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Structural phase transitions of a successive type and the two-dimensional nature of the antiferromagnetic ordering in La_2NiO_4 single crystal

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Abstract. The heat capacities of a single crystal of the stoichiometric compound La_2NiO_4 were measured over the temperature range 14–500 K with an adiabatic calorimeter. Three heat capacity anomalies were observed. The two anomalies taking place at around 80 K and 150 K were interpreted as being due to first-order and second-order structural phase transitions, respectively, potentially of the locked-in-commensurate–incommensurate–normal-commensurate type. The third anomaly at 330 K was indicated to be a three-dimensional antiferromagnetic phase transition found commonly in two-dimensional antiferromagnets of the K_2NiF_4 type. The two-dimensional antiferromagnetic short-range order is discussed on the basis of the magnetic contribution to the heat capacity curve on the high-temperature side of the transition temperature.

1. Introduction

Since the discovery of superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ crystal by Bednorz and Müller [1], the crystal structure of La_2CuO_4 as its prototype compound has been of interest to many research groups. In view of the facts that the substitutions for the cations with different ions produce different crystal structures [2, 3] and that a structural phase transition changes the superconducting properties appreciably at lower temperatures [2–4], it appears quite important to examine what kinds of structural variation are permissible and how the electronic/magnetic properties appear in the two-dimensional layered perovskite compounds of La_2MO_4 (M: transition metals).

La_2NiO_4 crystal has the same structure, of K_2NiF_4 type with space group $I4/mmm$ at high temperatures, as La_2CuO_4 . While La_2CuO_4 crystal shows only a structural phase transition of second order from the $I4/mmm$ to the $Bmab$ phase at 530 K [5], La_2NiO_4 crystal is known to show a second-order structural phase transition from the $I4/mmm$ to the $Bmab$ phase at 650 K [6] and a first-order structural phase transition at around 80 K [6–12]. The two structural phase transitions have been considered as characterized by variations in the tilts of NiO_6 octahedra, and discussed on the basis of Landau theory [2]. The following two cases of successive phase transitions have been found by analysis by Axe *et al* [2] to

potentially occur:

$$\text{case 1: } P4_2/ncm \stackrel{(b)}{\leftrightarrow} Bmab \stackrel{(a)}{\leftrightarrow} I4/mmm$$

and

$$\text{case 2: } P4_2/ncm \stackrel{(a)}{\leftrightarrow} Pccn \stackrel{(a)}{\leftrightarrow} Bmab \stackrel{(a)}{\leftrightarrow} I4/mmm$$

where (a) and (b) denote that the two space groups relevant to each phase transition are and are not connected, respectively, by a relation between the group and subgroup with respect to their symmetry elements. The $Bmab$ – $P4_2/ncm$ transition should be of first order because the two space groups are not linked by the group–subgroup relation, but all of the other transitions could be of second order. For the low-temperature phase below 80 K, there have been two different space groups proposed. Rodríguez-Carvajal *et al* [6] found the space group of the low-temperature phase to be $P4_2/ncm$ by refinement, and the conclusions of many research groups are in agreement with this refinement result [7–9]. However, it was noted by Lander *et al* [11] that the space group $Pccn$ could not be discarded because it gave the same results as $P4_2/ncm$ within the experimental error, while they did not observe any splitting of the reflections due to the orthorhombic structure. On the other hand, Hayashi *et al* [12] have clearly observed in the low-temperature phase the splitting of the reflections (133) and (313) based on the orthorhombic structure. The proposal of different structures would indicate that some complex process proceeds in the phase transition at 80 K, and considering that a similar transition has been reported to occur in cation-substituted La_2CuO_4 crystal [2, 3], the appearance of the transition needs to be examined through different properties.

La_2CuO_4 and La_2NiO_4 crystals are antiferromagnets at room temperature. The magnetic properties are expected, from the layered perovskite structure, to show a two-dimensional character. The two-dimensional antiferromagnetic properties have been studied in detail for K_2NiF_4 crystals [13–16]. Neutron diffraction experiments [13, 14] have disclosed that a three-dimensional antiferromagnetic phase transition occurs at around 97 K and is accompanied by two-dimensional critical scattering, and that the in-plane antiferromagnetic order remains up to rather high temperatures. The heat capacity curve [15, 16] showed a small peak at the transition temperature 97 K and a broad hump rather on the high-temperature side, as is consistent with the results of the above neutron diffraction experiments [13, 14]. The magnetic properties of La_2NiO_4 crystal have been studied by many research groups [6, 11, 17]. Rodríguez-Carvajal *et al* [6] and Yamada *et al* [17] reported that the three-dimensional antiferromagnetic phase transition took place at 330 K and 325 K, respectively. However, it is still open to question how high a temperature the in-plane short-range order remains up to. The knowledge of the temperature dependence of the spin ordering over the whole temperature range in La_2NiO_4 crystal is important in order to clarify the electronic state, electric conductivity, and superconductivity of the La_2MO_4 crystal system, and is attractive also in comparison with the properties of K_2NiF_4 crystal. The magnetic properties of La_2CuO_4 crystal have been studied by Yamada *et al* [18] and found to show an antiferromagnetic phase transition at 298 K, and reported by Shirane *et al* [19] to exhibit no critical scattering at the transition temperature. The character is different from that of K_2NiF_4 . Furthermore, in view of the fact that, while the in-plane nearest-neighbour Cu–Cu exchange interaction, $J \sim 1300$ K [20], is much higher than that, $J \sim 340$ K, for the Ni–Ni interaction in the La_2NiO_4 system [21], three-dimensional antiferromagnetic phase transitions occur at almost the same temperature, there would appear to be some difference between the heat capacity curves of La_2NiO_4 and La_2CuO_4 crystals.

Recently Castro and Burriel [22] measured heat capacities of La_2NiO_4 powder crystal with adiabatic and ac calorimeters over the ranges 90–350 K and 20–100 K respectively, and observed the following three anomalies: a small peak at 328 K in the heat capacity curve; excess heat capacities over the whole range above 90 K; and a peak at 56 K. The first is due to the three-dimensional antiferromagnetic phase transition, the temperature of which is in reasonable agreement with the values reported by Rodríguez-Carvajal *et al* [6] and Yamada *et al* [17]. The second was indicated as being due to the magnetic contribution from Ni spins. However, the detailed behaviour of the magnetic contribution above 350 K and the similarity/dissimilarity of the magnetic properties to those of K_2NiF_4 or La_2CuO_4 crystals have remained open to question. The third anomaly was interpreted as being due to a first-order structural phase transition. This transition temperature is, however, much lower than the value of 80 K obtained previously by different methods [6–12], and the reason for the inconsistency has not been mentioned.

In the present study, the heat capacities of a La_2NiO_4 single crystal were remeasured with an adiabatic calorimeter over the temperature range 14–500 K to solve the above problems. It is found that the phase transition at 80 K proceeds in two steps, and the transition temperature is sensitive to the oxygen content probably because of the locking-in nature of the transition. Furthermore, the characters of the magnetic properties are found to be similar to those for K_2NiF_4 crystal.

2. Experiment

La_2NiO_4 single crystal was grown by the procedure described previously [23]. The amount of excess oxygen content, δ , was adjusted through high-temperature treatment under an atmosphere of controlled oxygen-gas pressure [24].

The heat capacities of the sample were measured over the temperature range 14–500 K by an intermittent-heating method with a high-precision adiabatic calorimeter [25]. The initial temperature, T_i , is rated for 12 min; some known quantity of electrical energy, ΔE , is supplied into a calorimeter cell loaded with the sample; and the final temperature, T_f , is rated for 12 min. The gross heat capacity of the cell is evaluated to be $\Delta E/(T_f - T_i)$ at $T_{\text{av}} = (T_f + T_i)/2$. The latter temperature rating serves as the former rating in the next set of heat capacity measurements.

The mass of La_2NiO_4 crystal used was 15.537 g (≈ 0.038794 mol). The imprecision and the inaccuracy of the measurements with the apparatus were estimated to be less than $\pm 0.04\%$ and $\pm 0.4\%$, respectively [25].

3. Results

Experimental molar heat capacities of La_2NiO_4 are shown graphically in figure 1. Three heat capacity anomalies were observed at around $T_2 = 80$ K, $T_1 = 150$ K, and $T_N = 330$ K, due to a first-order structural phase transition reported before [6–12], to a second-order phase transition, and to a three-dimensional antiferromagnetic phase transition, respectively. The anomaly at around 150 K was newly revealed in the present study, but a sign of the anomaly might be found as the kinks at around 150 K in the magnetization curve (A) in figure 5 of reference [17] and in the $\delta = 0$ curve in figure 4 of reference [26].

Lattice molar heat capacities at constant pressure, $C_{p,m}^{\text{lat}}$, as represented by a solid line in figure 1, were calculated in order to estimate the excess molar heat capacities due to the phase transitions. A dashed line in figure 1, representing the lattice molar heat capacity curve

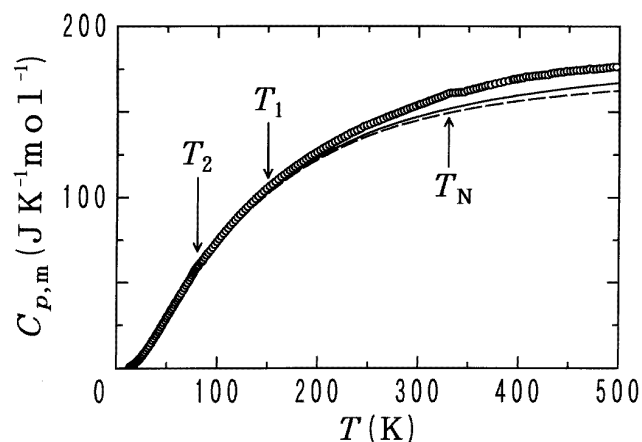


Figure 1. Experimental heat capacities of La_2NiO_4 crystal. Dashed and solid lines represent the calculated lattice heat capacities at constant volume and at constant pressure, respectively. See the text for details.

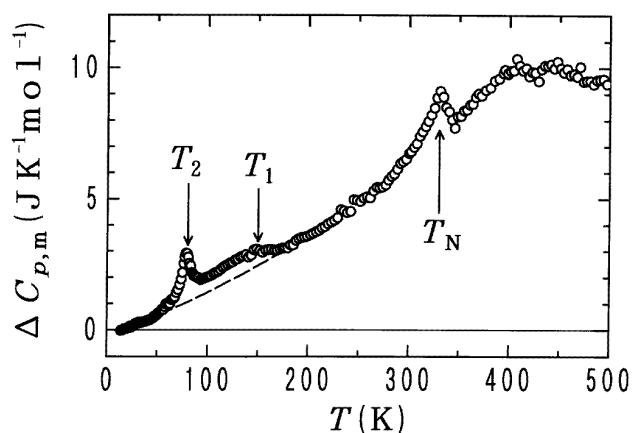


Figure 2. Excess heat capacities of La_2NiO_4 crystal as referred to the values of the solid line in figure 1. A dashed line represents the baseline of the contribution from the structural phase transitions at T_1 and T_2 . The baseline was drawn by smoothly linking the values in the ranges 14–40 K and 200–300 K.

at constant volume, $C_{v,m}^{\text{lat}}$, was first evaluated from the phonon density of states obtained by inelastic neutron scattering measurements and by analysis on the basis of a rigid-ion model [27], and a $C_{p,m}^{\text{lat}} - C_{v,m}^{\text{lat}}$ correction term was calculated according to the following equation:

$$C_{p,m}^{\text{lat}} - C_{v,m}^{\text{lat}} = A(C_{p,m}^{\text{lat}})^2 T. \quad (1)$$

Here the constant A was determined from the structural and other data at 300 K as follows.

The correction term can be estimated by using formally a thermodynamic relation:

$$C_{p,m}^{\text{lat}} - C_{v,m}^{\text{lat}} = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p = B V_m \alpha^2 T \quad (2)$$

where B , V_m and α are the bulk modulus, molar volume, and volume thermal expansion coefficient, respectively. The bulk modulus $B = 1.13 \times 10^{-5} \text{ J cm}^{-3}$ was taken from the result of Brill *et al* [28], and $V_m = 57.21 \text{ cm}^3 \text{ mol}^{-1}$ and $\alpha = 3.31 \times 10^{-5} \text{ K}^{-1}$ were calculated from the data on the temperature dependence of the unit-cell volume obtained by Hayashi *et al* [12]. $C_{v,m}^{\text{lat}}$ at 300 K was derived from the phonon density of states as mentioned above to be $C_{v,m}^{\text{lat}}(300 \text{ K}) = 145.16 \text{ J K}^{-1} \text{ mol}^{-1}$, and thus $C_{p,m}^{\text{lat}}$ at 300 K was evaluated to be

$$C_{p,m}^{\text{lat}}(300 \text{ K}) = 147.29 \text{ J K}^{-1} \text{ mol}^{-1}. \quad (3)$$

Substituting the evaluated values of $C_{p,m}^{\text{lat}}$ and $C_{v,m}^{\text{lat}}$ into equation (1) gave the result $A = 3.26 \times 10^{-7} \text{ J}^{-1} \text{ mol}$.

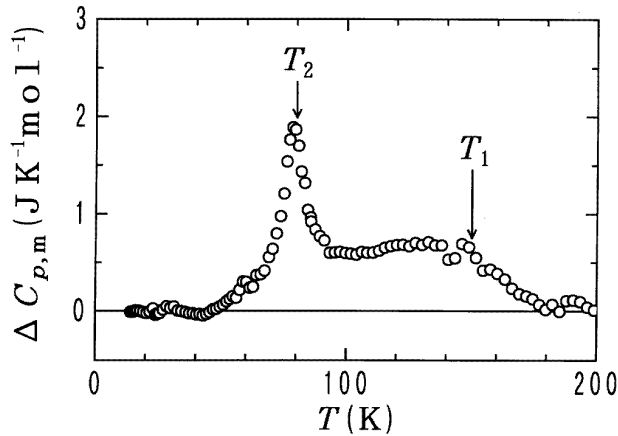


Figure 3. The heat capacities assessed as due to the structural phase transitions at T_1 and T_2 on an enlarged scale.

Figure 2 shows excess heat capacities of La_2NiO_4 crystal obtained by subtracting the solid-line values in figure 1 from the experimental heat capacities. A new heat capacity anomaly at around 150 K is clearly demonstrated to exist. A dashed line in the figure stands for a baseline, obtained by smoothly interpolating the values in the ranges 14–40 K and 200–300 K to the structural phase transitions at T_1 and T_2 . Figure 3 shows the excess heat capacities on an enlarged scale. The total entropy of the transitions was estimated to be $0.8 \text{ J K}^{-1} \text{ mol}^{-1}$, which was quite small, which is consistent with the fact that the transitions were of the displacive type. No appreciable spontaneous temperature drift nor sharp heat capacity peak were observed at around T_1 in the heat capacity measurements made during heating. The phase transition at T_1 was thus determined to be of second order.

Circles in figure 4 represent excess heat capacities, due mainly to the antiferromagnetic ordering of spins, for the normalization of the three-dimensional antiferromagnetic phase transition temperature, 330 K, on an enlarged scale. The transition point, determined as the temperature of the small heat capacity peak, was rather close to the literature values given

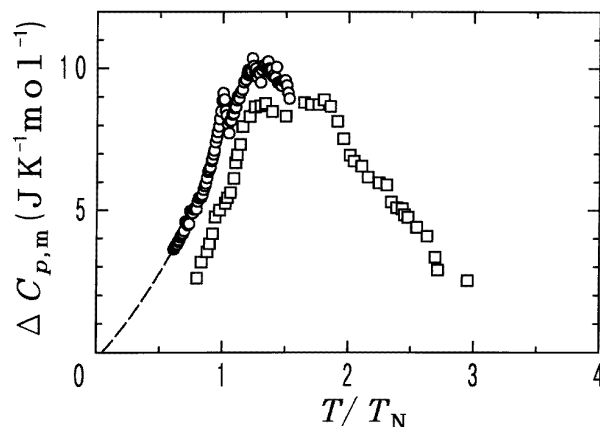


Figure 4. Excess heat capacities due to magnetic contributions: \circ , the present result; \square , the result for K_2NiF_4 obtained by Salamon and Ikeda [15].

by Rodríguez-Carvajal *et al* [6] and Yamada *et al* [17]. The heat capacity curve showed a wide tail on the low-temperature side of the transition, and is expected to exhibit a tail on the high-temperature side as well, while showing a hump a little above the transition temperature.

4. Discussion

4.1. Successive structural phase transitions at around 80 K and 150 K

First, let us number the phases in the order of decreasing temperature for clarity:

V ($T_2 = 80$ K) IV ($T_1 = 150$ K) III ($T_N = 330$ K) II ($T_{OT} = 650$ K) I.

The V–IV and IV–III phase transitions are interpreted as being due to variations in the tilts of NiO_6 octahedra as stated above. Each tilt can be characterized by displacements of apical oxygen atoms of NiO_6 octahedra [2, 3]. With the displacements of the apical oxygen atom along the $[110]$ and $[\bar{1}10]$ directions in the space group $I4/mmm$ designated by Q_1 and Q_2 , respectively, the magnitudes of Q_1 and Q_2 in each space group are given as follows and shown graphically in figure 5:

$$\begin{aligned}
 I4/mmm &: & |Q_1| &= |Q_2| = 0 \\
 Bmab &: & |Q_1| &\neq 0, |Q_2| = 0 \\
 P4_2/ncm &: & |Q_1| &= |Q_2| \neq 0 \\
 Pccn &: & |Q_1| &\neq |Q_2|, |Q_1| \neq 0, |Q_2| \neq 0.
 \end{aligned}$$

The heat capacity curve and the characters of the successive (V–IV and IV–III) phase transitions, as shown in figure 3, are quite similar to those of a type of locked-in-commensurate–incommensurate–normal-commensurate phase sequence [29–33]. The first transition is known to have a first-order character, showing the mixed phases at around T_2 [7–9, 12] and a relatively sharp heat capacity peak. The second transition, on the other hand, showed a heat capacity anomaly of second-order type as described above. Such

types of anomaly have been found in some systems such as Rb_2ZnCl_4 [29, 30], thiophene [31, 32] and chlorocyclohexane [33]. In most of the systems, a remarkable impurity-doping effect has been observed with respect to the locked-in-commensurate–incommensurate phase transition; namely, the heat capacity anomaly due to the transition broadens and then disappears with doping with a small amount of impurity. The reason for this is that a number of different configurational structures are allowed as the incommensurately modulated states, but with only a little difference between their energies, and thus different structures can be pinned easily by the presence of impurities. It is anticipated for the same reason that point defects will show the same effect. On the other hand, there is usually no remarkable impurity-doping effect observed with respect to the incommensurate–normal-commensurate phase transition.

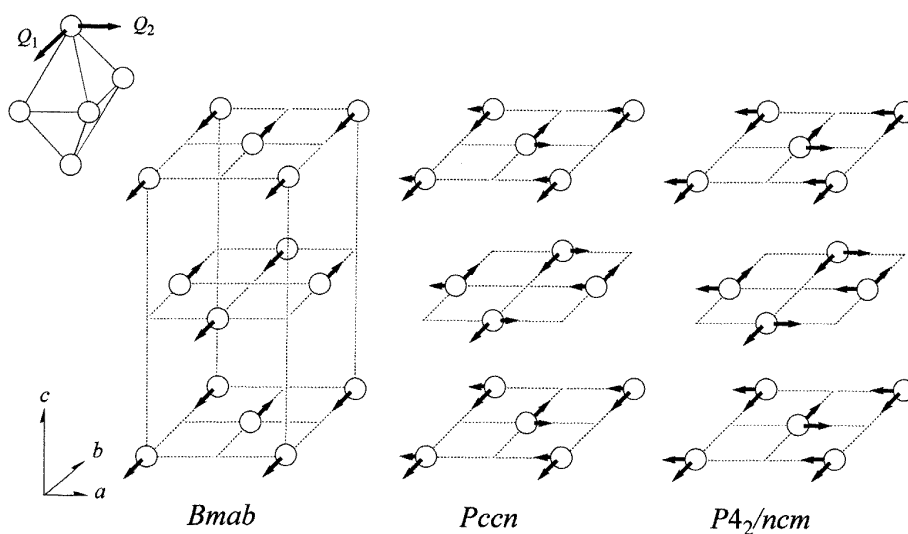


Figure 5. Arrangements of tilts of NiO_6 octahedra represented by the displacements of apical oxygen atoms in different structural modifications, as viewed along the c -axis. The magnitudes of the displacements along the a - and b -axes, $|Q_1|$ and $|Q_2|$, are different from and equal to each other for the space groups $Pccn$ and $P4_2/nm$, respectively.

Closed circles in figure 6 show excess heat capacities obtained by subtracting the solid-line values in figure 1 from the data of Castro and Burriel [22]. It is found that the anomaly at around 150 K clearly exists in their result as well as in our result. It should be noticed that the temperatures T_N and T_1 are the same as in our results, but that the temperature T_2 is lowered to 56 K for their sample. Considering that preparation of stoichiometric samples is difficult, it is possible that the oxygen nonstoichiometries of Castro and Burriel's samples were different to those of our samples. In view of the fact that T_N is sensitive to oxygen nonstoichiometry [26], the oxygen contents must be almost same for the two samples. However, the fact that the temperatures T_2 are rather different from each other potentially indicates that there might have been a very slight difference between the oxygen contents and/or the homogeneities of the two samples. This is just a characteristic of the locked-in-commensurate–incommensurate phase transition as stated above. Therefore the interpretation that the successive (V–IV and IV–III) phase transitions are to be classified as being of the type having the locked-in-superstructural-commensurate–incommensurate–

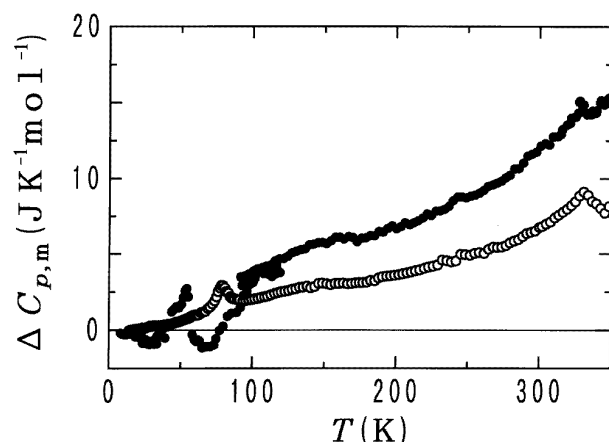


Figure 6. Excess heat capacities obtained by subtracting the solid-line values of figure 1 from the experimental data: ○: the present result; ●: the result obtained by Castro and Burriel [22].

normal-commensurate phase sequence appears reasonable at present. It is noted that a similar incommensurate phase has been observed for a compound, $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{MnCl}_4$, with the same K_2NiF_4 -type structure at high temperatures [34].

In view of the facts that the IV–III phase transition is of second order and that the space group of phase III is $Bmab$ [6], the only possible choice of the space group for phase IV is $Pccn$, a subgroup of $Bmab$ with respect to the symmetry elements. There are two possibilities for the space group of phase V: $Pccn$ and $P4_2/nm$. A conclusive choice is difficult on the basis of just the present data, but from the consideration of the following structural results, the phase V is rather likely to be in the space group $Pccn$. Though Lander *et al* [11] suggested $P4_2/nm$ for the space group because there was no observation of orthorhombic splitting, they did not discard the possibility of $Pccn$. Hayashi *et al* [12] definitely observed orthorhombic splitting, and indicated that the space group is $Pccn$ —being orthorhombic—rather than $P4_2/nm$ —being tetragonal. Then the following sequence of successive space groups is indicated for La_2NiO_4 :

locked-in superstructural, $Pccn$ (T_2) IC, $Pccn$ (T_1) $Bmab$

(where IC = incommensurate).

In passing, it is noted that the absolute values of the heat capacities obtained by Castro and Burriel are larger by 3–4% than the present ones. The reason for this is considered to be as follows. When the heat capacities of as-prepared samples were measured during heating, a heat evolution effect was observed above room temperature. Then the sample was annealed at around 400 K within the calorimeter until the effect disappeared. The heat capacity values obtained after the annealing were smaller than those obtained before the annealing. The heat evolution should not be thought to originate from absorption of oxygen, because the sample was located within a calorimeter cell filled with He gas, nor from decomposition into La_2O_3 , NiO and/or other compounds, because such reactions do not proceed under the He atmosphere at around 400 K. The reasonableness of this explanation is indicated by the fact that the annealed sample showed the antiferromagnetic phase transition at 330 K and the first-order structural phase transition at 80 K, as reported already by many research groups. Thus, the origin of the heat evolution is considered to be a certain stabilization of

the as-prepared sample to a more stable state potentially in the respect of the homogeneity of the oxygen content over the whole sample, and Castro and Burriel are considered to have measured the heat capacities of a sample that was instead in a quasi-stable state. A little inhomogeneity in the as-prepared sample is potentially caused by the nonstoichiometry of the oxygen composition.

4.2. The three-dimensional antiferromagnetic phase transition and the two-dimensional antiferromagnetic short-range order

Circles and squares in figure 4 represent the heat capacities due to magnetic ordering in La_2NiO_4 and K_2NiF_4 crystals, respectively, for the normalization of the three-dimensional antiferromagnetic transition temperature, T_N . Both sets of results show a small peak at T_N and a hump on the high-temperature side of the peak. The hump is interpreted as being attributable to two-dimensional antiferromagnetic short-range ordering. The two sets of results are thus quite similar to each other and the heights of the humps are almost same, indicating that the magnetic properties of La_2NiO_4 crystal are those which generally appear in the crystals of K_2NiF_4 type.

The total entropy estimated from the heat capacities in figure 4 below 500 K is about $13 \text{ J K}^{-1} \text{ mol}^{-1}$. Even if the heat capacity tail on the high-temperature side is taken into account, the entropy does not exceed $15 \text{ J K}^{-1} \text{ mol}^{-1}$. Considering that the baseline of the heat capacities was derived from the phonon density of states via a neutron scattering experiment, the value is rather close to $R \ln 3$ expected from the spin of the nickel ion.

It is noticed, in comparison with the results for La_2CuO_4 crystal, that there was a heat capacity peak observed at the three-dimensional antiferromagnetic phase transition at 330 K. The heat capacity curve of La_2CuO_4 , which we reported previously [23], showed no appreciable anomaly at the corresponding phase transition, 316 K. As the transitions take place at almost the same temperatures, the difference between the thermal anomalies of La_2NiO_4 and La_2CuO_4 crystals is understood as being due to the difference in the magnitude of the in-plane exchange interaction [20, 21]. In La_2CuO_4 , nearly complete ordering of the spins would be accomplished above the three-dimensional antiferromagnetic phase transition temperature of 316 K, and the degree of ordering would not change through the transition. In view of the remarkable similarity of the heat capacity curves of La_2NiO_4 and K_2NiF_4 crystals, the phase transition at $T_N = 330 \text{ K}$ would be expected to show two-dimensional critical scattering as in the case of K_2NiF_4 . This also indicates a difference between La_2NiO_4 and La_2CuO_4 crystals. The reason, based on the electronic orbitals, for the difference between copper and nickel compounds remains to be clarified.

5. Concluding remarks

New aspects have been found concerning the structural and magnetic properties of La_2NiO_4 crystal. The indication of the presence of an incommensurate phase with respect to the modulation in the tilts of NiO_6 octahedra is particularly noticeable in that various modulations of the tilts are potentially allowed in two-dimensional perovskite compounds. Superconductivity in cuprates is produced on the two-dimensional CuO_2 plane formed by edge sharing of the CuO_6 octahedra, and thus the detailed arrangement of the tilts of the octahedra at low temperatures has an important effect on the properties of superconductivity; the structural phase transition at 222 K in $\text{La}_2\text{CuO}_{4.011}$ crystal is known to change the superconducting transition temperature by 7 K [4], and the mechanism of the transition would be linked to the change in the modulation of the tilts.

The magnetic properties of La_2NiO_4 were indicated to be quite similar to those of K_2NiF_4 but not to those of La_2CuO_4 . The difference between La_2NiO_4 and La_2CuO_4 —as regards features such as the magnitude of the exchange interaction and the presence/absence of the critical scattering—needs to be clarified in relation to the issue of the emergence of superconductivity.

Acknowledgments

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