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Thermal Anomalies Associated with the Antiferromagnetic Ordering of FeF_2, CoF_2, and NiF_2

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FROM measurements of the magnetic susceptibility of powdered materials, Bizette[1] concluded that MnF_2 and FeF_2 are antiferromagnetic, but that the isomorphous compounds CoF_2 and NiF_2 are not. The neutron diffraction studies of Erickson[2] show, however, that at low temperatures all four compounds are antiferromagnetically ordered and magnetic anisotropy measurements[3] on a single crystal of CoF_2 indicate an antiferromagnetic behavior. We have measured the heat capacity of FeF_2, CoF_2, and NiF_2 over the temperature range 12–300°K. Each of these salts shows a pronounced thermal anomaly of the lambda-shape characteristic of processes where there is cooperative ordering. The experimental heat capacity data in the neighborhood of the anomalies are shown in Figs. 1, 2, and 3 for FeF_2, CoF_2, and NiF_2, respectively. In order to determine the shape of the curves, the points in the regions of rapidly changing heat capacity were taken with small temperature increments (about 0.1°). The temperatures of the heat capacity maximum are: FeF_2, 78.3°K; CoF_2, 37.7°K; NiF_2, 73.2°K. A similar anomaly in MnF_2 with a heat capacity maximum at 66.5°K has been reported previously.[4] There seems to be no doubt that these anomalies represent the loss in entropy upon passing from the disordered paramagnetic state to the ordered antiferromagnetic state.

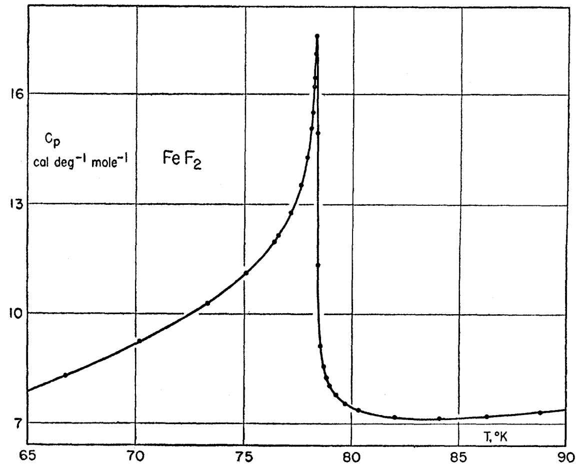

FIG. 1. Molal heat capacity of ferrous fluoride *versus* temperature.

The antiferromagnetic Curie temperatures deduced by Erickson[2] from the temperature variation of the magnetic structure factor are higher than those of the maximum in heat capacity by factors ranging from 1.1 to 1.3. However, the neutron diffraction measurements are a relatively imprecise method for determining the Curie temperature and also it seems probable that near the Curie point the magnetic form factor is varying much more rapidly with temperature than the Brillouin function used by Erickson in his extrapolation. We do not believe, therefore, that there is a significant disagreement.

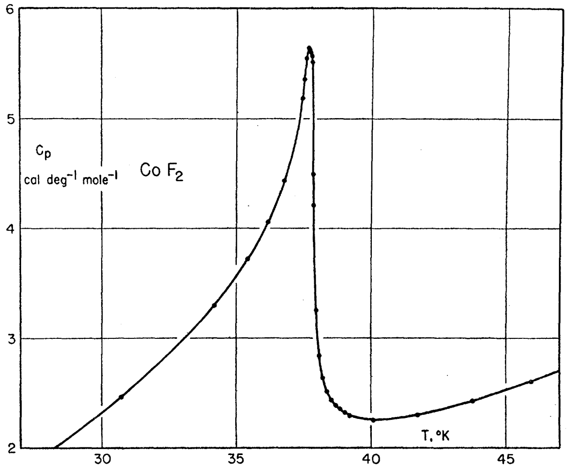

FIG. 2. Molal heat capacity of cobalt fluoride *versus* temperature.

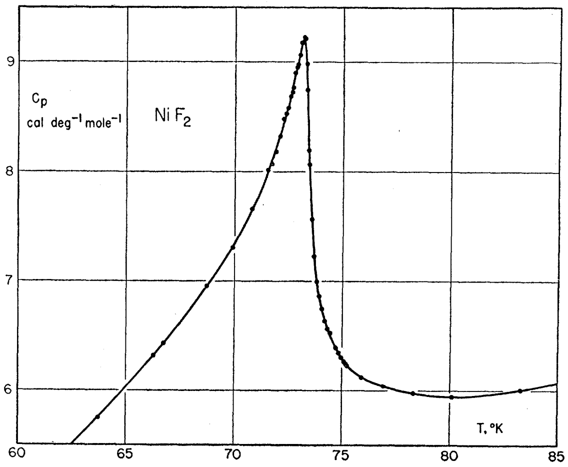

FIG. 3. Molal heat capacity of nickel fluoride *versus* temperature.

We have also made heat capacity measurements on the diamagnetic salt ZnF_2, which is isomorphous with the four antiferromagnetic fluorides. The data on ZnF_2 will permit an estimate of the entropy and heat capacity arising from lattice vibrations in the antiferromagnetic salts and thus enable the separation of the thermal effects caused by the magnetic ordering. The data and calculations will be published in detail elsewhere.

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