JOURNAL OF SOLID STATE CHEMISTRY 4, 1–3 (1972)

The Heat Capacity of $PrCo_2$ and $NdCo_2$ Between 8 and 300°K*

C. DEENADAS, R. S. CRAIG, N. MARZOUK, AND W. E. WALLACE

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213

Received February 3, 1971

Heat capacities of $PrCo_2$ and $NdCo_2$ are presented for the temperature region extending from 8 to 300°K and the resistivity-temperature behavior of $NdCo_2$ is given for the same temperature range. These materials are both ferromagnetic at helium temperatures. The heat-capacity data show that the magnetic order in both compounds is lost in two stages. The nature of the two stages for $PrCo_2$ is not clear: For $NdCo_2$ the results indicate that ferromagnetism exists only for $T < 42$°K and that between 42 and 116°K, the Curie temperature deduced from magnetic measurements, another ordered magnetic structure exists. The resistivity measurements clearly show the spin-disorder contribution and confirm that there are two transition temperatures.

This study represents a portion of an ongoing program being carried out in this laboratory dealing with the low-temperature heat-capacity behavior of intermetallic compounds in which one component is a lanthanide. Magnetic measurements of Farrell and Wallace (*1*) revealed Curie points for $PrCo_2$ and $NdCo_2$ at 50 and 116°K, respectively. The magnetization-temperature curve for $PrCo_2$ was of the shape expected for a ferromagnetic material (*2*) whereas that for $NdCo_2$ exhibited (*1*) an anomalous break at about 40°K, some 75°K below T_c.

In the present report we present heat-capacity data for $PrCo_2$ and $NdCo_2$. The compounds were prepared by levitation melting from rare earth metals stated to be of 99.9% purity (with respect to metallic contaminants) and from Johnson Matthey cobalt having an impurity content of less than 50 parts per million. The calorimetric procedure followed that described in an earlier paper from this laboratory (*3*).

The heat capacity data for $PrCo_2$ and $NdCo_2$ and, for comparison, the results (*4*) for the nonmagnetic isostructural compound $LaNi_2$[1] are presented in Figs. 1 and 2. There are thermal anomalies for these two cobalt compounds peaking at temperatures close to T_c obtained from magnetic measurements. It is to be noted that, as with $GdNi_5$, (*5*) magnetic order appears to be lost in two stages. The temperature of the lower-temperature thermal anomaly in $NdCo_2$ correlates well with the temperature of the break in the magnetization-temperature curve. The temperature at which the upper anomaly is maximal is in proper accord with T_c measured magnetically. Moon, Koehler, and Farrell (*6*) studied $NdCo_2$ by neutron diffraction techniques and established that it was ferromagnetic at 4.2°K. The present results suggest that it adopts another magnetic structure between 43 and 100°K. An alternative possibility is that the anisotropy changes with temperature and the easy axis of magnetization changes at 42°K. Still another possibility is that the anomaly at 42°K is a crystal field effect. In a cubic field the $(2J+1)$-fold degenerate ground state multiplet of Nd^{+3} is split (*7*) into two quartets and a doublet. The 42°K anomaly might be ascribed to redistribution within the crystal field spectrum. This possibility can be excluded on two grounds: first, on this basis the anomaly should be of the Schottky type whereas experimentally it is much sharper, suggesting a cooperative effect; second, if the anomaly were crystal field in origin the associated entropy would have to be $R\ln 2$ or larger. Experimentally, it is approximately $1/4\ R\ln 2$. The neutron diffraction results of Moon et al. (*6*) were interpreted to indicate a single magnetic structure for all temperatures below the Curie temperature, 116°K. This interpretation must now be questioned in the light of the present results. The neutron diffraction results were not obtained on single crystal materials and perhaps the assumed structural change thereby escaped observation. If the 42°K anomaly is due to a

* This work was assisted by a grant from the Army Research Office, Durham.

[1] Efforts to prepare $LaCo_2$ were unsuccessful.

1

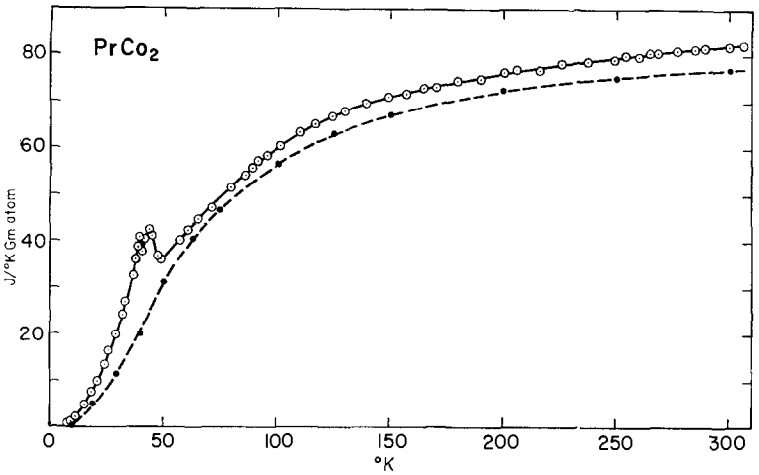

FIG. 1. Heat capacity v. temperature for $PrCo_2$. The dashed line gives results for $LaNi_2$, the isostructural, nonmagnetic counterpart of $PrCo_2$.

change in the direction of easy magnetization, this would not be evident in the powder neutron diffraction patterns. However, this latter possibility seems somewhat less likely in view of the sharpness (*8*) of the 42°K anomaly.

Resistivity-temperature data for $NdCo_2$ are shown in Fig. 3 together with corresponding results for its isostructural nonmagnetic counterpart $CeCo_2$. The loss of the $NdCo_2$ spin-disorder resistivity at $T < T_c$ is readily apparent. There is reasonably clear indication that this is lost also in two stages. The nature of the phenomenon which gives rise to the doublet thermal anomaly for $PrCo_2$ is as yet unclear. Lanthanide moments in both $NdCo_2$ and $PrCo_2$ are (*1*, *6*) well below gJ, the free ion moments. The discrepancy is particularly large for Pr^{+3}, 1.2 μB experimental compared to $gJ = 3.2$ μB. The Pr moment is largely quenched by the influence of the crystal field. Probably the doublet thermal anomaly for $PrCo_2$ and the low Pr moment are in some way interrelated. The entropy difference between $PrCo_2$ and $LaNi_2$ at 300°K is 17.7 J/mol °K and for $NdCo_2$ the corresponding quantity is 18.6 J/mol °K, which are 97 and 98 %, respectively, of the theoretical magnetic entropy $R\ln(2J+1)$. Although this agreement is impressive, it is largely fortuitous. The heat capacities of the $LnCo_2$ compounds differ substantially from that of $LaNi_2$ at 300°K indicating

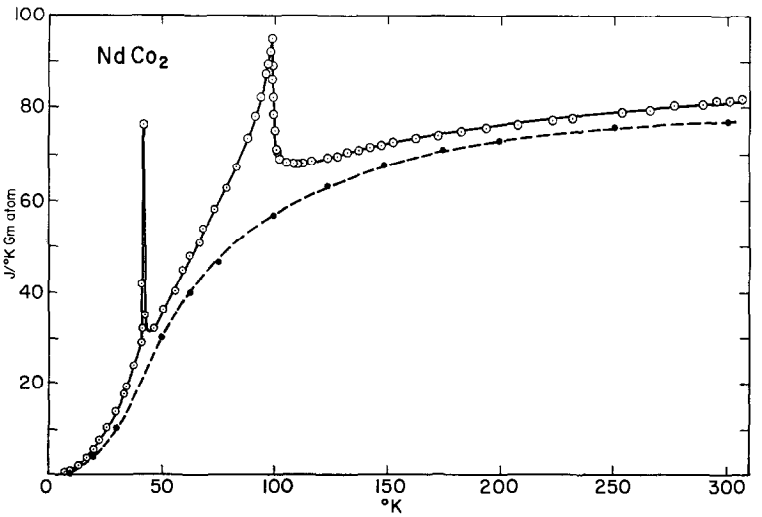

FIG. 2. Heat capacity v. temperature for $NdCo_2$ together with results for $LaNi_2$ (dashed curve).

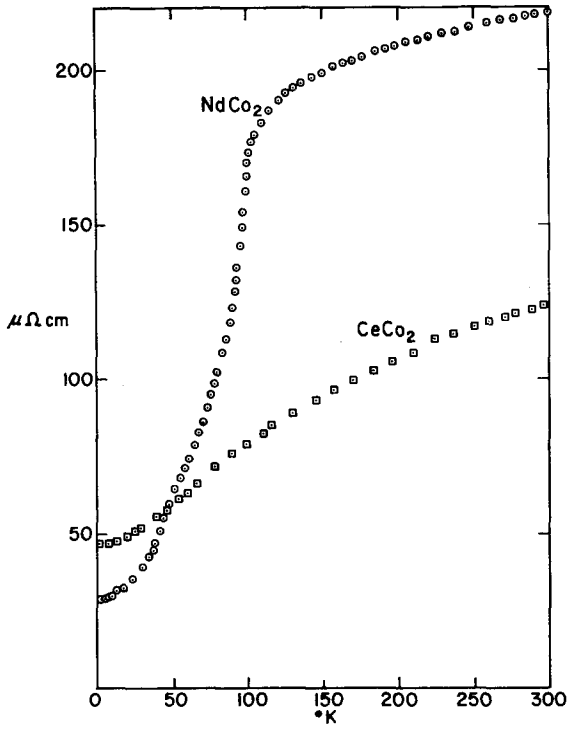

FIG. 3. Resistivity-temperature results for $NdCo_2$ and $CeCo_2$. $CeCo_2$ gives no evidence of magnetic ordering.

that the measured entropy differences contain significant nonmagnetic contributions, probably vibrational and electronic in nature.

References

1. J. FARRELL AND W. E. WALLACE, *Inorg. Chem.* **5**, 105 (1966).
2. J. FARRELL, "Magnetic Properties of $CeFe_2$, $LnNi_5$ and some 1:2 Intermetallic Compounds of Lanthanide Metals with Nickel and Cobalt," p. 45, Ph.D. Dissertation, University of Pittsburgh, Pittsburgh, Pa., 1964.
3. W. E. WALLACE, C. DEENADAS, A. W. THOMPSON, AND R. S. CRAIG, *J. Phys. Chem. Solids*, to appear.
4. S. NASU, N. MARZOUK, R. S. CRAIG, AND W. E. WALLACE, *J. Solid State Chem.*, to appear.
5. W. E. WALLACE, R. S. CRAIG, A. THOMPSON, C. DEENADAS, M. DIXON, M. AOYAGI, AND N. MARZOUK. Colloques Internationaux du Centre National de la Recherche Scientifique No. 180, Tome II, p. 427, Paris, 1970.
6. W. MOON, W. C. KOEHLER, AND J. FARRELL, *J. Appl. Phys.* **36**, 978 (1965).
7. B. BLEANEY, *Proc. Roy. Soc. London A* **276**, 28 (1963).
8. See W. G. SABA, W. E. WALLACE, and R. S. CRAIG, *J. Chem. Phys.* **35**, 689 (1961) for heat capacity data on $DyCo_5$. The easy axis of this material does change and the corresponding heat capacity anomaly is quite gradual compared to that for $NdCo_2$. This suggests that the 42°K anomaly for $NdCo_2$ originates otherwise.