Determination of λ Transition Temperatures in AgNO₃-Base NaNO₃ Alloys

WILLIAM KLEMENT JR.,*† ADRIANA BALBOA, AND PAULINA RUIZ

Universidad de Chile, Santiago, Chile

Investigation with a differential scanning calorimeter of $AgNO_3$-rich $NaNO_3$ alloys showed a λ transition occurring in alloys containing ~3–20 mole % $NaNO_3$, with data for more concentrated alloys not obtained because of the smearing-out of the signals. Temperatures of the first-order transitions, in the alloys containing $\lesssim 3$ mole % $NaNO_3$, were obtained on heating and on cooling. It was shown that the λ transition is associated only with the phase based on the high temperature polymorph of $AgNO_3$. The λ transition temperature increases linearly with alloying over the investigated range at the rate of $2.0 \pm 0.2°$/mole % $NaNO_3$ and, for pure $AgNO_3$, is estimated by extrapolation to be $346 \pm 2°K$. Lattice parameters for some alloys were obtained from Debye–Scherrer patterns at room temperature and it appears that there is ordering in the $AgNO_3$-rich alloys analogous to that in the $NaNO_3$-base alloys.

Introduction

The high temperature phase in $AgNO_3$ appears (*1–5*) to be isostructural with the high temperature phase in $NaNO_3$, which shows a lambda transition on cooling. Mazieres and van't Hoff (*3*) described a metastable phase transition in their thermal analyses and X-ray diffraction studies of $AgNO_3$ and the probable analog with the λ transition in $NaNO_3$ was explicitly (*3*) noted. But neither they (*3*) nor Levin (*5*) have established the isomorphism of the low temperature phases in these compounds. Rapoport and Pistorius (*6*) searched for such a transition in their high pressure investigation of $AgNO_3$ but could not establish its existence. A recent investigation (*7*) with a differential scanning calorimeter (DSC) showed that the λ transition temperature in $NaNO_3$ is lowered ~1.3°/mole % $AgNO_3$ upon alloying and similar techniques were used in the present work to search for a λ transition in $AgNO_3$-rich $NaNO_3$ alloys.

* School of Engineering and Applied Science, University of California, Los Angeles, California 90024.

† Now on leave at National Physical Research Laboratory, P.O. Box 395, Pretoria, South Africa.

DSC Experiments and Results

AR materials from Merck were dried under $<10^{-2}$ Torr at $\gtrsim 115°C$ for $\gtrsim 10$ hr before mixtures of integral molar percentages were weighed out in 1–2 g quantities. Other details of the alloy preparations were similar to the previous techniques (*7, 8*). Freshly encapsulated samples of 20–40 mg were used with a Perkin–Elmer DSC-1B and an empty aluminum capsule was used in the reference sample holder, as before (*7, 8*). Samples were initially annealed at 450°K in the DSC for ~½ hr before the runs were begun. The DSC was frequently calibrated against room temperature, with the melting points of indium and tin and with the λ transition of $NaNO_3$ (*9*); temperatures are perhaps accurate to $\pm 1°C$. A precision of the order of 1° seems to have been maintained and this is also the order of the reproducibility of duplicate runs, unless otherwise stated.

(i) Lambda Transition

For runs with alloys containing $\geqslant 3$ mole % $NaNO_3$, cusp-like signals were observed

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and the maximum in the thermal effect was taken as T_λ. Heating and cooling rates of 4, 8, 16, 32 and 64 deg min^{-1} were used where possible. As with the $NaNO_3$-base alloys (7), it was found that T_λ increased with heating and decreased with cooling in direct proportionality to the rate; the proportionality factor was 0.22 ± 0.03 deg per (deg min^{-1}) of heating or cooling rate and extrapolations to zero rate were made in order to bound the equilibrium transition temperature. The signals became smeared out at the lower rates with increased alloying and, also, the instrument was unable to maintain the highest rates of cooling at the lower temperatures. Thus much of the data had to be taken at the 8, 16, and 32 deg min^{-1} rates, with consequent uncertainties in the extrapolations to zero rate. The supposition that the transition encountered in these alloys is indeed a λ transition rests, so far, on the symmetry of the signals observed on heating and cooling at the different rates and the essential coincidence of the transition temperatures, extrapolated to zero rate, for the less concentrated alloys; both these results are consonant with the experience (7) with the $NaNO_3$-base alloys but contrary
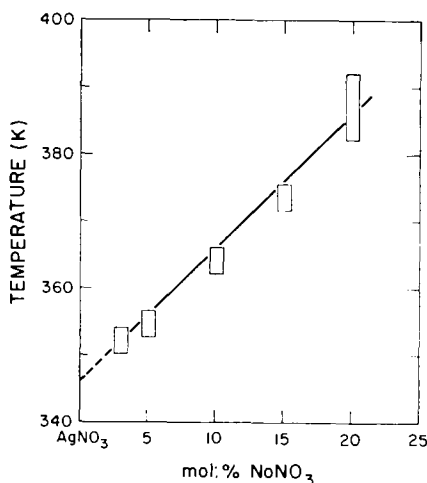
to the present experience with the first order transition in $AgNO_3$ and its dilute alloys, which is discussed below.

Shown in Fig. 1 are the λ transition temperatures found, by extrapolation to zero rate, for the $AgNO_3$–$NaNO_3$ alloys. The variation of transition temperature with composition appears to be linear over the investigated range, with a slope of 2.0 ± 0.2° /mole % $NaNO_3$. Linear extrapolation (Fig. 1) to pure $AgNO_3$ suggests a metastable λ transition temperature of 346 ± 2°K. The increasing indistinctness of the signals with increased alloying set the practical limit to the compositions investigated. A run with a 25 mole % $NaNO_3$; $AgNO_3$ alloy suggested a transition temperature compatible with that expected by linear extrapolation from Fig. 1 but the signals were quite poor.

(ii) First-Order Transition

For pure $AgNO_3$, the temperatures, at zero rate, corresponding to the peak for the first-order transition were in the range ~435–440°K on heating and in the range ~410–418°K on cooling. For the alloys, the temperatures on heating and cooling, at zero rate, were respectively, 1 mole % $NaNO_3$, ≈ 433°K, ~400°K; 2 mole % $NaNO_3$, ≈ 427°K, ~385°K; 3 mole % $NaNO_3$, ~422°K, >300°K. The slope of the transition temperatures vs rate, obtained for the alloys on heating, was similar to that for the λ transition, whereas the analogous slopes obtained for pure $AgNO_3$ and for the alloys on cooling were numerically greater and not as well defined due to scatter, which could not be eliminated (also see below). For the 3 mole % $NaNO_3$ alloy, the λ transition was obtained, after the initial anneal, on both heating and cooling unless one cooled the sample very slowly—usually manually—to ~300°K, the lowest temperature obtainable with the DSC; then one could always obtain the first order transition on heating. Cooling at very low rates to 300°K with the instrument did not yield recognizable signals but it was expected that the signal would be quite diffuse at those rates; cooling to 300°K at higher rates was not possible since the DSC could not maintain the rate.

FIG. 1. Lambda transition temperatures, extrapolated to zero heating/cooling rate, for $AgNO_3$–$NaNO_3$ alloys. Uncertainties in temperature are denoted by error bars or by size of the symbols. The drawn line corresponds to an intercept, at pure $AgNO_3$, of 346°K and a slope of 2.0°/mole % $NaNO_3$.

Thus it can only be concluded here that the first-order transition on cooling occurs at >300°K for the 3 mole % NaNO₃ alloy. These experiments also clearly confirm that the λ transition is associated with the phase based on the high-temperature polymorph of AgNO₃. The first order transition temperature on heating decreases ~5°/mole % NaNO₃ upon alloying, whereas the decrease of transition temperature on cooling is more. The transition temperatures obtained here on heating agree well with the phase boundary given by Hissink in his 1900 paper (*10*), which appears to be the most recent comprehensive report on the AgNO₃–NaNO₃ system near equilibrium.

(iii) Other Results

The long but easy linear extrapolation of the λ transition temperatures in AgNO₃-rich alloys (Fig. 1) to pure NaNO₃ yields a λ transition temperature not far removed from the accepted value (e.g., 7) of ≈ 548 1/2°K. However, the slope suggested (7) for the variation of λ transition temperature in NaNO₃-base alloys is −1.3°/mole % AgNO₃ which appears to be different, beyond experimental errors, from the slope obtained here for the AgNO₃-base alloys. A 15 mole % AgNO₃; NaNO₃ alloy was prepared in the usual way and run in order to check the previous results (7). Acceptable signals were obtained, the extrapolations to zero rate were in accord with previous experience (7) and the value obtained for T_λ of this alloy—572 1/2 ± 2°K—was in acceptable agreement with the previous work (7).

The temperature corresponding to the onset of melting of pure AgNO₃ was determined, from several runs, as 482 ± 2°K which agrees with others' results (*6, 10*). Because of reaction with the aluminium capsule, only the first melting point was accepted for each AgNO₃ sample. There was some evidence of deterioration of the encapsulated AgNO₃-rich alloys in the solid state because of the generally poorer signals observed on rerunning samples. Hence almost all of the data here are from samples which were encapsulated immediately before the runs. It did not seem feasible to eliminate the initial anneals at 450°K because,

without the anneal, there were several closely spaced peaks, each presumably corresponding to the first-order transition, whereas, after the anneal, only a single well-defined peak was observed.

Most of the present experiments in the DSC were completed before the paper (*3*) by Mazieres and van't Hoff ("MvH") could be obtained and studied. Since MvH used samples of only ~1–6 mg, some further experiments were made with smaller AgNO₃ samples—of ca. 10, 5, and 2 mg. For these samples, the behavior on heating and on cooling was comparable to that observed for the larger samples studied previously, except for the 2 mg sample on cooling. For the 2 mg sample, the powder was insufficient to cover the bottom of the capsule and so the sample was encapsulated into disconnected portions. On cooling, several signals were usually observed and could usually be reproduced in subsequent cycles. No signals attributable to the λ transition could be obtained with pure AgNO₃ and, despite some effort, the first-order transition on cooling always occurred at temperatures above where the signal for the λ transition would be expected. No attempt was made to study large AgNO₃ crystals because, in the process of ensuring good thermal contact by encapsulation, it seemed almost certain that the crystals would have been deformed or fractured.

Further Discussion

The characteristics of the metastable phase transition in AgNO₃ investigated by MvH (*3, 11*) are quite similar to the characteristics of the λ transition studied here in AgNO₃-rich NaNO₃ alloys. MvH state that the transition is "practically without hysteresis" (*3*) which is in accord with the present experience; hysteresis of ~4° is evident in their (*3*) Figs. 3 and 4 but the rates of temperature change are not given. The X-ray diffraction work (*3*) by MvH satisfies the necessary condition for the transition being similar to that in NaNO₃ but is not sufficient to establish the similarity. The temperature of 80°C ≈ 353°K that MvH (*3*) give for the transition temperature (for samples of unspecified

purity) differs somewhat from the present result of 346 ± 2°K, which is from an extrapolation, to be sure, but one based on linear variation with alloying over some 20 mole % (Fig. 1). Too many details are lacking in the MvH report (3) to attempt a sufficiently detailed comparison with the present work.

From the experiments (13) of Kennedy and Schultz, there is good understanding of the growth characteristics for the first-order transition in AgNO₃. For nucleation, the present results corroborate the Kennedy-Schultz conclusions (13) on heating; on cooling, the present experience, especially with the smaller samples, definitely indicates heterogeneous nucleation. The temperatures of the first-order transition on cooling, from the present work, all lie in the range of appreciable growth rates (13). On the other hand, the growth rates at temperatures near the λ transition temperature are relatively low (and there is no indication (13) of any anomalous variation due to the λ transition). It is not understood why the high temperature phase of AgNO₃ could not be retained to low enough temperatures to show the λ transition in the present experiments, especially since others (1, 3, 5) have succeeded in metastably retaining the high temperature phase at room temperature. Some X-ray diffraction work showed that the transition from the phase based on the high temperature phase of AgNO₃ to that based on the low temperature AgNO₃ phase was also difficult to suppress at room temperature for the AgNO₃-rich NaNO₃ alloys.

X-Ray Diffraction Experiments and Results

Debye–Scherrer patterns were obtained for some of the AgNO₃–NaNO₃ alloys at room temperature using Ni-filtered CuKα radiation with a 114.6 mm diam CGR camera, the film being positioned in the Straumanis arrangement. Samples were put inside fused silica capillaries of 0.5 mm diam and 0.01 mm wall thickness, which were always sealed since the samples were hygroscopic. Usually the samples were prepared by being heated in the DSC at 16 deg min⁻¹ to 450°k, then ½ hr annealing followed by cooling at 16 deg

min⁻¹ to room temperature so that the λ transition temperature could be verified. In the effort to retain the metastable phases, the samples were not ground. Within a few hours after preparation, the samples had been mounted and were undergoing exposure. Unfortunately, and despite much effort, it was usually not possible to obtain patterns for the AgNO₃-rich alloys free of the low temperature orthorhombic phase based on AgNO₃. Mixtures of orthorhombic and trigonal phases were usually found for the 15, 20, and 25 mole % NaNO₃; AgNO₃ alloys (the latter was often annealed at 475°K in cognizance of Hissink's phase diagram (10)).

Lines on the films were many, of course, and usually not too sharp, doublets never being resolved. Linear corrections for shrinkage were made, when necessary. The high angle lines were indexed in conjunction with the Nelson–Riley extrapolations and methods of successive approximations used in determining the lattice parameters. Results for the trigonal structures in these alloys are summarized in Table I (referred to an hexagonal unit cell). For 20 mole % NaNO₃; AgNO₃ samples in which no traces of the orthorhombic phase were discernable, Table II shows the d-spacings, visual intensities and indices for lines on the Debye–Scherrer films (many of the very very weak high angle lines could not be indexed with confidence and have been omitted). It is especially to be noted (Table II) that the (11.3) line has been detected thus lending credence to the widely expected isomorphism with the low temperature NaNO₃ phase.

The lattice parameters for NaNO₃ (Table I) agree with the standard values (14) and the lattice parameters (Table I) for the AgNO₃-rich NaNO₃ alloys seem compatible with the values (1, 5) for pure AgNO₃. With respect to linear variations of c and a with composition between NaNO₃ (14) and AgNO₃ (1, 5), the present values (Table I) show positive deviations for both c and a in the AgNO₃-rich alloys and a positive deviation for c in the NaNO₃-rich alloy. It is likely that the different effects of alloying upon lattice parameters for the AgNO₃-rich and NaNO₃-rich alloys, respectively, are intertwined with the different

TABLE I

LATTICE PARAMETERS FOR TRIGONAL STRUCTURES (REFERRED TO HEXAGONAL UNIT CELL)
IN $AgNO_3$–$NaNO_3$ ALLOYS

Composition	c(A)	a(A)	c/a
$NaNO_3$	16.83 ± 3	5.070 ± 5	3.319 ± 9
15 mole % $AgNO_3$; $NaNO_3$	16.87 ± 2	5.077 ± 5	3.323 ± 7
25 mole % $NaNO_3$; $AgNO_3$	16.686 ± 6	5.149 ± 1	3.2406 ± 18
20 mole % $NaNO_3$; $AgNO_3$	16.694 ± 10	5.152 ± 3	3.2403 ± 40

slopes for λ transition temperature vs composition. Obviously, though, lattice parameter measurements at temperatures near the transitions would be more useful than room temperature data in this question. It should also be noted that the variations of lattice parameters with temperature are undoubtedly more complex near the λ transition in $AgNO_3$

TABLE II

D-SPACINGS, VISUAL INTENSITIES AND INDICES (HEXAGONAL UNIT CELL) FOR LOWER ANGLE X-RAY DIFFRACTION LINES FROM 20 MOLE % $NaNO_3$; $AgNO_3$ ALLOY

d(Å)	Visual intensity[a]	$kh\cdot l$
3.87	S	01·2
3.01₈	VS	10·4
2.75₅	M	00·6
2.55₂	S	11·0
2.31₈	VVW	11·3
2.13₆	S	20·2
1.95₀	S	02·4
1.87₇	VS	01·8, 11·6
1.64₀	S	12·2
1.55₅	S	21·4
1.51₆	VW	20·8
1.47₉	W	03·0
1.306	M	12·8
1.21₈	W.	11·12
1.18₂	W	21·10
1.16₅	VVW	22·6
1.061₆	VVW	31·8
1.013	VVW	10·16, 30·12
0.97₁	VVW	12·14
0.917	VVW	14·6

[a] S = strong, M = medium, W = weak; V = very.

and its alloys, as for $NaNO_3$ (e.g., 15) than is currently suggested by Levin's exploratory work (5).

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