0.7$ , which may be the  $\text{Cd}_2\text{Nb}_2\text{O}_7$  case. However, the  $\text{NbO}_6$  octahedra are not all in equivalent positions in these structures so that only some fraction of the octahedra may contribute to the low-lying mode. This seems to be the case of the remaining niobates. Along this line, it is interesting that the 20-mole %-Pb substitution on the Cd site in  $\text{Cd}_2\text{Nb}_2\text{O}_7$  reduces the  $r$  value by almost exactly one-half (Table I).

The Schottky contribution, Fig. 5 and Table II, is present in all the ferroelectric members but is present in just one nonferroelectric,  $\text{CdNb}_2\text{O}_6$ . It is difficult to reconcile this Schottky term as an impurity effect because all the samples were prepared from the same reagent-grade chemicals, care being taken to avoid impurities. Moreover, the  $\delta$  values in Table II are very similar.

The smallness of the  $\delta$  values suggests a nuclear effect. Since  $\text{Nb}^{5+}$  has a finite electric-quadrupole moment, it is tempting to attribute the Schottky effect to the quadrupole-moment interaction with the electric-field gradient at the  $\text{Nb}^{5+}$  site, and it is expected that this gradient is strongest in the ferroelectrics. Furthermore, the field gradient should be larger in the Pb-containing materials, and the  $\delta$  values in Table II are in accord with this (i.e.,  $\delta$  is proportional to the quadrupole coupling constant which is related to the field gradient). Presumably, the field gradients in the nonferroelectric lead niobates are not large enough for the Schottky term to contribute above 2 K, but the case of  $\text{CdNb}_2\text{O}_6$  is not clear.

Along this line, it is interesting to review the case of  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ : Specific-heat measurements on single crystals of these ferroelectrics were reported previously,<sup>1</sup> and a steep rise in  $CT^{-3}$  with decreasing temperature was found in both cases below  $\sim 4$  K. The  $\text{LiNbO}_3$  data very accurately follow a  $T^{3/2}$  law below 4 K,<sup>1,10</sup> but the  $\text{LiTaO}_3$  data do not.

These  $\text{LiTaO}_3$  data do, however, give an excellent Schottky plot, equivalent to the plots in Fig. 5, with the fitting result that  $\delta = 11.9$  mK. This is significant for the interpretation of the Schottky term given

above because Ta<sup>5+</sup> has a much larger electric-quadrupole moment than Nb<sup>5+</sup> (4.0 for <sup>181</sup>Ta compared to -0.16 for <sup>93</sup>Nb, in units of  $e \times 10^{-24} \text{ cm}^2$ ). Presumably, then, the Schottky contribution dominates in LiTaO<sub>3</sub> and the  $T^{3/2}$  contribution dominates in LiNbO<sub>3</sub> (both crystals are rhombohedral).

Measurements of PbTa<sub>2</sub>O<sub>6</sub> would be illuminating here because of the similarity of this orthorhombic ferroelectric and PbNb<sub>2</sub>O<sub>6</sub>.<sup>15</sup> If the explanation of the Schottky term is correct, then the  $\delta$  value for PbTa<sub>2</sub>O<sub>6</sub> should be  $\sim 1$  K.

In conclusion, the calorimetric measurements reported here and previously<sup>1,2</sup> have shown that ferroelectric-type materials have specific heats which are dominated by phenomena other than the long-wavelength acoustic waves in the elastic continuum. These non-Debye contributions arise from a large density of low-lying phonons that occur in these crystal structures, which are either favorable for the oc-

currence of a soft mode or closely related to structures that are favorable. Two other contributions have been demonstrated which are important below about 4 K: A Schottky term demonstrated here which appears due to the Nb electric-quadrupole moment in a field gradient, and a  $T^{3/2}$  term which was originally believed due to domain walls<sup>10</sup> but later postulated to be due to surface wave phenomena.<sup>16</sup> Specific-heat measurements below 2 K and thermal-conductivity measurements are needed to clarify the many questions posed by what has thus far been found from these calorimetric measurements.

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<sup>11</sup>A nonlinear regression analysis was used in fitting these data to Eq. (1), and the Debye-function table given in

Ref. 12 was incorporated. The index of regression for these fits was typically  $\sim 0.999$ . The experimental uncertainty in  $CT^{-3}$  is  $< \pm 5\%$ , and the uncertainty in the parameters of Table I is  $< \pm 2\%$ .

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