ENERGY LEVELS OF THE MAGNETIC RARE EARTHS

Rare-earth ions can also contribute to the magnetic properties of the compounds. The ground-state multiplet of unfilled 4f shells splits due to the influence of electrostatic and magnetic fields.

In the low-temperature tetragonal phase, the R3+ ions are on a site of D4h symmetry. Consequently, the ground-multiplet of Pr3+ splits into five singlets and two doublets due to the electric field created by the crystal, and the ground-multiplet of Nd3+ splits into five doublets. The energies of the resulting levels are in the thermal range, and substantial heat-capacity contributions can be expected due to their thermal population. The energy splitting of the ground-multiplet can be measured by inelastic neutron scattering.

The application of a magnetic field produces a further shift of some levels and a splitting of the doublets. In addition to external fields, an effective magnetic field can be induced on the R3+ sites by the ordered Ni2+ magnetic moments. The effective field acting on the Nd3+ sites has been estimated to be \( H = 5.2 \, T \) on Nd2NiO4 at 4.2 K (6).

For Pr3+, a shoulder on the heat-capacity curve appears at around 20 K as shown in Fig. 6 after subtraction of the lattice heat capacity. A preliminary inelastic neutron scattering experiment (14) has shown a crystal-field transition at 4.4 meV with additional levels at higher energies. This level splitting would account for the experimental shoulder. Additional higher energy levels would contribute to the anomalous heat capacity at higher temperatures. The height of the anomaly indicates that the ground and first-excited levels have the same degeneracy. Moreover, the shape of the low-temperature magnetic susceptibility (Fig. 5) and the absence of any heat-capacity peak down to 2 K are consistent with a singlet ground-state for Pr3+.

Measurements on Nd2NiO4 showed excited levels at 8, 23, 38 and 49 meV (7) with an energy resolution of 1 meV. A large broadening of the absorption lines was observed and attributed to doubling of the lines due to the additional interaction of the internal magnetic field. The Schottky anomaly calculated with excited doublets at the energies given by the neutron scattering experiment is illustrated in Fig. 7. The experimental heat-capacity points have been drawn after subtracting the lattice contribution as estimated above. They show two bumps with maxima at 8 and 27 K, and differ from the Schottky calculation.

In view of the additional Zeeman splitting of the Nd3+ energy doublets induced by the internal magnetic field, our heat-capacity results predict \( \Delta = 17 \, K \) for the energy splitting of the ground-doublet. The previously reported levels, together with this splitting and minor adjustments of \( \pm 1 \, meV \) in the next two levels lead to excellent agreement with the experimental data as shown by the dashed line in Fig. 7. The doubling of the excited doublets would not appreciably affect the shape of the curve.

Fig. 6. Anomalous heat capacity of Pr2NiO4. The dashed line represents a Schottky anomaly for two levels with equal degeneracy and separated by \( \Delta = 50 \, K \). Combinations of one doublet and one singlet would give the dotted lines.

Fig. 7. Anomalous heat capacity of Nd2NiO4. The full curve represents the Schottky anomaly from the inelastic neutron scattering levels (7). The dashed curve includes a splitting of the ground-doublet, \( \Delta = 17 \, K \).