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Addendum to “The heat capacity of $NdAlO_3$ from 0 to 900 K [R.R. van der Laan, et al., Thermochim. Acta 329 (1999) 1]”

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Recently we have reported an experimental study of the heat capacity of $NdAlO_3$ in the 0 to 900 K temperature range by combined low-temperature adiabatic calorimetry and high-temperature drop calorimetry [1]. The two sets of measurements were in good agreement and the enthalpy and entropy for this compound were derived by integration of the heat capacity curve. However, it was not taken into account that the lanthanide compounds often exhibit an excess term to heat capacity and entropy due to the electronic contribution, which will affect the entropy recommendation.

Nd^{3+} has a $^4I_{9/2}$ ground state that is split due to the crystal field in most ionic crystals. The ground state of $NdAlO_3$ was found to split into five Kramer’s doublets at 0, 122, 148, 595 and 595 cm^{-1} [2]. Also data for the higher states ($^4I_{11/2}$, $^4I_{13/2}$ and $^4I_{15/2}$) of Nd^{3+} are available [2]. The heat capacity and entropy calculated from these data are shown in Fig. 1. The heat capacity curve shows a maximum around 50 K caused by the ground state splitting, followed by a gradual increase after about 500 K due to the contribution of the higher electronic states. The excess entropy S_{xs} varies from 5.763 $J\,K^{-1}\,mol^{-1}$ at low temperatures to about 20.5 $J\,K^{-1}\,mol^{-1}$ at 900 K. The former value is equal to $R\ \ln(g_0)$ where $g_0 = 2$, the degeneracy of the ground state. Calorimetric measurements for $NdAlO_3$ in the 0.2–6 K range by Bartolomé et al. [3] have confirmed this value. These authors found a transition at (0.93 ± 0.01) K, below which an antiferromagnetic ordering of the Nd^{3+} ions occurs, with a total entropy change equal to $\Delta S = R\ln(2)$.

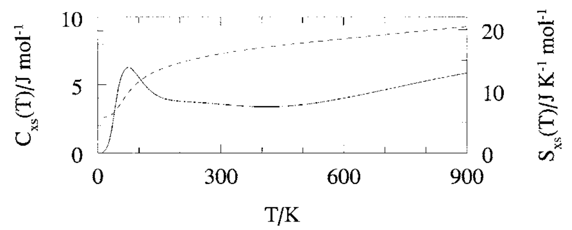

Fig. 1. Left axis: the calculated excess heat capacity (—) for $NdAlO_3$; right axis: the calculated entropy (– – –) for $NdAlO_3$.

The ‘practical’ entropy of $NdAlO_3$ is then obtained by adding $R\ \ln(2)$ to the entropy derived from the calorimetric measurements ($99.3 \pm 0.3\ J\,K^{-1}\,mol^{-1}$) to give

$$S^0(NdAlO_3,\ cr,\ 298.15\,K) = (105.0 \pm 0.3)\,J\,K^{-1}\,mol^{-1}$$

References

[1] R.R. van der Laan, R.J.M. Konings, A.C.G. van Genderen, J.C. van Miltenburg, Thermochim. Acta 329 (1999) 1.

[2] E. Finkman, E. Cohen, L.G. van Uitert, Phys. Rev. B 7 (1973) 2899.

[3] F. Bartolomé, J. Bartolomé, J. Blasco, J. Magn. Magn. Mater. 157/158 (1996) 491.

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