Particle Size Dependence of the Magnetic Heat Capacity of $Ni(OH)_2$ Crystal at Low Temperatures

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The heat capacities of $Ni(OH)_2$ crystals with three kinds of particle sizes [*i. e.* (1) (~20 Å) × (~130 Å), (2) (30—1000 Å) × (200—10000 Å), and (3) (0.2—0.5 μ) × (1—3 μ), where we designate their particle size as (average distance in <001> direction) × (distance in <100> direction)] have been measured in the temperature region form 1.5 to 300°K. Each of these crystals showed a heat capacity anomaly associated with the spin ordering of the metal ions at 23.0±0.1°K, 24.25±0.05°K, and 24.80±0.05°K for the $Ni(OH)_2$-(1), -(2), and -(3), respectively.

The magnetic heat capacities of these substances were separated from the total heat capacities by a rather reasonable method. The reduced plots of the magnetic heat capacities thus obtained are shown in Fig. 1. The magnetic entropies of the Ni-salts associated with the spin ordering effect agreed well with the value of 9.134 J/°K·mol from $\boldsymbol{R}\cdot\ln(2S+1)$ where $S=1$ for the spin of the Ni^{2+} ion, and about 50% of this was acquired in the region above the Néel point, T_N, indicating the characteristic behaviours due to much stronger two-dimensional interactions predicted from their layer lattice structures (the CdI_2-type).

The variation of the transition temperatures form sample to sample observed in the Ni-salts may be the largest effect ever known[1] and clearly regarded as the particle size effects on the magnetic heat capacity. Additional effect of the particle size could be observed in the rounding of the heat capacity maxima with decreasing size of the crystal particles (see Fig. 1). This particle size effect has long been one of the unsolved problems which could help to fulfill the gaps between theory and experiment.

The particle size effect was also reflected in the surface heat capacities. The excess heat capacity was estimated to be about 1.2 J/°K·mol at 100°K for $Ni(OH)_2$ with the surface area of 314 m²/g. This magnitude of excess heat capacity is the largest effect ever known and is compared with the data for NaCl, MgO, and BeO crystals[2] in Fig. 2.

The detailed results and discussions will be published in due course.

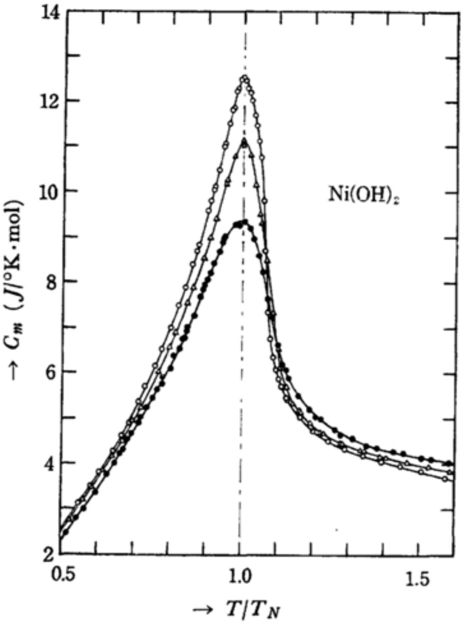

Fig. 1. The magnetic heat capacity C_m *versus* reduced temperature curves for $Ni(OH)_2$ with different crystal sizes. ●, the $Ni(OH)_2$-(1); △, the $Ni(OH)_2$-(2); ○, the $Ni(OH)_2$-(3)

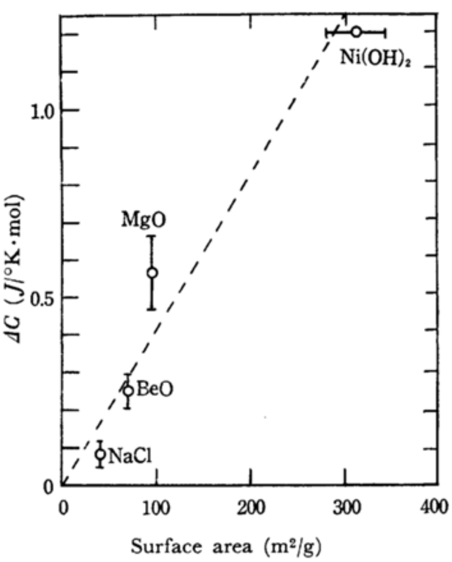

Fig. 2. The excess heat capacity ΔC for several kinds of crystals at 100°K as a function of surface area per unit mass.

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2) A. C. Victor, *J. Chem. Phys.*, **36**, 2812 (1962).