

SHORT COMMUNICATIONS

COMMENT ON THE PHASE TRANSITIONS OF CAESIUM AND RUBIDIUM NITRATE BELOW ROOM TEMPERATURE

By W. R. OWEN* and C. H. L. KENNARD†

[Manuscript received September 22, 1970]

It has been reported¹ that the performance of electrical measurements on anhydrous univalent nitrates, where the cation is Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ag^+ , Tl^+ , and NH_4^+ , showed that they exhibit solid state transitions below room temperature. Samples used "were formed by cooling molten p.a. grade compounds between plane electrode assemblies of silver". Anomalous dependence of the dielectric constant ϵ and resistivity ρ_D on temperature was claimed as evidence of a phase transition.

However, thermal analysis using a differential scanning calorimeter on both CsNO_3 and RbNO_3 from -90°C to room temperature failed to reveal any transitions. No structural change, compared to the room temperature phase, was detected when the neutron powder spectrum of CsNO_3 was run at -195°C . This evidence suggests that the anomalous electrical behaviour of these nitrates is not due to a phase transition of CsNO_3 and RbNO_3 , but to the violent thermal history in the preparation of the electrode assemblies. The reported effects could probably be ascribed to thermal hysteresis.

The univalent nitrate (approximately 10 mg) was subject to a temperature programme in a Perkin-Elmer DSC-1B, at $0.5^\circ\text{C}/\text{min}$ with a sensitivity of 1 mcal s^{-1} for a full scale deflection from 26°C to -90°C . The sample was held at -90°C for 30 min, and rescanned back to 26°C . No exotherm or endotherm was observed. The maximum noise level was approximately 0.02 mcal s^{-1} (peak to peak) and any transitions should have been observed.

Measurement of the known transitions of RbNO_3 and CsNO_3 , under the same experimental conditions, gave:

	Phase Change	Temp. (lit. ²) ($^\circ\text{C}$)	Temp. (this work) ($^\circ\text{C}$)
RbNO_3	IV \rightarrow III	164	163.1(5)
	III \rightarrow II	219	222.2(5)
	II \rightarrow I	291	284.3(5)
CsNO_3	II \rightarrow I	154, 161	152(1)

Numbers in parentheses refer to the estimated standard deviation for a particular observation.

* Department of Pharmacy, University of Queensland, St. Lucia, Qld. 4067.

† Department of Chemistry, University of Queensland, St. Lucia, Qld. 4067.

¹ Fermor, J. H., and Kjekshus, A., *Acta chem. scand.*, 1968, **22**, 2054.

² McLaren, A. C., *Rev. pure appl. Chem.*, 1962, **12**, 54.

The III \rightarrow II phase change of RbNO_3 at 222°C was unusual. The transition occurred over a range of 5°C , probably due to the slow establishment of the thermodynamic equilibrium.

The calorimeter was calibrated before and after analytical scans by observing the melts of samples of zone-refined lead (327.4°C , $1.22 \text{ kcal mol}^{-1}$)³ and indium (157.0°C , $0.78 \text{ kcal mol}^{-1}$).³

A sample of CsNO_3 was contained in a vanadium can surrounded by a liquid nitrogen cryostat. This assembly was mounted on a neutron powder diffractometer installed at the Australian Atomic Energy Commission's reactor HIFAR at Lucas Heights in New South Wales.

The spectrum was run at a slow scan over 12 hr up to $2\theta = 60^\circ$, wavelength 1.083 \AA . The powder spectra of both phase I⁴ and phase II⁵ have previously been recorded using this equipment. Consequently if significant structural changes had occurred, it should be detected using this technique.

Acknowledgments

We wish to thank Drs D. W. James and W. H. Leong for the samples of caesium and rubidium nitrates, the Australian Research Grants Committee (DSC-1B) and the Australian Institute for Nuclear Science and Engineering (A.I.N.S.E.) for financial support. We are also grateful to A.I.N.S.E. for access to the neutron diffraction facilities, and to the members of its Neutron Diffraction Group for their assistance.

³ National Bureau of Standards Circ. 500. pp. 653, 660. (U.S. Govt. Printing Office: Washington 1952.)

⁴ Delacy, T. P., and Kennard, C. H. L., unpublished data.

⁵ Delacy, T. P., and Kennard, C. H. L., *Aust. J. Chem.*, 1971, **24**, 165.