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HEAT CAPACITIES OF RARE EARTH ISOTHIOCYANATE HEPTAHYDRATES, $[M(NCS)_3(H_2O)_6] \cdot H_2O$ (M = Ce, Pr, Nd), AT VERY LOW TEMPERATURES: NEW FINDING OF MAGNETIC PHASE TRANSITIONS AND SCHOTTKY ANOMALIES*

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SUMMARY

Heat capacities of the rare earth isothiocyanate heptahydrates, $[M(NCS)_3(H_2O)_6] \cdot H_2O$ (M = Ce, Pr, Nd), have been measured in the temperature region from 50 mK to 20 K by using a very low temperature calorimeter workable with a $^3He/^4He$ dilution refrigerator. Appreciable increases of the heat capacities were observed below 100 mK for the Ce and Nd compounds. These heat capacity anomalies were interpreted in terms of the high-temperature tail of a magnetic phase transition located at lower temperature. Temperature dependences of these heat capacity tails were compared with the results of high-temperature expansion for some theoretical models. Above 2 K, the heat capacity of the Pr compound showed a remarkable hump beyond those of the Ce and Nd compounds. This excess contribution was well accounted for by a crystalline field splitting which might exist.

INTRODUCTION

Lanthanoid compounds exhibit various interesting properties owing to their partially occupied 4f shells. Especially their magnetic properties provide attractive problems and have been intensively studied by various experimental methods. Since 1950's, lanthanoid metals and alloys have become easily available and hence many studies of their metals and alloys are currently being progressed. Studies of lanthanoid compounds were started later on. Many kinds of lanthanoid compounds have been examined nowadays, for example, halides[1,2], pnictides[3], sesquioxides[4,5], borides[6], hydrides, carbides and superconducting copper double oxides.

Heat capacity is one of the important properties for understanding of magnetism because magnetic materials often exhibit magnetic phase transitions and/or Schottky heat capacity anomaly due to thermal excitation between discrete energy levels. Low temperature heat capacity measurements are especially informative in the sense that the contribution of the lattice vibrations to heat

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capacity becomes negligibly small and hence separation of the magnetic contribution from the observed values can be made with minimal ambiguity.

The excess heat capacities of rare earth compounds often appear as remarkable humps[7]. They are the Schottky anomalies due to thermal excitation among finite number of energy levels caused by the crystalline field splitting. Those results are favorably compared with spectroscopic data and consistently interpreted. On the other hand, sharp heat capacity peaks sometimes appear as the magnetic phase transitions[8-11] arising from energy-level splitting of the ground state manifold by the superexchange and/or magnetic dipolar interactions.

Purpose of the present paper is to closely examine heat capacities of the rare earth isothiocyanate heptahydrates, $[M(NCS)_3(H_2O)_6] \cdot H_2O$ (M = Ce, Pr, Nd). Since these compounds contain many crystal water molecules, magnetic interactions would be weak. Therefore, the magnetic heat capacity anomalies would be expected at very low temperatures, if any. The crystal structures of those compounds have already been determined. Each lanthanoid ion is nine-coordinated forming a coordination polyhedron of a distorted capped square antiprism (space group $P\ 2_1/c$) as shown in Fig. 1[12].

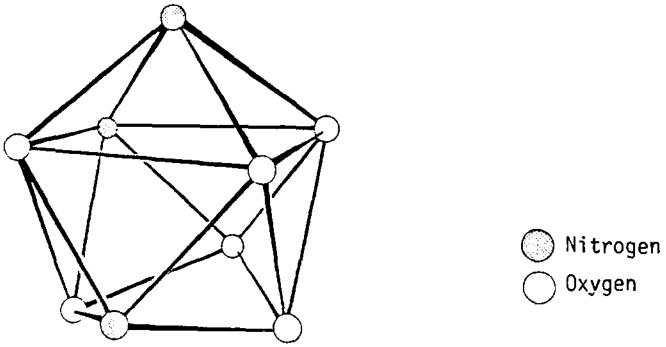

Fig. 1. The coordination polyhedron
in the present rare earth compounds[12].

EXPERIMENTAL

All the present compounds were prepared at Dalian Institute of Chemical Physics. Crystalline compounds were obtained by concentration of the aqueous solution of $M(NCS)_3$ below 55 °C. Anal. Calcd. for the Ce compound: Ce, 31.81; NCS, 39.55; H_2O, 28.63%. Found: Ce, 31.90; NCS, 39.48; H_2O, 28.62%. Calcd. for the Pr compound: Pr, 31.93; NCS, 39.49; H_2O, 28.58%. Found: Pr, 31.99; NCS, 39.34; H_2O, 28.62%. Calcd. for the Nd compound: Nd, 32.44; NCS, 39.19; H_2O, 28.36%. Found: Nd, 32.50; NCS, 39.01; H_2O, 28.48%.

Heat capacity measurements were carried out by using a very low temperature calorimeter workable with a $^3He/^4He$ dilution refrigerator, which was operated as either an isoperibol calorimeter from 50 mK to 2 K or an adiabatic one from 1 to 20 K [13]. Silicone oil was mixed with the samples as a heat-exchange medium. The amounts of the sample and silicone oil used for the heat capacity measurements were 9.8879 and 7.0513 g for the Ce compound, 9.6111 and 5.0669 g for the Pr compound, and 11.8546 and 5.3399 g for the Nd compound, respectively.

RESULTS

The results of the heat capacity measurements of the Ce, Pr and Nd compounds are plotted in Figs. 2-4, respectively. Open circles represent the present results while closed circles indicate the previous ones which have been measured between 13 and 300 K by Matsuo *et al.*[14]. Below 80 mK, the thermal relaxation time necessary for the thermal equilibration after an energy input elongated to 1 h. For the Ce and Nd compounds, the heat capacities were increased with decreasing temperature below 100 mK, indicating the existence of heat capacity anomalies arising from the magnetic interactions. Although the heat capacities of the Ce and Nd compounds were substantially the same in the range from 2 to 20 K, the heat capacities of the Pr compound were remarkably large around 20 K in comparison to those of the Ce and Nd compounds. This fact indicates the existence of a Schottky anomaly centered around 20 K for the Pr compound.

In order to determine these excess heat capacities, we should estimate normal heat capacities arising from lattice vibrations. It is generally difficult to estimate the contribution of lattice vibrations by *a priori* calculation based on lattice dynamics. Thus for estimate of normal heat capacities, we adopted an approximation following the law of corresponding states. The best way for the law of corresponding states is to use heat capacities of the diamagnetic, isostructural homologue, $[La(NCS)_3(H_2O)_6]\cdot H_2O$, as the normal heat capacities of the paramagnetic compounds, in which the temperature should be suitably scaled. However, the data of the La compound are available only in the temperature region from 13 to 300 K[14]. Therefore, it was impossible to extrapolate the normal heat capacities down to 50 mK only by means of these data. Alternatively we used the heat capacities of the Nd compound in the temperature region from 1 to 20 K as the normal heat capacities for the present three compounds because the heat capacities of the La and Nd compounds between 13 and 20 K agreed well each

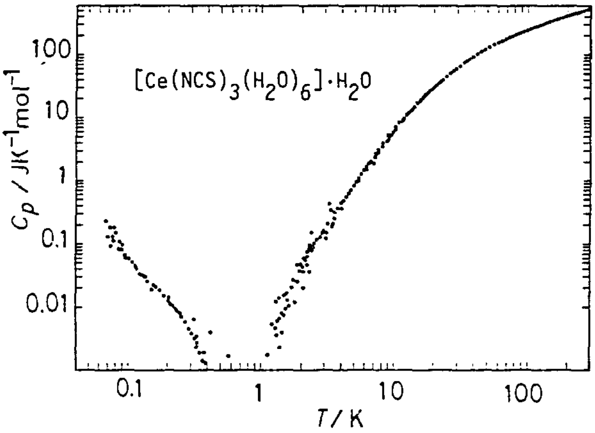

Fig. 2. Molar heat capacities of $[Ce(NCS)_3(H_2O)_6]\cdot H_2O$.

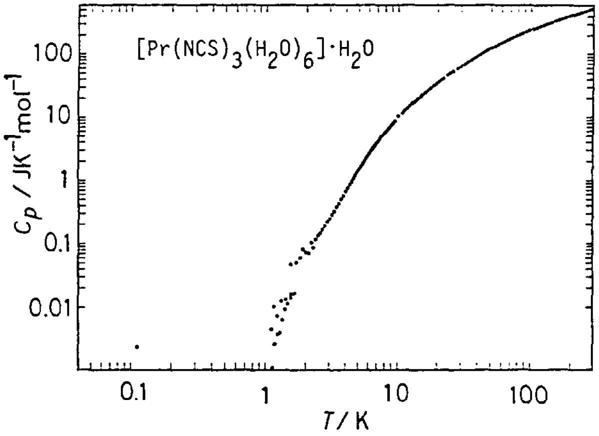

Fig. 3. Molar heat capacities of $[Pr(NCS)_3(H_2O)_6]\cdot H_2O$.

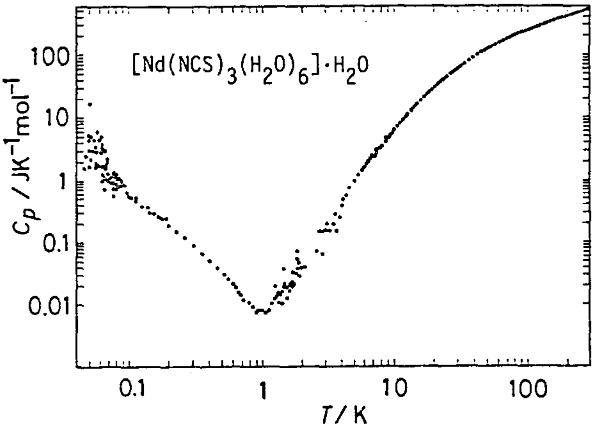

Fig. 4. Molar heat capacities of $[Nd(NCS)_3(H_2O)_6]\cdot H_2O$.

other. The excess heat capacities thus obtained were shown in Fig. 5 for the Pr compound, and in Fig. 6 for the Ce and Nd compounds.

DISCUSSION

Two pronounced features are encountered in the present three lanthanoid compounds: one is the heat capacity anomaly found for the Pr compound around 20 K and the other is the very low temperature anomalies of the Ce and Nd compounds. We shall discuss first the electronic states of the Pr^{3+} ion under a crystalline field.

Judging from spectroscopic data of several other Pr(III) compounds[15], it is very likely that the observed hump centered around 20 K in the heat capacity of the Pr compound may be attributed to a Schottky anomaly arising from a crystal-field level-splitting of the ground term $^3H_4$ of a free Pr^{3+} ion. The crystalline field can lift the multiplet $^3H_4$ into nine or less levels. Consequently we fitted the Schottky anomaly with a nine-level scheme to the data of excess heat capacity and obtained the energy-level scheme shown in Fig. 5. The resultant energy-level scheme seems to be adequate for the present system at least up to the second excited level because it is comparable with the energy-level schemes found for other Pr(III) compounds, as shown in Table 1.

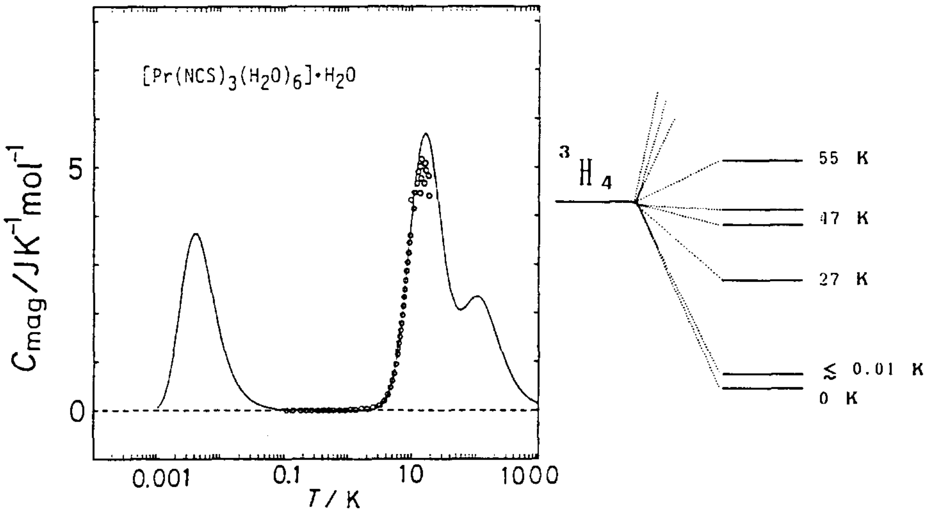

Fig. 5. Excess heat capacities of $[Pr(NCS)_3(H_2O)_6] \cdot H_2O$ and the theoretical curve for the Schottky anomaly of the system with nine energy-level scheme shown on the right hand side.

TABLE 1. First and second excited levels arising from crystalline field splitting for several Pr(III) compounds. The energy levels are given in the unit of K.

Compound	$Pr(OH)_3$	$Pr(C_2H_5SO_4)_3 \cdot 9H_2O$	$Pr:LaCl_3$	$Pr(NCS)_3 \cdot 7H_2O$
1st excited state	0	0.53	0	≤ 0.01
2nd excited state	15.8	16.7	47.6	27
reference	[1]	[16]	[17]	This work

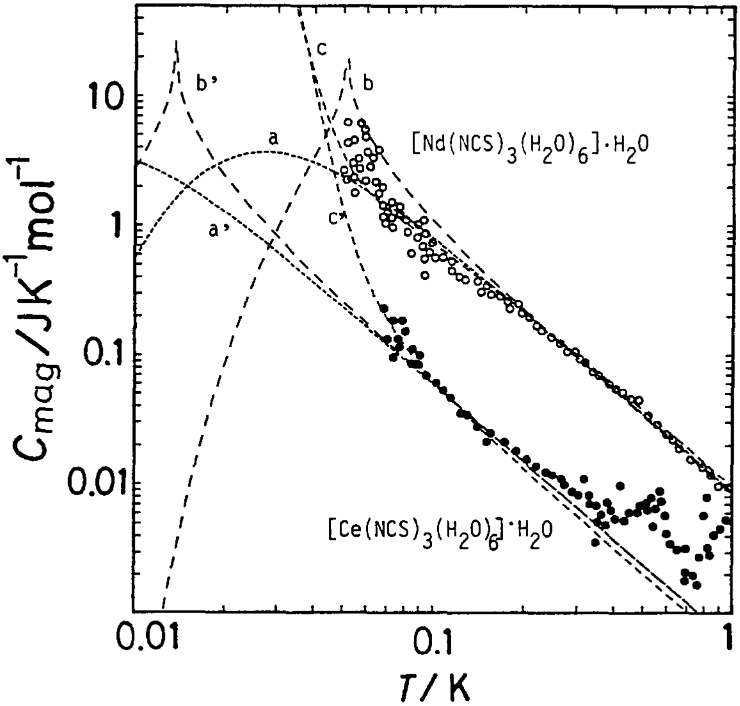

Fig. 6. Excess heat capacities of $[Ce(NCS)_3(H_2O)_6] \cdot H_2O$ (closed circles) and $[Nd(NCS)_3(H_2O)_6] \cdot H_2O$ (open circles) with several theoretical curves.; (a) Schottky anomaly with the degeneracy ratio of the ground and excited states being 1:1 ;(b) Ising model of a square lattice with exchange integral parameter J/k = 0.012 K; (c) Ising model of a simple cubic lattice with J/k = 0.013 K; (a') Schottky anomaly with the degeneracy ratio of 1:2 ;(b') Ising model of a square lattice with J/k = 0.045 K; (c') Heisenberg model of a simple cubic lattice with J/k = 0.023 K.

Except for a few levels at low energies, higher excited levels were ill-determined only from the heat capacity data, owing to the uncertainty involved in the separation of lattice heat capacities. The nearly degenerate ground levels were inevitable to reproduce the heat capacity data at the low-temperature side of the Schottky peak centered around 20 K. The upper limit of the ground level splitting was estimated to be 0.01 K from the fact that there exists essentially no effect of the Schottky anomaly due to it in the temperature region down to 100 mK.

For the Ce and Nd compounds, the observed increases of the excess heat capacities below 1 K are shown in Fig. 6 together with several theoretical curves. The steep rises in the excess heat capacities of the Ce and Nd compounds below 60 mK cannot be described by any Schottky anomalies. They should be reasonably attributed to a magnetic phase transition. Even if any crystalline field with the lowest symmetry would act on the Ce^{3+} or Nd^{3+} ion, the resultant degeneracies cannot be completely lifted because they belong to the Kramers doublets characteristic of a system consisting of odd electrons. However the super-exchange interaction or the magnetic dipolar interaction between the neighboring lanthanoid ions can lift the Kramers doublet to give rise to a magnetic phase transition, unless the interactions are limited within a finite membered system such as dimer, tetramer, *etc.* In such a case, the crystal manifests a magnetically ordered state below a critical temperature. It is, however, difficult to determine only from the heat capacity data whether the ordered state is ferromagnetic or antiferromagnetic. To this end, magnetic susceptibility measurements and/or spin-polarized neutron diffraction would play more useful roles. Although the mechanism of the present phase transitions have not been yet explicated as to whether they come from superexchange or magnetic dipolar interaction, and as to whether the magnetic behavior can be described by the Heisenberg or Ising model, the present calorimetric study has clearly demonstrated the existence of a magnetic phase transition at very low temperatures for the Ce and Nd compounds. Further detailed studies are now going on.

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