Calorimetric investigation of successive phase transitions in $Cd_2Nb_2O_7$

Makoto Tachibana, Hitoshi Kawaji, and Tooru Atake
Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan
(Received 23 October 2003; published 10 August 2004)

We report the heat capacity (C_p) measurements on single crystals of pyrochlore $Cd_2Nb_2O_7$ over the temperature range of 0.3 to 420 K. A peak in C_p appears at $T_s = 204$ K, where a small anomaly is observed in the dielectric constant. Below T_s, there is a broad C_p anomaly that corresponds to the relaxor-like behavior in the dielectric constant. At lower temperatures, the shape of C_p anomalies around the continuous transition at 85 K and the first-order transition at 46 K is consistent with normal-incommensurate and incommensurate-commensurate transition, respectively, as suggested in previous Raman studies. In the lowest temperature region, C_p of $Cd_2Nb_2O_7$ is compared with that of typical relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN). While the low-temperature C_p of PMN exhibits a glasslike behavior with the linear temperature-dependent coefficient of 1.6 $\mu J\,K^{-2}\,g^{-1}$, C_p of $Cd_2Nb_2O_7$ shows the crystalline behavior. This suggests that polar clusters associated with the relaxor-like behavior in $Cd_2Nb_2O_7$ develop into normal ferroelectric domains below the incommensurate transitions.

DOI: 10.1103/PhysRevB.70.064103 PACS number(s): 82.60.Fa, 64.70.Kb, 64.70.Rh, 77.84.Dy

I. INTRODUCTION

Recent heat-capacity measurements[1] on the relaxor ferroelectrics $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT) demonstrated that the formation of polar nanoregions is accompanied by an extremely broad heat-capacity anomaly, and a glassy ground state was suggested from the observed values of entropy. Although Pb-based complex oxides such as PMN and PMT are typical representatives of relaxors, recent studies indicate that many other disordered oxides exhibit similar relaxor behavior—a large, broad peak in the dielectric constant with low-frequency dispersion. The studies of cation substitutions into $SrTiO_3$ and $BaTiO_3$,[2,3] and the systematic behavior[4,5] of neighbors to $KTaO_3$ provide good examples of how the subtle physics of relaxor behavior is ultimately determined by details of local structure and polarization mechanism. On the other hand, there exist major disagreements among the proposed interpretations of relaxor behavior,[6–9] and there is still no satisfactory model capable of describing the general behavior of all relaxors. As such, it may be desirable to study structurally simpler systems which still display similar relaxor behavior.

Pyrochlore $Cd_2Nb_2O_7$, which has long been known to exhibit unusual ferroelectric behavior,[10–13] may perhaps be considered as one such system. $Cd_2Nb_2O_7$ shows relaxor-like behavior[10–13] despite the lack of cation mixing, and a number of successive phase transitions have been reported to occur in different temperature regions.[14] Although the details of the relaxor behavior in $Cd_2Nb_2O_7$ remain unclear and might differ from those of typical relaxors,[3,11] a better understanding of this structurally simple system may provide important insights into the relaxation properties of disordered ferroelectrics. In this study, we examine the relaxor behavior and the nature of successive phase transitions in $Cd_2Nb_2O_7$, using high-precision heat capacity (C_p) measurements over a wide temperature region of 0.3 to 420 K. In addition, in order to correlate the dielectric properties with the ground-state thermal properties, we extend our previous C_p measurements[1] on PMN down to 0.3 K, and compare the results with those of $Cd_2Nb_2O_7$.

In the room-temperature paraelectric phase, $Cd_2Nb_2O_7$ is cubic and belongs to the space group of $Fd\bar{3}m$. With the general formula of $A_2B_2O_7$, the pyrochlore structure is composed of three-dimensional network of corner-sharing BO_6 octahedra, and the O-B-O chains follow zigzag lines along the $\langle 110 \rangle$ direction. The framework has the composition $(B_2O_6)_\infty$, leaving the seventh set of oxygen atoms and the A ions to occupy the open spaces. At $T_s \sim 205$ K, $Cd_2Nb_2O_7$ undergoes a structural transition into an orthorhombic phase (mmm), which has been classified as an improper ferroelastic transition.[15] This transition is marked by a small anomaly in dielectric constant, and domain structures were observed in a number of studies. As the crystal is cooled further, the real part of the complex dielectric constant shows a rounded peak around 190 K, with a frequency dependence reminiscent of relaxors.[10–13] The dielectric relaxation time has been described with the Vogel-Fulcher relation.[10,12] The electric-field dependence of the dielectric constant indicated the presence of nanometer-sized cluster polarization,[11] though perhaps of different nature from that of typical relaxors.[10,11] The new symmetry group of $mm2$ was suggested below this temperature region,[16] yet the extremely small distortion has precluded detailed structural studies. Also, previous heat-capacity measurements[17,18] showed a broad anomaly in this temperature region, but the results were not discussed in detail.

On cooling down still further, $Cd_2Nb_2O_7$ exhibits additional transitions at $T_i = 85$ K and $T_c = 46$ K.[14] The dielectric constant shows a peak at T_i, which also shows thermal hysteresis between T_i and T_c. Below T_i, the damping of some new Raman modes shows anomalous temperature dependence down to T_c, where the integrated intensity of Raman modes shows a steep drop.[19,20] These features were shown to resemble closely the incommensurate (IC) phases in the well-known systems K_2SeO_4 and Rb_2ZnBr_4, and IC phase was speculated for $Cd_2Nb_2O_7$ between T_i and T_c.[19,20] How-

ever, identification of the IC phase in $Cd_2Nb_2O_7$ has been limited to dielectric and Raman scattering experiments, and no diffraction data showing the satellites peaks of the IC phase have been reported.

The low-temperature thermal properties of $Cd_2Nb_2O_7$, and of ferroelectrics in general, have been a controversial and confusing problem. More than 20 years ago, Lawless reported that ferroelectrics exhibit a $T^{3/2}$ dependence of C_p at low temperatures.[21] This feature was attributed initially to a domain-wall contribution and later to surface excitations. However, subsequent studies by different authors have shown conclusively that no such anomaly in C_p exists.[22] Instead, the low-temperature C_p of ferroelectrics showed the usual Debye behavior of crystalline solids. On the other hand, Lawless and co-workers[23,24] and others[25] reported glasslike behavior in low-temperature C_p and thermal conductivity for *some* ferroelectrics, $Cd_2Nb_2O_7$ being one of them.[23] Glasslike behavior[26] is observed universally in glasses and amorphous solids, and it is very different from the properties of the Debye model. Below 1 K, glasslike behavior is marked by a linear T dependence in C_p and T^2 dependence in thermal conductivity. Above 1 K, C_p still deviates strongly from the Debye T^3 dependence, and the thermal conductivity shows a plateau. These features in glasses can be explained by the two-level tunneling model[27] and its extended models.[28]

The observation of glasslike behavior in ferroelectrics was critically examined by De Yoreo *et al.*,[29] who proposed that there are two kinds of ferroelectrics: Normal ferroelectrics with sharp ferroelectric transition exhibit crystalline thermal properties at low temperatures, whereas relaxors display glasslike behavior. This proposal was correlated with the observation of local and randomly oriented polarization in the latter systems,[30] although it is still not clear how glasslike excitations arise from such polarization, without explicit structural disorder as in glasses and amorphous solids. While many ferroelectrics were categorized by De Yoreo *et al.* into one of the two classes, it was not concluded[29] whether $Cd_2Nb_2O_7$ exhibits glasslike or crystalline behavior for the following reasons: (1) Lawless's C_p data on $Cd_2Nb_2O_7$ showed T^{-2} dependence below 4 K,[31] which has led Lawless *et al.*[23] to argue that a possible glasslike linear term is masked by this contribution. (2) While thermal conductivity data on ceramic $Cd_2Nb_2O_7$ were originally interpreted by Lawless *et al.*[23] to be glasslike, De Yoreo *et al.* pointed out that the data are better interpreted as a characteristic of small-grain-size ceramics. However, it must also be kept in mind that (1) the reported C_p data on $Cd_2Nb_2O_7$ should be viewed with some caution, since many of the low-temperature C_p data reported by the same author have been dismissed,[32] and (2) De Yoreo *et al.* considered $Cd_2Nb_2O_7$ as a normal ferroelectric, and its unusual ferroelectric properties were not mentioned. Also, even for those relaxors in which glasslike behavior was corroborated by different authors, most of the reported C_p data deviate from the linear T dependence in the lowest temperature region. This is most likely to be due to impurities,[29] and no reliable value of the energy-independent density of states has been extracted from these C_p data. With these features in mind, we have carried out C_p measurements down to 0.3 K on high-quality single crystals of $Cd_2Nb_2O_7$ and PMN.

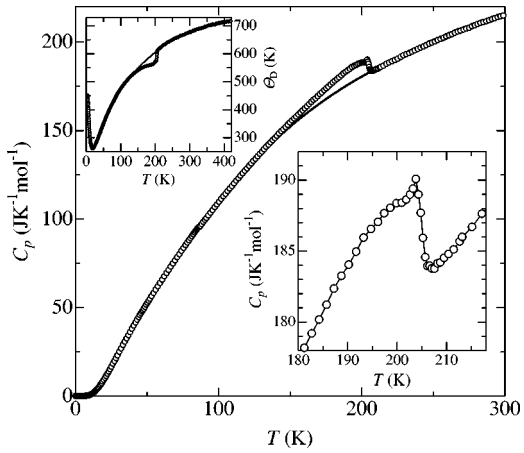

FIG. 1. Heat capacity C_p of $Cd_2Nb_2O_7$. The solid line is the estimated lattice contribution. The lower inset shows C_p around 200 K. The upper inset shows the effective Debye temperature $\Theta_D(T)$, calculated from C_p assuming three degrees of freedom for each atom. The solid line in the upper inset corresponds to the solid line in the main figure.

II. EXPERIMENT

Single crystals of $Cd_2Nb_2O_7$ were prepared by a flux method using cadmium borate as the flux. We followed the procedure reported by Meldrum *et al.*,[33] with the mixture ratio of $Cd_2Nb_2O_7:Cd_3B_2O_6=2:3$. The crystals are colorless and transparent with the maximum size of ~ 5 mm wide $\times 1$ mm thick. The powder x-ray diffraction patterns showed that the sample is single phase with the cubic pyrochlore structure. An inductively coupled plasma analysis indicated the Cd/Nb ratio of 0.98. The heat capacity of $Cd_2Nb_2O_7$ was measured on heating direction using three different apparatuses. Data from 13 to 420 K were taken by an adiabatic calorimeter, which is the same apparatus used in previous measurements of the heat capacity of PMN and PMT.[1] Data from 3 to 30 K were obtained with Quantum Design PPMS employing the relaxation method. Data in the lowest temperature region from 0.3 to 5 K were obtained by the relaxation method in a ^{3}He-^{4}He dilution refrigerator, with a RuO_2 chip as the thermometer. This apparatus was also used to measure the heat capacity of single crystals of PMN between 0.3 and 5 K, which has been measured previously in the temperature range of 2 to 420 K.[1] Dielectric complex-permittivity of $Cd_2Nb_2O_7$ was measured with an HP 4284A LCR meter operating between 1 and 1000 kHz. The sample was first heated up to 330 K, and the measurements were carried out on cooling direction down to 15 K.

III. RESULTS AND DISCUSSION

We describe the results of C_p measurements in descending order of temperature region. Figure 1 shows C_p versus T from 0.3 to 300 K. The most pronounced anomaly occurs around 200 K, where C_p shows a sudden change. The lower inset exhibits the same data on an expanded scale around 200 K, which clearly shows a small peak at 204 K superimposed on another anomaly with a broad peak at slightly

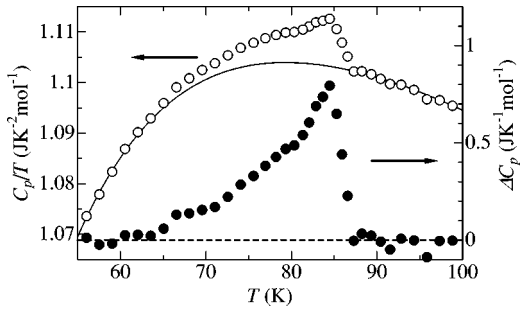

FIG. 2. Heat capacity, divided by temperature, for $Cd_2Nb_2O_7$ (open circles). The solid line is the estimated lattice contribution, which was used to obtain the excess heat capacity ΔC_p (closed circles).

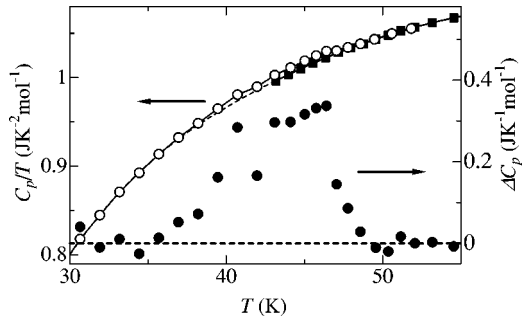

FIG. 3. Heat capacity, divided by temperature, for $Cd_2Nb_2O_7$. Open circles and closed squares correspond to data obtained on heating direction after the sample was cooled down to 4.2 and 42 K, respectively. The dashed line is the estimated lattice contribution. Also shown in closed circles is the excess heat capacity ΔC_p.

lower temperature. The overall shape of the anomaly is consistent with the previous reports,[17,18] though the present results clearly demonstrate two separate peaks of different nature. The peak at $T_s = 204$ K corresponds to a small anomaly in dielectric constant, to be discussed later, and this transition has been classified as an improper ferroelastic transition.[15] There was no sign of latent heat or thermal hysterisis across this transition, indicating that the transition is second-order. It was not possible to extract critical exponents for this peak, since the low-temperature side is masked by the broad anomaly, and there are a limited number of data points covering the sharp drop on the high-temperature side. The broad peak, on the other hand, corresponds to the large, relaxor-like peak in the dielectric constant (see Fig. 5). The details of this broad peak will be discussed later.

We can estimate the entropy involved in both transitions by subtracting a smooth background from the C_p data, as shown in Fig. 1. This background was determined by fitting the C_p well above and below the anomalous region by a polynomial function. The upper inset of Fig. 1 shows that this background can also smoothly fit the lattice part of the effective Debye temperature curve, which was calculated assuming three degrees of freedom for each atom. The obtained excess entropy ΔS is 2.0 J K^{-1} mol^{-1}. It is to be noted in passing that we did not find any sign of C_p anomaly around 312 K, where isostructural transition has been reported.[34] This is consistent with the recent infrared[14] and x-ray[35] studies, which did not observe any important change in this temperature region.

The C_p data in Fig. 1 show that the broad anomaly extends down to ~120 K, indicating that this anomaly does not overlap with much smaller anomalies around 85 and 46 K. In Fig. 2, the heat capacity is plotted in C_p/T with open circles, which shows a peak at $T_i = 84.5$ K with a long tail on the low-temperature side. We have also measured C_p after the sample was cooled from 100 K to T_i and also from 100 K to $T_i - 5$ K, and the data coincided with those in Fig. 2. This indicates that there is no supercooling nor hysteresis associated with this transition. Also, there was no sign of latent heat at the transition. These results, together with the shape of anomaly, indicate that the transition is second-order. In order to examine the shape of C_p anomaly more closely, a smooth background curve was subtracted from the data. The results, plotted in ΔC_p, are shown in Fig. 2 with closed circles. On the high-temperature side, ΔC_p does not drop vertically but shows a small rounding. On the low-temperature side, ΔC_p shows a long tail which extends close to the transition at $T_c = 46$ K. These features of this C_p anomaly are very similar to normal (N)-incommensurate (IC) transitions in K_2SeO_4,[36] Rb_2ZnCl_4,[37] and Rb_2ZnBr_4,[38] suggesting similar mechanism of transition. The entropy of the transition is estimated to be 0.11 J K^{-1} mol^{-1}.

The critical behavior of C_p around $T_i = 84.5$ K was also investigated with the logarithmic plot of ΔC_p as a function of reduced temperature. A linear slope was obtained in the range $|T - T_i| < 5$ K on the low-temperature side, and the critical exponent of $\alpha \sim 0.26$ was obtained. This is significantly greater than the theoretical value of $\alpha = -0.007$ for the three-dimensional *XY* model, which is usually believed to represent most N-IC transitions. However, it should be noted that experimental values of $\alpha = 0.20$ for Rb_2ZnCl_4 (Ref. 37) and $\alpha = 0.13$ for K_2SeO_4 (Ref. 36) have been reported, which were obtained with similar experimental setups and data analysis to the present study. Several studies[40,41] have suggested that detailed fitting procedures are needed to make the data conform to the theoretical expectations; these are beyond the scope of the present study.

Figure 3 shows C_p in the vicinity of the transition at $T_c = 46$ K. The open circles correspond to a series of measurements in which the sample was heated from the liquid He temperature. A small anomaly is visible between 35 and 50 K, and the temperature drift during the relaxation periods of the measurement was observed up to 46 K. The closed squares correspond to the C_p values taken after the sample was cooled from 53 to 42 K. In this case the data extend smoothly across T_c, indicating that the high-temperature phase is supercooled. These observations indicate that the transition is first-order. The dashed line in the figure represents a baseline, which was established by extrapolating the closed-square values into the low-temperature region. This baseline was then used to obtain the excess heat capacity ΔC_p, which is plotted with closed circles. The entropy of the transition is estimated to be 0.054 J K^{-1} mol^{-1}. To date, all IC-commensurate (C) transitions have been shown to be first-order, with small C_p anomaly similar to the present case.[42] A tail on the high-temperature side of the transition,

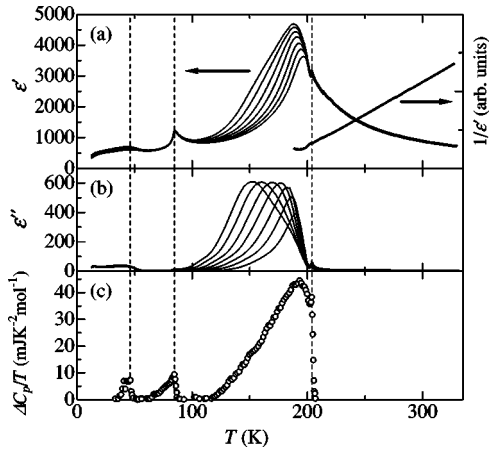

FIG. 4. The real ϵ' (a) and imaginary ϵ'' (b) part of dielectric constant at measurement frequencies of 1, 3, 10, 30, 100, 300, and 1000 kHz (left to right) and excess heat capacity $\Delta C_p/T$ (c) in $Cd_2Nb_2O_7$. The inverse of the dielectric constant at 100 kHz is also shown in (a), which shows the Curie-Weiss behavior above 204 K. Dashed lines are drawn at 46, 84.5, and 204 K to locate the anomalies associated with each transition.

which is observed in the present data, is also considered as a characteristic of IC-C transition.[39] Ideally, a first-order transition should be accompanied by a sharp peak in C_p, due to the latent heat of transition. A broad C_p anomaly at first-order transition is usually associated with internal inhomogeneities produced by strain or impurities, and IC-C transitions are known to be extremely sensitive to such effects.[42]

The C_p anomalies discussed so far are plotted as $\Delta C_p/T$ in Fig. 4, which also shows the real and imaginary parts of the dielectric constant. As discussed above, the peak in C_p at $T_s = 204$ K corresponds to a small anomaly in the dielectric constant. Above T_s, the dielectric constant follows the Curie-Weiss behavior and there is no excess contribution in C_p. These results, together with the presence of ferroelectric soft mode in this temperature region,[14] are the expected behavior of paraelectric phase in normal displacive-type ferroelectrics. For the prototypical relaxor PMN, the dielectric constant deviates from the Curie-Weiss behavior below the Burns temperature $T_d \sim 600$ K.[43] This is several hundred of degrees higher than $T_{max} \sim 280$ K, where the dielectric constant shows a broad peak. It is widely believed that randomly oriented regions of local polarization, of several unit cells in size, gradually condense within the nonpolar matrix below T_d. This is seen in the heat capacity of PMN as an extremely broad anomaly, which starts at above 500 K and extends down to 150 K.[1] Absence of such features in $Cd_2Nb_2O_7$ above T_s suggests that local polarization does not develop in this temperature region.

In contrast to the normal-ferroelectric behavior above T_s, both C_p and dielectric constant below T_s show many features that are characteristics of relaxors. As in relaxors, the magnitude of the real part of the dielectric constant decreases with increasing frequency and the maximum shifts to higher temperatures. In addition, the low-frequency data develop a shoulder at ~150 K, which has been described previously as an extra relaxation mode.[10] The absence of a singularity in the broad C_p anomaly below T_s suggests that there is no true phase transition in this temperature region.[44] Moreover, the close resemblance of the shape of the broad anomaly to that of PMN (Ref. 1) implies a similarity in polarization mechanism. However, whether there is a proper paraelectric to ferroelectric transition in this system[14] remains unclear from the present C_p measurements, and further structural studies are needed to shed light on this matter.

It is perhaps worth pointing out that the transition at T_s shows some resemblance to the role of Burns temperature T_d in Pb-based relaxors. In both cases, normal-ferroelectric behavior with soft TO mode is observed above these temperatures,[14,45] and the formation of polar clusters starts only below these temperature points. However, while most Pb-based relaxors show no reduction in macroscopic symmetry at T_d, a real structural phase transition occurs at T_s in $Cd_2Nb_2O_7$. Previously, the orientational disorder of the seventh set of oxygen and off-center Cd dipoles has been suggested as a possible explanation of dielectric relaxation in $Cd_2Nb_2O_7$.[12,13] Although the nature of the transition at T_s is not understood in detail, the dipoles may couple effectively with the formation of domains at T_s to produce the cluster polarization.[11]

The anomalies in dielectric constant and C_p around 85 and 46 K are also evident from Fig. 4. The transition at 46 K is accompanied by dielectric relaxation in the kHz region, which is widely observed in IC-C transition.[42] It is not clear how IC transitions appear on cooling in $Cd_2Nb_2O_7$. However, it should be pointed out that the observation of IC structures is widely reported in $(PbLa)(ZrTi)O_3$ (Ref. 46) and also in $Pb(Sc_{1/2}Ta_{1/2})O_3$,[47] which exhibit relaxor behavior for some compositions in the former and under certain preparative conditions in the latter. Both IC structure and polar clusters are characterized by frustration of competing interactions, and both states may become very close in free energy.[46] Also, spontaneous relaxor to normal-ferroelectric transformation on cooling is observed in a number of oxides,[4] which may be related to the present case.

Finally, we discuss the low-temperature C_p of $Cd_2Nb_2O_7$, which is shown in Fig. 5. The results of C_p measurements on PMN are also shown, and the published results[1] are used above 3 K. The data have been normalized to per mole of *A*-site atom for a meaningful comparison. Note that this is equivalent to one mole for PMN, and 0.5 mole for $Cd_2Nb_2O_7$. In order to clarify the existence of various contributions to C_p from different mode of excitations, the data are plotted as C_p/T^3 vs T in Fig. 5. When C_p is plotted this way, a Debye contribution with the T^3 dependence will appear constant up to the Debye temperature Θ_D, above which it drops to zero. This behavior can be seen in $Cd_2Nb_2O_7$ from the lowest temperature up to ~5 K, indicating the absence of the reported T^{-2} term.[31] The absence of a linear T term can also be seen from the C_p/T vs T^2 plot in the inset, which extrapolates to zero for $T=0$. The data above 4 K are consistent with the published results,[31] and the broad peak at 18 K can be described by an Einstein term with $\omega = 53$ cm^{-1}.[31] Therefore, the low-temperature C_p of $Cd_2Nb_2O_7$ can be satisfactorily described by a combination of Debye and Einstein contributions, indicating that $Cd_2Nb_2O_7$ exhibits a crystalline behavior. This crystalline behavior suggests

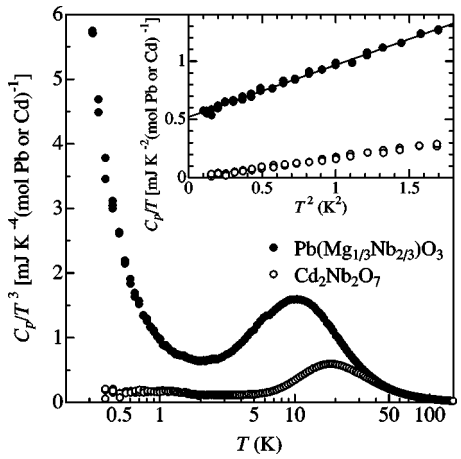

FIG. 5. Heat capacity divided by T^3 for $Cd_2Nb_2O_7$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) vs T in semilog scale. The inset shows C_p/T vs T^2 for $Cd_2Nb_2O_7$ and PMN. The solid line is the fit to the data.

that polar clusters develop into normal ferroelectric domains below the incommensurate transitions for $Cd_2Nb_2O_7$.

In contrast to $Cd_2Nb_2O_7$, a sharp upturn is observed in PMN below 2 K, which is indicative of contribution from linear-temperature component. This component corresponds to the finite intercept in the C_p/T vs T^2 plot. For PMN, the best fit to $C_p=\gamma T+\beta T^3$ requires $\gamma=0.52$ mJ K^{-2} mol^{-1} or 1.6 μJ K^{-2} g^{-1} for the linear coefficient. If the coefficient γ in PMN is analyzed within the two-level-system model used for glasses, the energy-independent density of states is $D(\epsilon)=6.7\times10^{21}$ states/eV cm^3. This is within the range widely observed in amorphous solids.[26] Also to be noted is the large size of the peak at 10 K in the C_p/T^3 plot for PMN. If this peak is treated within the context of lattice vibration in crystals, unusually large contributions from low-energy optic modes are obtained.[1] On the other hand, the peak may be more closely related to the low-frequency vibrational modes in glasses, which has been considered previously.[24]

IV. CONCLUSION

In conclusion, we have measured the heat capacity of $Cd_2Nb_2O_7$ over the temperature range of 0.3 to 420 K, and extended previous measurements on PMN down to temperatures low enough to investigate the region dominated by the linear term in T. In $Cd_2Nb_2O_7$, the normal-ferroelectric behavior is observed down to $T_s=204$ K, where a sharp transition marks the onset of relaxor-like behavior. The close resemblance of the broad C_p anomaly to that of PMN suggests the formation of cluster polarization, despite the lack of chemical disorder (cation mixing) in $Cd_2Nb_2O_7$. The shapes of C_p anomalies around the second-order transition at 85 K and the first-order transition at 46 K support the previous conjecture of N-IC and IC-C transition, respectively. In contrast to the glassy behavior of low-temperature C_p for PMN, crystalline behavior is observed for $Cd_2Nb_2O_7$. This result suggests that polar clusters associated with the relaxor-like behavior develop into normal ferroelectric domains below the incommensurate transitions. Further experimental efforts, especially structural studies, are warranted in this unique ferroelectric system.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the technical assistance of Naoki Abe and stimulating conversations with Dr. Yosuke Moriya.

[1] Y. Moriya, H. Kawaji, T. Tojo, and T. Atake, Phys. Rev. Lett. **90**, 205901 (2003).
[2] C. Ang, Z. Yu, and Z. Jing, Phys. Rev. B **61**, 957 (2000).
[3] C. Ang and Z. Yu, J. Appl. Phys. **91**, 1487 (2002).
[4] J. Toulouse, B. E. Vugmeister, and R. Pattnaik, Phys. Rev. Lett. **73**, 3467 (1994).
[5] G. A. Samara, Phys. Rev. Lett. **53**, 298 (1984).
[6] V. Westphal, W. Kleemann, and M. D. Glinchuk, Phys. Rev. Lett. **68**, 847 (1992).
[7] D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttig, J. Appl. Phys. **68**, 2916 (1990).
[8] A. E. Glazounov, A. K. Tagantsev, and A. J. Bell, Phys. Rev. B **53**, 11 281 (1996).
[9] R. Pirc and R. Blinc, Phys. Rev. B **60**, 13 470 (1999).
[10] C. Ang, R. Guo, A. S. Bhalla, and L. E. Cross, J. Appl. Phys. **87**, 7452 (2000).
[11] C. Ang, L. E. Cross, R. Guo, and A. S. Bhalla, Appl. Phys. Lett. **77**, 732 (2000).
[12] N. N. Kolpakova, P. P. Syrnikov, A. O. Lebedev, P. Czarnecki, W. Nawrocik, C. Perrot, and L. Szczepanska, J. Appl. Phys. **90**, 6332 (2001).
[13] N. N. Kolpakova, R. Margraf, and M. Polomska, J. Phys.: Condens. Matter **6**, 2787 (1994).
[14] E. Buixaderas, S. Kamba, J. Petzelt, M. Savinov, and N. N. Kolpakova, Eur. Phys. J. B **19**, 9 (2001).
[15] The transition has also been classified as improper ferroelectric; see, e.g., F. M. Salaev, L. S. Kamzina, and N. N. Krainik, Sov. Phys. Solid State **34**, 982 (1992).
[16] Z. G. Ye, N. N. Kolpakova, J. P. Rivera, and H. Schmid, Ferroelectrics **124**, 275 (1991).
[17] G. A. Smolensky, N. N. Kolpakova, S. A. Kizhaev, I. G. Siny, V. V. Tikhonov, M. Polomska, R. Margraf, and E. S. Sher, Sov. Phys. Solid State **26**, 604 (1984).
[18] F. M. Salaev, L. S. Kamzina, N. N. Krainik, A. L. Kholkin, and V. M. Egorov, Sov. Tech. Phys. Lett. **10**, 253 (1985).
[19] N. N. Kolpakova, B. Brezina, and E. S. Sher, Jpn. J. Appl. Phys., Suppl. **24-2**, 823, (1985).
[20] G. A. Smolensky, N. N. Kolpakova, S. A. Kizhaev, and E. S. Sher, Ferroelectrics **73**, 161 (1987).
[21] W. N. Lawless, Phys. Rev. Lett. **36**, 478 (1976); Phys. Rev. B **14**, 134 (1976); **23**, 2421 (1981); **25**, 1730 (1982).
[22] M. C. Foote and A. C. Anderson, Ferroelectrics **62**, 11 (1985); R.

Villar, E. Gmelin, and H. Grimm, *ibid.* **69**, 165 (1986).
[23] W. N. Lawless, A. C. Anderson, and F. Walker, Ferroelectrics **37**, 627 (1981).
[24] D. A. Ackerman, D. Moy, R. C. Potter, A. C. Anderson, and W. N. Lawless, Phys. Rev. B **23**, 3886 (1981).
[25] For references, see E. Gmelin and G. Burns, Phys. Rev. B **38**, 442 (1988).
[26] For a review, see *Amorphous Solids: Low Temperature Properties*, edited by W. A. Phillips (Springer, Berlin, 1981); W. A. Phillips, Rep. Prog. Phys. **50**, 1657 (1987).
[27] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1, (1972); W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).
[28] L. Gil, M. A. Ramos, A. Bringer, and U. Buchenau, Phys. Rev. Lett. **70**, 182 (1993).
[29] J. J. De Yoreo, R. O. Pohl, and G. Burns, Phys. Rev. B **32**, 5780 (1985)
[30] G. Burns and F. H. Dacol, Phys. Rev. B **28**, 2527 (1983); Solid State Commun. **48**, 853 (1983).
[31] W. N. Lawless, Phys. Rev. B **19**, 3755 (1979).
[32] In the case of $Cd_2Nb_2O_7$, C_p data below 4 K were excluded in the following review article; W. N. Lawless, Ferroelectrics **43**, 223 (1982).
[33] A. Meldrum, C. W. White, V. Keppens, L. A. Boatner, and R. C. Ewing, Phys. Rev. B **63**, 104109 (2001).
[34] N. N. Kolpakova, L. Bobrowicz, A. Pawlowski, and W. Nawrocik, Solid State Commun. **75**, 461 (1990); N. N. Kolpakova, A. Pietraszko, S. Waplak, and L. Szczepanska, *ibid.* **79**, 707 (1991).
[35] K. Lukaszewicz, A. Pietraszko, J. Stepien-Damm, and N. N. Kolpakova, Mater. Res. Bull. **29**, 987 (1994).
[36] T. Atake, K. Nomoto, B. K. Chaudhuri, and H. Chihara, J. Chem. Thermodyn. **15**, 383 (1983).
[37] T. Atake, K. Nomoto, B. K. Chaudhuri, and H. Chihara, J. Chem. Thermodyn. **15**, 339 (1983).
[38] K. Hamano, Y. Ikeda, T. Fujimoto, K. Ema, and S. Hirotsu, J. Phys. Soc. Jpn. **49**, 2278 (1980).
[39] K. Nomoto, T. Atake, B. K. Chaudhuri, and H. Chihara, J. Phys. Soc. Jpn. **52**, 3475 (1983).
[40] Z. Y. Chen, Phys. Rev. B **41**, 9516 (1990).
[41] H. Haga, A. Onodera, Y. Shiozaki, K. Ema, and H. Sakata, J. Phys. Soc. Jpn. **64**, 822 (1995); H. Haga, R. Nozaki, Y. Shiozaki, and K. Ema, *ibid.* **64**, 4258 (1995).
[42] H. Z. Cummins, Phys. Rep. **185**, 211 (1990).
[43] D. Viehland, S. J. Jang, L. E. Cross, and M. Wuttig, Phys. Rev. B **46**, 8003 (1992).
[44] Broad C_p anomalies are observed in, e.g., spin glasses; K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).
[45] S. Wakimoto, C. Stock, Z.-G. Ye, W. Chen, P. M. Gehring, and G. Shirane, Phys. Rev. B **66**, 224102 (2002).
[46] D. Viehland, X. H. Dai, J. F. Li, and Z. Xu, J. Appl. Phys. **84**, 458 (1998).
[47] C. A. Randall, S. A. Markgraf, A. S. Bhalla, and K. Baba-Kishi, Phys. Rev. B **40**, 413 (1989).