Inverse Isotope Effect on the Melting Temperature of $LiNO_3$

Takehiko Hidaka

Electrotechnical Laboratory, MITI, 1-1-4, Umezono, Tsukuba, Ibaraki 305, Japan

Arnold Lundén

Department of Physics, Chalmers University of Technology, S-41296 Göteborg, Sweden

An inverse isotope effect on the melting temperature, T_m, of lithium nitrate has been observed: T_m is by 0.7 °C higher for a sample with 98.6% ^6Li than for one with 92.6% ^7Li. The abnormal sign of the isotope effect on T_m has already previously been found in fractionation experiments. Our results are in agreement with Holmberg's finding for T_m of $LiNO_3 \cdot 3H_2O$ (30 °C) that the isotope effect is inverse for $^6Li-^7Li$ but normal for H-D. Different types of experimental methods have been compared also for lithium sulfate, where a normal isotope effect has been found for both T_m (860 °C) and T_c (577 °C), the temperature of a monoclinic-cubic phase transition. Otherwise, nonhydrogen isotope effects at solid-solid transitions are usually inverse for displacive transitions, or nearly zero for order-disorder transitions.

I. Introduction

Generally the melting temperature, T_m, increases with the mass of the involved isotopes. For example, T_m is 0 °C for H_2O while it is 3.82 °C for D_2O. Such an isotope shift is to be expected because light isotopes show larger thermal fluctuations than heavy ones. Thus, at a certain temperature the long-range lattice ordering of the solid state is destroyed more effectively by thermal fluctuation in a crystal rich in light isotopes than in one rich in heavy isotopes. Therefore the sign of the isotope effect on T_m has been predicted to be the same as for water for all materials including metals (normal isotope effect) [1–3]. However some exceptions were discussed already in the late thirties. Thus for methane [4], hydrogen sulfide and hydrogen selenide [5] the isotope effect on the melting temperature is inverse, while it is normal for the five investigated solid-solid transitions (two for hydrogen sulfide and hydrogen selenide and one for methane) [5, 6].

In principle, isotope effects can be studied in two different ways. One is to prepare two samples that do not have the same isotopic composition and to measure the property in question for them. The other is to start with a sample with natural isotope composition and determine the isotope fractionation that can be obtained by means of some physical or chemical pro-

cess. The studies mentioned above [4–6] were performed in these first way. The detection of an inverse isotope effect on the critical temperature of superconductivity of metals has played an important role for the understanding of superconductivity [7]. Hidaka and Oka have recently studied non-hydrogen isotope effects for various types of solid-solid phase transitions [8–10]. The phase transition temperature, T_c, was measured for samples with different isotope compositions. The result was that either there was no significant effect (the upper limit being of the order of 0.2 °C for order-disorder type transitions) or that T_c was higher in ceramic samples with a high abundance of light isotope for displacive-type transitions (inverse effect). It is of interest in this connection to mention that Goodrich has found that there is no significant lithium isotope effect for the superconducting transition of $LiTiO_2$ [11].

Regarding isotope fractionation at phase transitions, a couple of studies has concerned isotope effects in some hydrates of lithium salts. Thus, ^6Li was slightly enriched in the solid phase when some hydrates were crystallized [12]. Partial phase diagrams have been determined for lithium nitrate-water by Holmberg [13]. The melting point (30 °C) was found to be 1.1 °C higher for $LiNO_3 \cdot D_2O$ than for $LiNO_3 \cdot H_2O$, and 0.22 °C higher for $^6LiNO_3 \cdot H_2O$ than for $^7LiNO_3 \cdot H_2O$. Thus, these two isotope effects have opposite signs.

Jansson and Lundén obtained a slight but significant fractionation of ^6Li and ^7Li at the melting point

of LiNO₃ (about 260 °C) by means of two related techniques, namely segregation during normal freezing and zone melting [14]. It was estimated that T_m was about 0.03 °C higher for ⁶LiNO₃ than for ⁷LiNO₃, i.e. the isotope effect had the same sign for anhydrous lithium nitrate as for the hydrate. (The investigations [13] and [14] had been performed independently.)

Lundén et al. have also demonstrated that an isotope fractionation can be obtained for Li₂SO₄ at both T_m and the monoclinic-cubic phase transition temperature, T_c, i.e. at about 860 °C and 577 °C, respectively [15, 16]. Segregation during normal freezing as well as zone melting were applied, and it was found that both transitions occurred at a lower temperature for ⁶Li₂SO₄ than for ⁷Li₂SO₄. On the other hand, Lundén et al. could not obtain any significant fractionation of lithium isotopes with the two mentioned techniques at T_m of LiF and LiCl, or at $T_c = 518$ °C of LiNaSO₄ [16].

The examples given above show that normal as well as inverse isotope effects have been detected on solid-solid and solid-liquid phase transitions, and that different experimental techniques have been used. We have considered it important to investigate a few compounds with more than one technique. Regarding nonhydrogen isotope effects, a comparison can readily be done for the melting of lithium nitrate, for which the isotope effect is inverse according to the above-mentioned fractionation experiments.

This paper reports a direct measurement of the ⁶Li–⁷Li isotope shift of T_m of LiNO₃. Several other materials, such as <u>Li</u>₂SO₄, Na<u>N</u>O₃ and Na<u>Cl</u>, were also tested to see whether any of the underlined elements showed the inverse isotope effect found for T_m of LiNO₃.

II. LiNO₃

LiNO₃ enriched in ⁶Li was obtained as follows: 98.6% ⁶Li (rest is ⁷Li) enriched (nominal data) Li₂SO₄ was supplied by ISOTEC Inc. LTD. U.S.A. (Lot No. MT-0695). We denote it hereafter as ⁶Li₂SO₄. Natural Li has 92.58% ⁷Li. We denote it as ⁷Li. ⁷Li₂SO₄ for a reference was supplied by Furu-Uchi Chemical Co. LTD. (Lot No. 47941; chemical impurity content < 0.1%). Ba(NO₃)₂ was also supplied by Furu-Uchi Chemical Co. LTD. (Lot No. 262201); chemical impurity content < 0.01%). Stoichiometric amounts of solutions of ⁶Li₂SO₄ and Ba(NO₃)₂ were mixed. BaSO₄
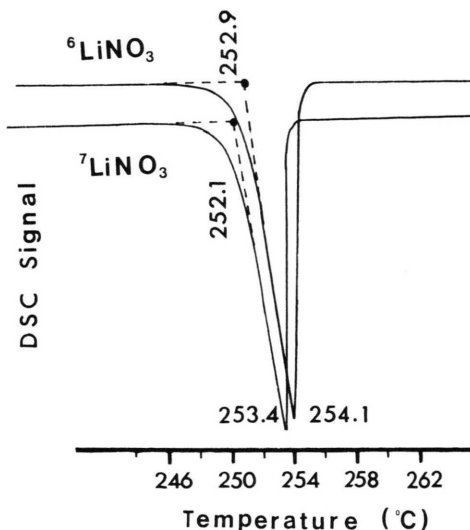
Fig. 1. DSC signals for the melting of ⁶LiNO₃ and ⁷LiNO₃. T_m is about 0.7 °C higher for ⁶LiNO₃ than for ⁷LiNO₃, i.e. the isotope effect is inverse. The resolution of T_m is better than 0.2 °C.

precipitated and the remaining aqueous solution contained only ⁶LiNO₃. ⁶LiNO₃ polycrystals were obtained by slow evaporation of the aqueous solution. By the recrystallization the material was thus purified enough to determine the isotope shift of T_m. We also obtained ⁶LiNO₃ as a reference from natural Li₂SO₄ with the same method as for ⁶LiNO₃. T_m of ⁶LiNO₃ and ⁷LiNO₃ were determined with a DSC (differential scanning calorimetric) apparatus, Seiko model DSC 300. The sample weight was 3.5 mg for ⁶LiNO₃ and 3.6 mg for ⁷LiNO₃. The temperature was increased at a rate of 2 °C/min. The results are shown in Figure 1. The peaktop temperature of the DSC signal of ⁶LiNO₃ (254.1 °C) is about 0.7 °C higher than that of ⁷LiNO₃ (253.4 °C), and the knee point (melt onset temperature) of ⁶LiNO₃ (252.9 °C) is 0.8 °C higher than that of ⁷LiNO₃ (252.1 °C). The error range for this temperature difference is of the order of 0.2 °C. We repeated the DSC measurements three times to define these T_m for ⁶LiNO₃ and ⁷LiNO₃. Every repeating gave coincident results for the respective materials.

The same sign has thus been found for the isotope effect on T_m, independent of whether it is measured separately for two isotope abundances, or if a temperature difference is calculated from an observed isotope fractionation [14]. In the latter case it was estimated that the isotope effect lies in the range 0.02 to 0.04 °C [14], which is lower than what the above-mentioned
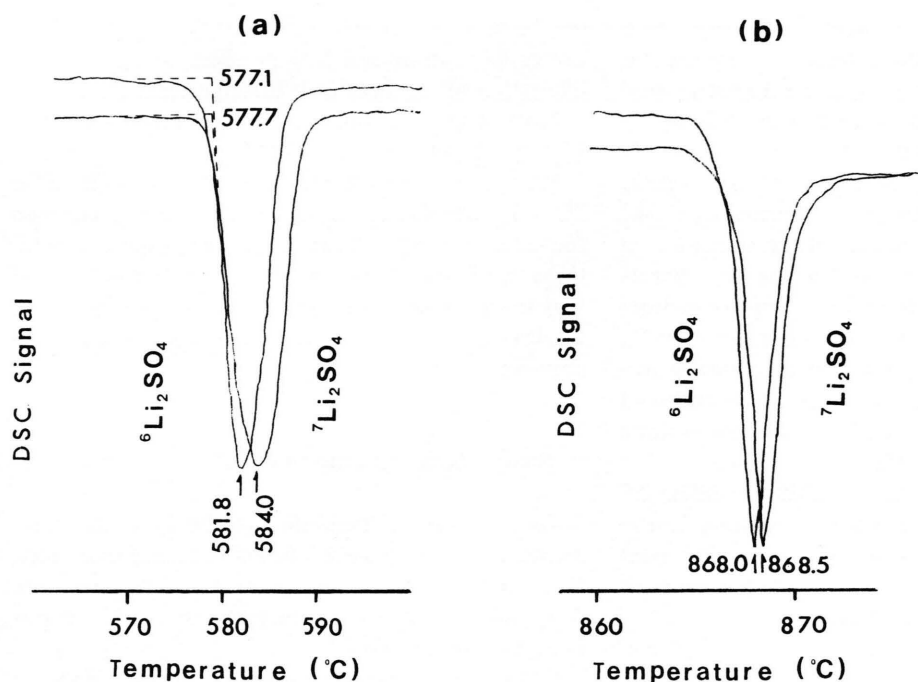
Fig. 2. DSC signals for lithium sulfate at a structural phase transition, T_c, near 580 °C (a), and for melting, T_m near 870 °C (b). The isotope effect is normal in both transitions, i.e. the transition occurs at a lower temperature for the light isotope. For T_c the recorded difference is 0.6 °C for the onset temperature, but about 2 °C for the peak temperature. The difference is about 0.5 °C for T_m.

temperature measurements give. It might be mentioned that deviations from the assumed ideal conditions tend to reduce the fractionation of isotopes during an experiment. It is in principle possible to achieve very large isotope fractionations by repeating the zone melting procedure many times, but there might be considerable complications in the case considered because the volume of $LiNO_3$ increases by 21% when the salt melts [5].

III. Li_2SO_4

As mentioned above, normal isotope effects for Li_2SO_4 on both T_c and T_m were found in fractionation experiments [15, 16], and we decided to measure the isotope shift for both transitions.

$^6Li_2SO_4$ and $^7Li_2SO_4$ were obtained from ISOTEC Inc. and Furu-Uchi Chemical Co., respectively; see above. The samples were recrystallized from their aqueous solutions. The sample weight for the DSC measurements was in both cases about 6 mg. The DSC signals are shown in Fig. 2, where (a) corre-

sponds to the structural transition near 580 °C, while (b) is for melting near 870 °C. For the structural transition of $^6Li_2SO_4$, the peaktop is at 581.8 °C (and the onset temperature at 577.1 °C), whereas the corresponding temperatures for $^7Li_2SO_4$ are 584.0 °C and 577.7 °C, respectively. The peaktop temperatures for melting are 868.0 °C for $^6Li_2SO_4$ and 868.5 °C for $^7Li_2SO_4$.

For both transitions we thus find that the direct measurement gives the same sign for the isotope effect as calculations from fractionation experiments do. In the original evaluation of the latter experiments for T_c three zone refining experiments were considered. The number of zone passes was 10 in one of these, while the other two were single pass experiments. The temperature difference is about 0.08 °C if the two single-pass experiments are considered, while it is of the order of 0.8 °C, if one considers only the 10-pass experiment [14, 15]. The latter is close to the 0.6 °C difference between the onset temperatures of Fig. 2 (a), where the peak temperatures differ by 2.2 °C.

It is of importance that we have confirmed the sign of the isotope effect on T_c of Li_2SO_4, since the inverse

isotope effect is far more common for nonhydrogen isotope effects on solid-solid transitions in ionic compounds. Thus, inverse isotope effects have been found for a number of dielectric (ceramic) crystals [8, 9], while no significant isotope effects were found for N or Li in the above-mentioned studies of ALiSO$_4$ (A = Rb, Cs, NH$_4$) [10]. This is not surprising if one considers the very special nature of the transition of Li$_2$SO$_4$; it might be sufficient to mention here that its entropy is 3.7 times larger than the entropy of melting [17]. Similar solid-solid transitions occur in LiNaSO$_4$ and LiAgSO$_4$, and one might expect a similarity also when it comes to isotope effects, but, as mentioned above, a preliminary check did not show any isotope effect on T_c for LiNaSO$_4$ [16].

Regarding the isotope effect of lithium sulfate on T_m, a precise evaluation of the fractionation experiments was not possible so far. The only numerical result is thus the difference of 0.5 °C between the peak temperatures shown in Figure 2 (b).

IV. Comparison with Hydrates of Lithium Salts

As mentioned in the introduction, Holmberg [13] has studied phase equilibria for the system of lithium-nitrate-water, for which only one hydrate is known, namely LiNO$_3$ · 3 H$_2$O with T_m 30 °C. When H$_2$O is substituted by D$_2$O, the curve for LiNO$_3$ · 3 H$_2$O is shifted by slightly more than 1 degree upwards for the whole concentration range (7.7 to 29 mol% LiNO$_3$), with an isotope effect of 1.1 °C on the congruent T_m. A cross-over was obtained when the ^{6}Li–^{7}Li isotope effect was studied. Thus for temperatures above 10 °C (more than 13 mol% LiNO$_3$), the curve for ^{6}LiNO$_3$ · 3 H$_2$O lies above that for ^{7}LiNO$_3$ · 3 H$_2$O, while the displacement is in the opposite direction for lower temperatures. The congruent T_m is by 0.22 °C higher for the light isotope, i.e. the lithium isotope effect is inverse for the hydrate.

The phase-diagram study by Holmberg is in agreement with the enrichment of ^{6}Li that de Vries found for the first fraction of LiNO$_3$ · 3 H$_2$O that crystallized from an aqueous solution [12]. He also found an enrichment of ^{6}Li for the crystallization of anhydrous halides (LiCl, LiBr) and their hydrates. From a comparison with the phase diagrams [18], it seems likely that crystals of LiCl · H$_2$O, LiCl · 2 H$_2$O, LiCl · 3 H$_2$O and LiBr · 2 H$_2$O were obtained. These observations

can be taken as an indication that the mentioned hydrates have an inverse isotope effect on T_m. It seems likely that all of them melt incongruently [18].

No isotope fractionation for the crystallization of Li$_2$SO$_4$ · H$_2$O was detected [12].

We tried to determine the latent heat of melting for ^{6}LiNO$_3$ · nH$_2$O and ^{7}LiNO$_3$ · nH$_2$O. However, when the salts were crystallized from their respective solutions, we found that n deviated slightly from 3, and that there seems to be some difference depending on whether the light or the heavy isotope was the abundant one.

V. Some Checks on Other Crystals

To confirm the credibility of the DSC measurements, we checked the resolution limit and reproducibility of T_m and T_c of several crystals. The resolution of T_c and T_m is expected to be better than 0.2 °C in our DSC measurements.

Figure 3 (a) shows the results obtained for NaNO$_3$. Na^{15}NO$_3$ was supplied by CEA-ORIS Co. (Lot No. NMM 225; stated 96.1% of ^{15}N), and natural NaNO$_3$ (99.6% ^{14}N) by Furu-Uchi Co. LTD. The salts were recrystallized from aqueous solutions. The sample weighed about 4.5 mg, and the temperature rising rate was 10 °C/min. Very weak normal isotope shifts are indicated for both T_c and T_m, 0.2 °C and 0.3 °C, respectively (Figures (a) and (b)), but only the latter shift is considered to be significant.

Isotope enriched sodium chlorides were supplied by Oak Ridge National Laboratory, U.S.A. The Lot No. of Na^{35}Cl was 40-0942 (99.35% ^{35}Cl), and that of Na^{37}Cl was 38-0105-A (98.21% ^{37}Cl). The salts were recrystallized from aqueous solutions in order to reduce the chemical impurity. Both samples weighed 3.5 mg, and the temperature rising rate was 2 °C/min. As shown in Fig. 4, the melting point is about 0.5 °C lower for the sample enriched in ^{35}Cl than for the one enriched in ^{37}Cl.

Except for LiNO$_3$, all materials show normal isotope effects on T_m. However, we are confident that our results for LiNO$_3$ are not due to some error in our experiment. LiNO$_3$ is an abnormal material in its latent heat and the NO$_3^-$ structure in it. The latent heat of melting of LiNO$_3$ is about 2 times larger than of other nitrates such as KNO$_3$, NaNO$_3$ and so on [19]. Moreover, the structure of NO$_3^-$ in LiNO$_3$ differs somewhat from other nitrates [20, 21].
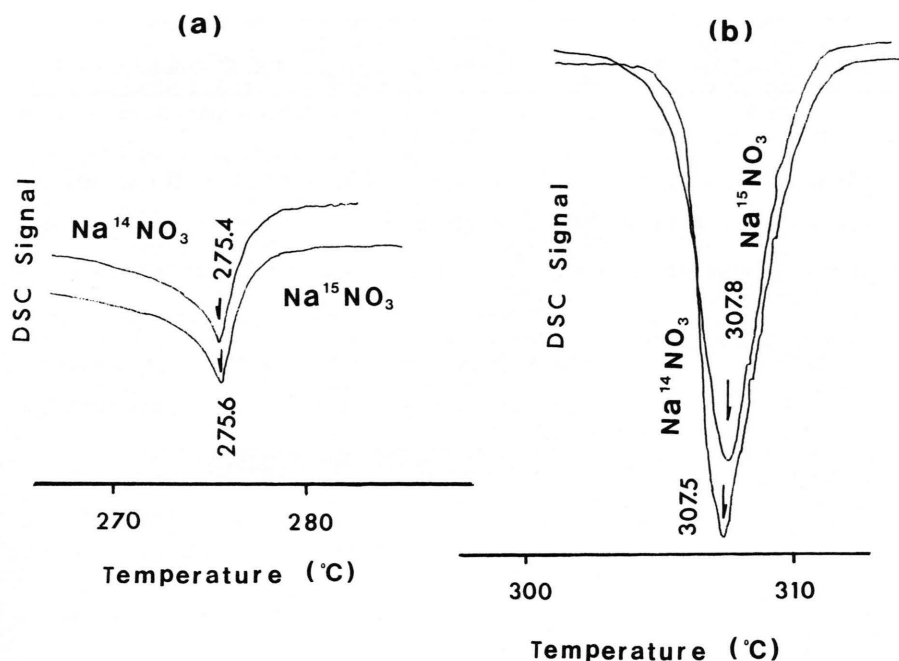
(a)

(b)

Fig. 3. DSC signals for $Na^{14}NO_3$ and $Na^{15}NO_3$ at a structural phase transition, T_c, near 275 °C (a), and at the melting point, T_m (b). Normal isotope effects are observed, and the recorded temperature differences are 0.2 °C and 0.3 °C, respectively.

Fig. 4. DSC signals for $Na^{35}Cl$ and $Na^{37}Cl$ at the melting point where the isotope effect is normal.

VI. Conclusion

Our conclusion is that the melting point of $^6LiNO_3$ is higher than that of $^7LiNO_3$, while the normal isotope effect on T_m has been found for other materials. It is also proven that a solid-solid phase transition occurs at a lower temperature for $^6Li_2SO_4$ than for $^7Li_2SO_4$, which, in turn, deviates from what has been observed in some other salts and oxides for non-hydrogen isotope effects of solid-solid transitions. It is now a challenge to find the physical reason of the reported isotope effects. A starting point might be theories of melting [22–25].

Acknowledgement

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