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STRUCTURAL TRANSITION STUDY OF $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$
BY SPECIFIC HEAT

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STRUCTURAL TRANSITION STUDY OF

 $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ BY SPECIFIC HEAT

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The specific heat of polycrystalline $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ measured in an adiabatic calorimeter by the heat-pulse method between 80 and 281 K indicates a first-order phase transition at $T_c = (220.0 \pm 0.5)$ K. This confirms a crystallographic transformation first detected by x-ray and EPR methods.

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In our previous work¹ we have reported EPR of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ and its known properties. A sudden broadening of EPR linewidth was observed in cooling runs at (200 ± 2) K and a reverse effect in heating runs at (220 ± 2) K. We have attributed this behavior to the crystallographic phase transition first detected by Bongaarts et al.² with x-ray experiments. They concluded that the monoclinic structure transforms into another similar one with doubled c axis below (230 ± 20) K. The specific heat of this substance is only known below 24.5 K.³

Using an adiabatic (two isothermal shields) liquid-nitrogen-cooled calorimeter and the heat-pulse method, we measured the specific heat of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ from 80 to 281 K. The temperature was determined with a platinum thermometer. 47.73 g of polycrystalline sample, with the largest crystal of size $0.5 \times 1 \times 6 \text{ mm}^3$, was used. They were grown from an aqueous solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in a temperature-controlled water bath at 70°C .

Our specific heat values were independent of the amount of added energy, which varied from 30 to 400 J, or of the rate of heating, which varied from 0.6 to 1.8 K/minute. The sample always reached thermal equilibrium after a heating pulse within one minute. As shown in Fig. 1 the transition temperature is well characterized by a sharp cooperative peak at $T_C = (220.0 \pm 0.5)$ K. Attempt made to observe latent heat indicated an endothermic process on heating beginning the study from

$T_C - 50^\circ$ to $T_C + 50^\circ$, although qualitatively. Below and above T_C the specific heat is approximately constant with C_p ratio 1:2. These features are typical of a first-order transition and consistent with the structural transformation indicated by our EPR work¹.

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FIGURE CAPTION

Fig. 1 Specific heat of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$.

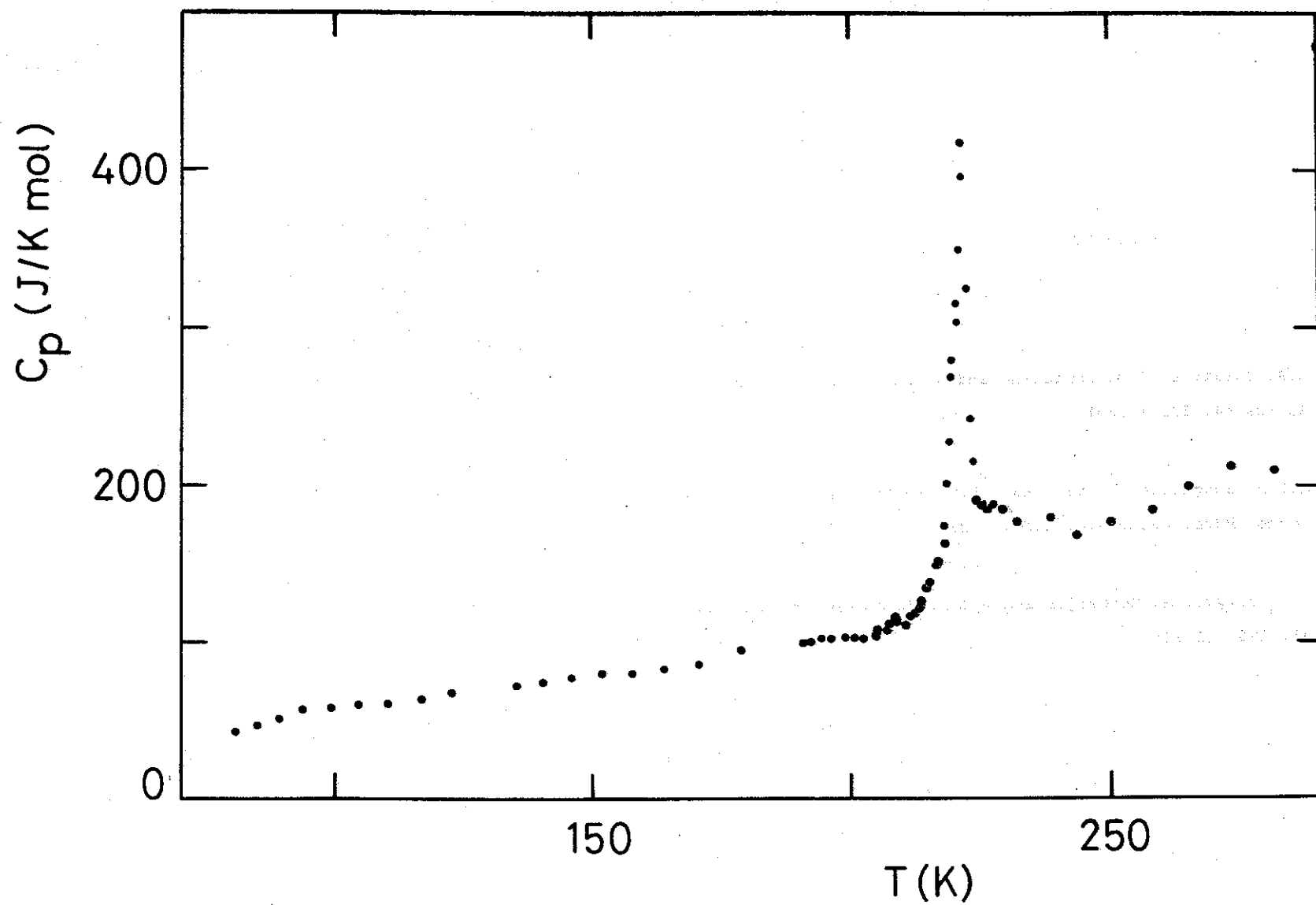


Fig. 1 Juraitis, Domidano and Sano