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2004 J. Phys.: Condens. Matter 16 8981

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Specific heat of cubic relaxor ferroelectrics

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Received 23 September 2004, in final form 23 September 2004

Published 26 November 2004

Online at stacks.iop.org/JPhysCM/16/8981

doi:10.1088/0953-8984/16/49/013

Abstract

The specific heat has been measured for the relaxor ferroelectrics $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ and the low-dielectric-constant material $\text{BaMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ over a temperature range of 2–420 K. The behaviours of the specific heat for $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ and $\text{BaMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ crystals have been qualitatively compared. A large excess of specific heat of $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ over that of $\text{BaMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ has been revealed. The behaviour of the low-temperature specific heat of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ has been analysed in the frameworks of the shell model, Debye model, Einstein oscillator, two-level systems approach, and fractal approach. The excess of the specific heat of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ over the harmonic phonon contribution has been estimated, and its possible origin is discussed.

1. Introduction

In recent years, considerable attention has been paid to studies of the influence of disordering on lattice dynamics and, hence, on thermodynamic properties of ferroelectric crystals. The low-temperature region is of primary importance in the case of ferroelectrics and related materials since it is populated mostly by low-energy modes which are, as a rule, responsible for phase transitions in these crystals [1]. It has been found for such ferroelectric crystals as BaTiO_3 , $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, triglycine sulfate, and some others that the behaviour of the specific heat C_p obeys the Debye law T^3 dependence predicted for crystals at sufficiently low temperatures.

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In some ferroelectrics, such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$, $\text{PbMn}_{1/2}\text{Ta}_{1/2}\text{O}_3$, $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$, and others, anomalous properties typical of glass-like systems have been revealed. In particular, the low-temperature specific heat has been found to considerably exceed the specific heat predicted by the Debye T^3 dependence [2–14]. Since the materials mentioned above have different structural motifs, no model adequately explaining the anomalous behaviour of the specific heat at low temperatures even qualitatively has been suggested so far.

In this connection, of particular interest is the investigation of crystals having the same structural motif, such as complex perovskites with the common formula $\text{AB}'_x\text{B}''_{1-x}\text{O}_3$ (where A and B are metal ions), whose thermodynamic properties have been intensively studied [4, 9, 13–22]. It was shown that there is an excess contribution to the specific heat of relaxor ferroelectrics $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ in the regions of dielectric anomalies at high temperatures [19]. At low temperatures, a specific heat of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ in excess of the Debye term was revealed [17, 18], in agreement with previous studies [4, 13]. This additional contribution cannot be described by an Einstein term or a two-level systems term (TLS) satisfactorily [17, 18]. To account for this excess specific heat, the fracton approach was used in [17, 18]. However, it is well known that the specific heat for a number of crystals does not obey the predictions of the Debye model approach [23]. This may just reflect the fact that the vibration spectra of real materials are more complicated than the assumptions of the Debye model [23–26].

Studies of complex perovskites frequently employ $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$, $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$, and $\text{BaMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ as model objects [27]. Crystals of this family are characterized by a chemical disordering arising due to the presence of ions of unlike valencies in the B sublattice. The PMN crystal is a relaxor ferroelectric whose dielectric permeability maximum is observed at $T_m \sim 270$ K at frequency $f = 10$ kHz [27]. PMN has the $Pm\bar{3}m$ symmetry though displacements of ions from centrosymmetric sites of a simple cubic cell already occur at fairly high temperatures [28]. The PMT crystal is a well known relaxor ferroelectric with a temperature of the dielectric permeability maximum of $T_m \sim 170$ K at $f = 10$ kHz [27]. Neutron scattering data point to the displacement of lead ions from centrosymmetric sites of the cubic cell of the PMT crystal [29]. A highly important difference between PMN and PMT crystals is their differing behaviours in an applied electric field. The PMN crystal experiences a structural phase transition at $T_c \sim 210$ K [30], while the PMT crystal preserves a cubic symmetry over the entire ranges of temperatures and applied electric fields studied [31, 32]. The BMT crystal is a material with a low dielectric permeability [33] and does not exhibit any structural instability [34–36].

Thus, investigation of the behaviours of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$, $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$, and $\text{BaMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ and comparison of the low-frequency properties of these materials having the same structural motif but fundamentally different dielectric properties can give valuable information about low-frequency lattice dynamics of relaxor ferroelectrics at low temperatures in the presence of chemical disordering. This paper presents results of calorimetric studies and model calculations for PMN, PMT, and BMT crystals.

2. Experimental details and results

Measurements of the specific heat were carried out on ceramic and single-crystal samples. Details of the sample preparation can be found elsewhere [17–19]. Precise specific heat measurements between 13 and 420 K were made using a homemade adiabatic calorimeter [37, 38]. The specific heat between 2 and 50 K was measured by a relaxation method using a PPMS (Quantum Design Inc.). The results obtained by the two methods were found to be in good agreement.

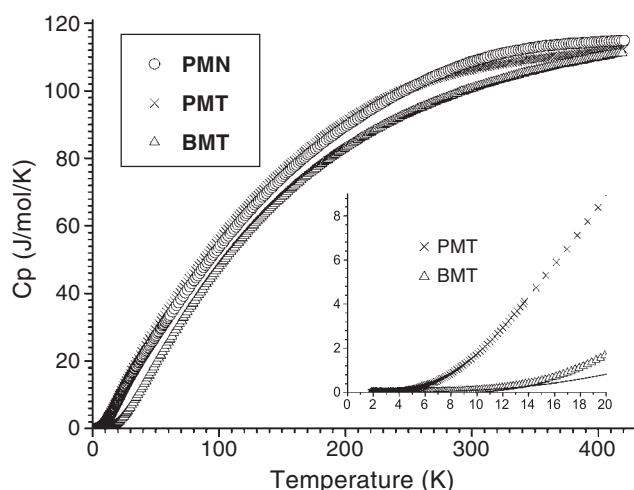


Figure 1. The specific heat for PMN, PMT, and BMT crystals. Symbols show the experimental data. The full curve in the inset is the Debye approximation of C_p for BMT crystal with $\Theta_D = 265$ K. Note that the difference between the specific heat of PMT and that of BMT tends to disappear at high temperature.

The measured specific heat in the range 2–420 K is shown in figure 1. It is readily seen that there is no pronounced anomaly of C_p in the vicinity of the temperatures where dielectric susceptibilities of PMN and PMT peak, consistently with earlier data [13, 17–19]. The behaviours of C_p for PMN and PMT are seen to be very similar to each other. Up to about 260 K, the specific heat of PMT exceeds that of PMN by less than 3%; at elevated temperatures, the specific heat of PMN becomes somewhat larger than that of PMT. As pointed out in [19], the behaviour of the specific heat in PMN and PMT in this temperature range can be due to the formation of a polar short-range order in these crystals. The specific heat of BMT behaves quite differently from C_p for PMN and PMT. Starting from $T \sim 30$ K and up to $T \sim 300$ K, C_p for BMT is lower by $\sim 8 \text{ J K}^{-1} \text{ mol}^{-1}$ than those for PMN and PMT. Such a drastic difference cannot be attributed just to the mass effects due to the different masses of Pb/Ba or Nb/Ta ions. An even more pronounced difference is observed at lower temperatures. The inset to figure 1 shows the behaviour of the specific heat of PMT and BMT crystals at $T < 20$ K. It is clear that C_p for PMT exceeds that for BMT by a factor of ~ 6 at $T = 20$ K.

It is possible to approximate the temperature dependence of C_p for BMT by the Debye function C_D with three degrees of freedom, with $\Theta_D = 265$ K at $T < 16$ K (the solid curve in the inset to figure 1). At higher temperatures, the experimental C_p for BMT increases more rapidly than the approximation using C_D . Formally, addition of the Einstein oscillator resolves this discrepancy and allows one to describe the experimental data. Therefore, in spite of chemical disordering of the B sublattice, the low-temperature specific heat of the BMT crystal does not exhibit any anomalies. Note that attempts to describe the behaviour of C_p of PMT using C_D failed even for such low temperatures. That is why one may conclude that there is some excess specific heat in the relaxor material PMT with respect to the low dielectric constant material BMT. A pronounced difference between C_p for PMT and that for BMT can be attributed to a higher density of vibration states at low energies of the PMT crystal compared to BMT. Indeed, the increase in density of states with decreasing temperature was observed for PMT and PMN crystals, while in BMT the density of states is constant for varying temperature within the experimental accuracy [34, 36].

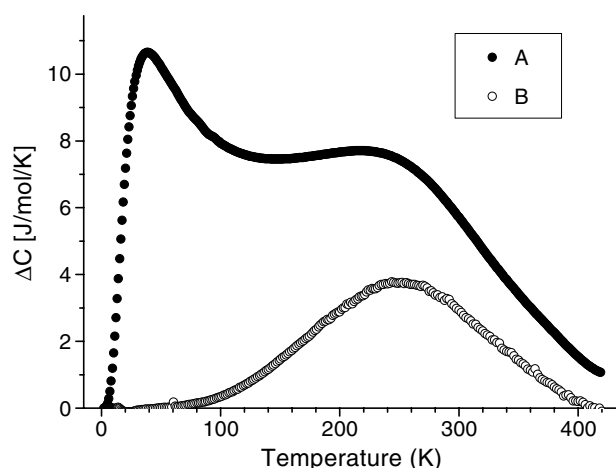


Figure 2. The behaviour of the excess specific heat ΔC for PMT crystal. Curve (A) holds for the excess specific heat of PMT with respect to BMT (see the text). Curve (B) denotes the anomalous specific heat inferred in [19].

The method used to estimate the additional contributions (besides the phonon ones) to the specific heat for the compounds containing magnetic ions involves subtraction of the specific heat of the compound without magnetic properties from that of the compound demonstrating magnetic properties (see, e.g., [39] and references therein). Since both PMT and BMT are cubic perovskites, they should contain equal numbers of phonon dispersion branches. So far, investigations of the BMT crystal by means of dielectric techniques [33, 35], light scattering [35, 40], neutron scattering [29, 34, 36], and adiabatic calorimetry have not revealed any ferroelectric properties and anomalies in the lattice dynamics. Thus, estimation of the excess specific heat of the PMT crystal relative to that of BMT can prove useful.

Figure 2 shows the behaviour of the difference $\Delta C \equiv C_p(\text{PMT}) - C_p(\text{BMT})$ in the temperature range studied. It is readily seen that the excess of the specific heat ΔC for PMT relative to that for BMT has a tendency to vanish at low (~ 3 K) and high temperatures (~ 420 K) and exhibits two anomalies with maxima at $T \sim 40$ and ~ 230 K. The high-temperature anomaly qualitatively corresponds to the excess specific heat for PMT obtained in [19] in the framework of a different approach. Since its temperature position approximately corresponds to the dielectric permeability peak, it is natural to suppose that the high-temperature anomaly is associated with the appearance of the short-range ferroelectric order in PMT [19]. Of interest is the high ΔC in the vicinity of both maxima: $\Delta C \sim 10.6 \text{ J mol}^{-1} \text{ K}^{-1}$ at $T \sim 39$ K and $\Delta C \sim 7.7 \text{ J mol}^{-1} \text{ K}^{-1}$ at $T \sim 217$ K. Note, for comparison, that the specific heat of the LaAlO_3 crystal at $T \sim 40$ K is $\sim 6.1 \text{ J mol}^{-1} \text{ K}^{-1}$ [41], and the specific heat of SrF_2 at $T \sim 40$ is $\sim 7.6 \text{ J mol}^{-1} \text{ K}^{-1}$ [42], while the specific heat of the cubic perovskite KZnF_3 at $T \sim 40$ is $\sim 16.6 \text{ J mol}^{-1} \text{ K}^{-1}$ [43], which is only 35% more than the excess of the specific heat of PMT over that of BMT at the same temperature.

Since C_p for PMN and that for PMT at low temperatures are close to each other (see figure 1), it is evident that the PMN crystal has an excess specific heat not only relative to the Debye contribution but also relative to the specific heat of the complex perovskite BMT. Unfortunately, there is a lack of data on the dispersion curves of phonons for PMT and BMT crystals. Therefore, we cannot analyse quantitatively the observed difference in value of C_p of PMT and BMT crystals. Below we analyse the behaviour of the specific heat in the relaxor

ferroelectric PMN for which there is some information on the dispersion of the phonons. Note that the thermodynamic behaviours of PMN and PMT are similar.

3. Excess specific heat in PMN

3.1. Different approaches to describing specific heat

Considerable attention has been paid to dynamic properties of PMN relaxor ferroelectric [44–47], and a simple model for lattice dynamics calculations for PMN was proposed [48]. It is worth considering different approaches to the description of the excess specific heat of PMN at low temperatures using the model of [48] to account for the phonon contribution to the specific heat of PMN. The basic models used in analysis of the temperature dependence of the specific heat of PMN at low temperatures are as follows.

The Debye model. In the case of the interpolation Debye scheme, only acoustic branches of the vibrational spectrum of a crystal are taken into consideration, and it is assumed that all of them are characterized by the same sound velocity. Then the Brillouin zone of the crystal is approximated by a sphere of the same volume in an inverse space [49, 50]. Under these assumptions, the formula for calculation of the specific heat acquires the form

$$C_D = 9R \left(\frac{T}{\Theta_D} \right)^3 \int_0^{E_D/k_B T} \frac{e^x x^4}{(e^x - 1)^2} dx \quad (1)$$

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant, k_B is Boltzmann's constant, Θ_D is the Debye temperature, and $E_D = k_B \Theta_D$ is the corresponding Debye energy. It is evident that if the Debye temperature is known from independent acoustic measurements (ultrasonic or Brillouin), expression (1) can be used to estimate the contribution of acoustic phonons to the specific heat of the crystal. In this paper we consider the specific heat at constant volume C_V in the low-temperature region. Since in this case the difference between C_V and C_P is small, we omit the subscript for C in the ensuing discussion.

The Einstein model. In the Einstein model [50–52] it is assumed that every atom vibrates similarly to a harmonic oscillator in a potential well formed by the forces of its interaction with the neighbours. The spectrum of a crystal consists of levels located at distance $\hbar\omega_E$ from each other. The contribution of the Einstein oscillator to the specific heat is given by

$$C_E = 3R \left(\frac{\hbar\omega_E}{kT} \right)^2 \frac{\exp\left(\frac{\hbar\omega_E}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega_E}{k_B T}\right) - 1\right)^2} \quad (2)$$

where $\omega_E = 2\pi\nu_E$ is the characteristic frequency of a corresponding oscillator. The Einstein model is rather well suited for taking into account the contribution of optical phonons to the specific heat [50]. Under certain conditions, local oscillations of a point defect are also well approximated by an Einstein oscillator [52–54].

The specific heat of a harmonic crystal. In the case where the phonon spectrum of a crystal is known, the specific heat in the harmonic approximation is given by [23, 50, 52]

$$C_H = R \frac{1}{N} \sum_{n,k} \left[\frac{\beta_{nk}}{2 \sinh(\beta_{nk})} \right]^2, \quad \beta_{nk} = \frac{\hbar\omega_n(\mathbf{k})}{2k_B T} \quad (3)$$

where N is the total number of atoms, and $\omega_n(\mathbf{k})$ denotes the phonon dispersion curve; other symbols have the same meaning as above. The subscript 'H' in equation (3) indicates

that calculations of phonon dispersion curves for the PMN crystal within the harmonic approximation [48] involved the use of the shell model [55].

The two-level-system model. The commonly accepted method of description of the low-temperature behaviour of the specific heat of canonical glasses and also of a number of related disordered systems is the two-level-system (TLS) formalism [56, 57]. In this case, at low temperatures (most often at $T < 1.5$ K), a linear dependence of the specific heat on temperature is predicted, i.e.,

$$C_{\text{TLS}} = BT, \quad (4)$$

where B is the normalizing parameter that depends on the density of states of the TLS. It should be noted that this approach to the description of specific heat is often successfully used for higher temperatures.

The fracton model. To describe the behaviour of such disordered condensed media as aerogels, the fractal approach is efficiently used [58, 59]. It assumes the self-similarity of an object on a definite scale of lengths [60]. In fractal structures, vibrational excitations, i.e., fractons, whose dispersion law differs from that of phonons can be realized. The density of vibrational states of fractons is characterized by a spectral (fracton) dimension \tilde{d} [59]: $G(\omega) \propto \omega^{\tilde{d}-1}$. There is a crossover frequency ω_{co} . At $\omega \ll \omega_{\text{co}}$, the Debye law characterizing the density of states of acoustic modes is fulfilled: $G(\omega) \propto \omega^2$. Under these assumptions, the specific heat of a disordered material can be written as [58]

$$C_{\text{fr}} = 9R \left(\frac{T}{\Theta_{\text{D}}} \right)^3 \int_0^{E_{\text{co}}/k_{\text{B}}T} \frac{e^x x^4}{(e^x - 1)^2} dx + AT^{\tilde{d}} \int_{E_{\text{co}}/k_{\text{B}}T}^{E_{\text{m}}/k_{\text{B}}T} \frac{e^x x^{\tilde{d}+1}}{(e^x - 1)^2} dx \quad (5)$$

where $E_{\text{co}} = \hbar\omega_{\text{co}}$ is the energy at which the Debye regime changes to the fracton one (crossover energy), $E_{\text{m}} = \hbar\omega_{\text{m}}$ is the maximum energy at which the fracton regime is realized. The first term in expression (5) is the contribution of acoustic vibrations to the specific heat of a disordered object. Equation (5) was used in [17, 18] to describe the specific heat of the PMN crystal at $T < 30$ K. The phonon contribution to the specific heat of PMN was estimated by using the Debye temperature $\Theta_{\text{D}} = 376$ K obtained from low-temperature acoustic measurements [61].

In this work we estimate the phonon contribution to the specific heat of PMN through equation (3) by using parametrization of the phonon spectrum of PMN taken from [48]. Then the expression for the fracton contribution to the specific heat acquires the form

$$C = R \frac{1}{N} \sum_{n,k} \left[\frac{\beta_{nk}}{2 \sinh(\beta_{nk})} \right]^2 + AT^{\tilde{d}} \int_{E_{\text{co}}/k_{\text{B}}T}^{E_{\text{m}}/k_{\text{B}}T} \frac{e^x x^{\tilde{d}+1}}{(e^x - 1)^2} dx \equiv C_{\text{H}} + C_{\text{fr}}, \quad (6)$$

and the possible contribution of two-level systems to the specific heat can be estimated in this approach as a sum $C_{\text{H}} + C_{\text{TLS}}$ (equation (3) + equation (4)), etc. Direct summation of contributions of different origins to the total specific heat of a crystal is justified if the contributions to the free energy corresponding to them are additive (see, e.g., [62]). Since harmonic phonons belong to vibrational degrees of freedom resulting from the long-range order in crystals, and the other contributions discussed above (with the exception of the Debye one) are determined by either local properties or short-range order, the approach that we use can be regarded as satisfactory.

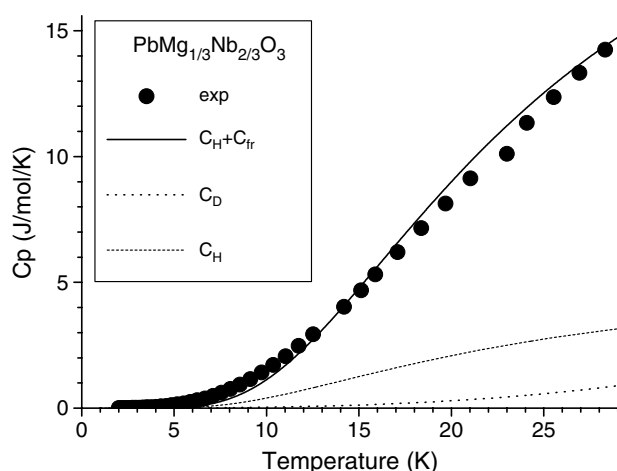


Figure 3. The specific heat of PMN crystal at low temperatures. Symbols show the experimental data. The dotted curve is the Debye approximation C_D , the dashed curve is C_H from formula (3), and the full curve is the specific heat fitted with the formula (6).

3.2. Results of model calculations and their comparison with experiment

To calculate the phonon contribution to the specific heat of PMN, the shell model of a classic perovskite with a virtual ion in the B sublattice having the mass $m_{MN} = (1/3)m_{Mg} + (2/3)m_{Nb}$ was used [48]. This model reproduces satisfactorily dispersion curves of acoustic and low-frequency optical phonons [45]. Therefore, it can be expected at low temperatures to describe well the contribution of harmonic phonons to the specific heat of PMN. Unfortunately, difficulties are encountered in description of the high-frequency dispersion curves for PMN because of problems in interpretation of experimental data [45] and imperfection of the model [48]. For this reason, it is impossible to compare the experimental specific heat and its calculated values C_H at higher temperatures, when the contribution of high-frequency optical phonons becomes significant. To calculate C_H , the software LADY for lattice dynamics simulation was used [63].

Figures 3 and 4 show the measured specific heat and results of approximation of the $C(T)$ dependence by the least-squares method in the framework of all the models discussed above and their combination for PMN at $T < 30$ K. It is readily seen that the Debye contribution to the specific heat of PMN is negligibly small as compared with the experimental value and is much lower than C_H . In particular, at $T = 25$ K the C_D/C_H ratio is equal to 0.1, which confirms the conclusion [26] that it is difficult to infer the presence of anomalous excess specific heat from consideration of the behaviour of the specific heat through the Debye expression (equation (1)).

As can be seen from figure 3, at $T = 25$ K $C_H/C_{exp} = 0.2$. At the same time, at low temperatures the values of C_H calculated for PMN and C_{exp} for BMT become close to each other: at $T = 20$ K $C_H = 2 \text{ J mol}^{-1} \text{ K}^{-1}$, and $C_{exp}(\text{BMT}) = 1.7 \text{ J mol}^{-1} \text{ K}^{-1}$. This means that the experimental specific heat of the complex perovskite BMT is close to the calculated specific heat of a classic cubic perovskite.

The Einstein oscillator with frequency $\nu_E = 1.8 \text{ THz} = 60 \text{ cm}^{-1}$ allows one to take into consideration the contribution to the specific heat of PMN additional to C_H only at $T > 17$ K (we recall that $1 \text{ meV} = 0.24 \text{ THz} = 8.06 \text{ cm}^{-1}$). At lower temperatures, the contribution of C_{EIN} decreases much faster than the experimental specific heat. Such a behaviour of C_{EIN} was

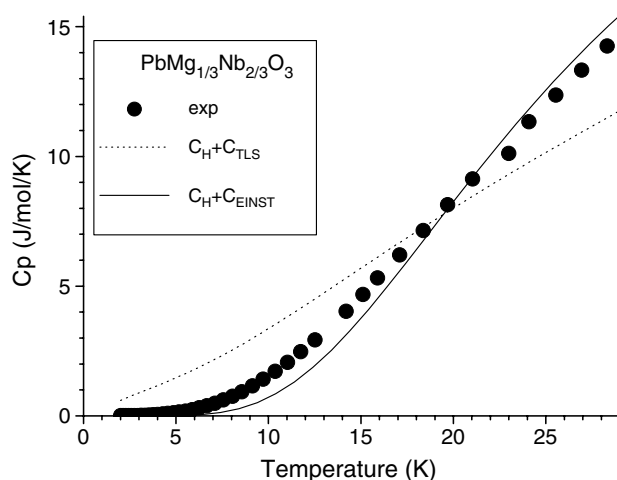


Figure 4. The specific heat of PMN crystal at low temperatures. Symbols show the experimental data. The full curve corresponds to the fit of Einstein oscillator contribution to the difference between the experimental specific heat and C_H . The dotted curve holds for the sum of C_H and the best fit of the TLS contribution with the formula (4).

also revealed in [17, 18] when the contribution of the acoustic phonons to the specific heat of PMN was described by using C_D (equation (1)). Thus, introduction of the Einstein oscillator cannot explain the observed behaviour of the specific heat in PMN at low temperatures as well. This is not surprising because at low temperatures C_{EIN} often decreases faster than the corresponding experimental data [23, 50].

The behaviour of the excess specific heat in PMN can be described in the framework of the fractal approach much better (compare figures 3 and 4). The calculated specific heat does not describe experimental results only at $T < 5$ K. The solid curves in figure 3 obtained at a fixed $E_m = 7.2$ meV correspond to the following parameters of the fractal model: $A = 0.054$, $\tilde{d} = 1.6$, $E_{co} = 5.1$ meV. These parameters are in good agreement with those obtained from inelastic neutron scattering data at $T = 50$ K [17, 18]: $E_{co} = 5$ meV, $E_m = 7$ meV, and $\tilde{d} = 1.7$. Note that the results of approximation through equation (6) are very close to the parameters obtained in [17, 18] where C_D was used to take into account the phonon contribution to the specific heat of PMN. An important difference between the results of these and earlier calculations [17, 18] is in the behaviour of the approximation function with free parameter E_m . Earlier [17, 18], the approximation with free parameter E_m made the agreement between the model and experiment much better. Now, when we use equation (6), the improvement is minor, and the model does not describe the data at $2 \text{ K} < T < 5 \text{ K}$ satisfactorily. One of the possible reasons for such a discrepancy between experimental and calculated data is the presence of another, additional contribution to the specific heat of PMN [4, 64].

4. Conclusion

A comparative analysis of the specific heat for the complex perovskites $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$, $\text{PbMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$, and $\text{BaMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ exhibiting different dielectric properties has shown that in the low-temperature region the excess specific heat is not a direct consequence of disordering of the B sublattice. Excess specific heat at low temperatures has been revealed in PMN and PMT crystals where lead ions are displaced from ideal sites of the perovskite cell.

Calculations for the PMN crystal in the framework of the shell model have shown that a simple approximation by a cubic lattice with a virtual ion yields a specific heat comparable with that of the low dielectric constant BMT crystal at low temperatures.

The use of different model approximations for description of the excess specific heat of PMN at low temperatures has shown that the best approximation of the experimental dependence is achieved in the framework of the fractal approach.

Analysis of calculations and experimental data obtained by complementary techniques (inelastic neutron scattering and experimental studies of the specific heat) has revealed, with a high reliability, the existence of an additional low-frequency excitation in the vibrational spectrum of the PMN crystal.

Acknowledgment

The work was supported in part by the RFBR grant No 02-02-17678.

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