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Isotope effects on structural phase transitions in several sulfates

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N and Li isotope effects on structural phase transitions in several sulfates, $(\underline{N}\underline{H}_4)_2SO_4$, $\underline{N}H_4\underline{Li}SO_4$, $Rb\underline{Li}SO_4$, and $Cs\underline{Li}SO_4$, are reported (underlined elements are those for which isotopes were substituted). No clear isotope effect has been observed in any of the sulfates studied. This result is similar to that obtained for $NaNO_2$, but in contrast to those obtained in other materials such as $BaTiO_3$.

The study of not only hydrogen—but also nonhydrogen—isotope effects on structural phase transitions in dielectric materials is very important to clarify the mechanisms of the transitions in relation to the phonon dynamics. From the viewpoint of classical lattice dynamics, the critical temperature, T_c (hereafter we will use T_c for all types of transitions), of structural phase transitions should *decrease* with the introduction of *lighter* isotope because of the larger thermal fluctuation present in light-isotope-enriched crystals.[1-3]

Recently, the author has reported nonhydrogen-isotope effects in many dielectric materials.[4,5] The essential point is that for displacive-type structural phase transitions such as $BaTiO_3$, T_c rises with the introduction of a lighter isotope. For example, ^{46}Ti-enriched $Ba^{46}TiO_3$ showed T_c to be about 132 °C, whereas ^{50}Ti-enriched $Ba^{50}TiO_3$ showed T_c about 111 °C; T_c is about 20 °C higher in the light ^{46}Ti-enriched $BaTiO_3$ than in the ^{50}Ti-enriched $BaTiO_3$.[4] This surprising fact is contrary to the prediction based on the classical theory. The force constant of the transverse-optical phonon in $BaTiO_3$ must be affected by the replacement of the Ti isotope, because $BaTiO_3$ shows a large Ti-isotope effect in its T_c. Equation (1) shows the force constant, k_{TO}, of the soft transverse-optical phonon relating to the ferroelectric phase transition;

$$\mu\omega_{TO}^2 = k_{TO} = k_{SR} - k_{LR} + f(T) , \quad (1)$$

where μ is the reduced mass of the soft phonon relating to the phase transition, ω_{TO} is the frequency of the soft phonon, k_{SR} is the short-range force constant (which is assumed to be independent of the isotope mass, as discussed later), k_{LR} is the long-range force constant (which is assumed to be affected by isotope mass), and $f(T)$ is a monotonic function of the temperature, T, arising from the nonlinearity of the lattice vibration. To explain the observed isotope effect in $BaTiO_3$ and other systems, it must be assumed that, at a same temperature, k_{LR} of the *light*-isotope-enriched material is *greater* in magnitude than that in the *heavy*-isotope-enriched one. The force constant of optical phonons in $BaTiO_3$ seems *soft* (the term "soft" means here that the force constant is influenced by the isotope mass and the temperature).

$NaNO_2$ was, however, a unique ferroelectric crystal in which the N-isotope effect (by heavy ^{15}N introduction) could not be observed within experimental error (Ref. 5). $NaNO_2$ is believed to be a representative crystal which shows a pure order-disorder-type phase transition. The phase transition in $NaNO_2$ is due to the dipole-dipole interaction. $NO_2{}^-$ ions in $NaNO_2$ have large permanent dipoles. The dipole on $NO_2{}^-$ seems not to depend upon the N-isotope mass. This means that the chemical-bond strength between N and O (due to short-range force only) in $NO_2{}^-$ is very stable (hard) regardless of the isotope mass and temperature. The short-range force constant, k_{SR}, of the soft phonon in $BaTiO_3$ is therefore assumed not to be affected by isotope mass and temperature, in analogy with the short-range force of $NO_2{}^-$ in $NaNO_2$.

The aim of this paper is to study such a weak N-isotope effect, as observed in $NaNO_2$, in several sulfates, which are believed to show order-disorder-type phase transitions. In the past study, only a very weak isotope effect in $NaNO_2$ was observed; the possibility that this observed weak isotope effect in $NaNO_2$ may be due to some other spurious impurity cannot be ignored. Thus, it is strongly desirable to confirm the isotope effect in other materials with order-disorder-type transitions. If the phase transitions in sulfates originate from the order-disorder interaction, it is then expected that the isotope effects in them will be weak, as they are in $NaNO_2$.

The materials studied are $(\underline{N}\underline{H}_4)_2SO_4$, $\underline{N}H_4\underline{Li}SO_4$, $Rb\underline{Li}SO_4$ and $Cs\underline{Li}SO_4$. Underlined elements (N, H, and Li) are those for which isotopes were substituted. $(NH_4)_2SO_4$, ammonium sulfate, henceforth designated as AS, shows a ferrielectric phase transition at about −50 °C.[6,7] The deuteron isotope effect in AS is very weak[7] compared to other materials with hydrogen bonds, such as KDP. In deuterated AS, T_c rises by an amount of about 0.5 °C. The weak hydrogen-isotope effect in AS suggests to us that the isotopic-mass effect in other elements such as N will be also weak. Hence, the nonhydrogen-isotope effect in AS is very interesting.

The ^{15}N-enriched AS powder was supplied by ISOTEC Inc. (Lot No. LR1726). The ^{15}N-enrichment degree was 99.3%; it was checked by an ir absorption measurement in our laboratory; to be in agreement with the nominal amount. We fabricated two different types of AS samples with ^{15}N isotopes using an aqueous-solution method.

One was ^{15}N fully enriched AS, and the other 50%-enriched $^{14}NH_4\,^{15}NH_4SO_4$. The latter was recrystallized from the mixture of two stoichiometric powders, $(^{14}NH_4)_2SO_4$ and $(^{15}NH_4)_2SO_4$. In AS, NH_4^+ ions can occupy two different crystallographic positions. We cannot rule out the possibility that in AS light $^{14}NH_4^+$ occupies one of the positions and heavy $^{15}NH_4^+$ occupies the other different crystallographic position (isotope ordering).[8,9] In such a crystal, several characteristics, for example, T_c can show values departing from the *average* of $(^{14}NH_4)_2SO_4$ and $(^{15}NH_4)_2SO_4$. Thus, it is worthwhile to study the properties of $^{14}NH_4\,^{15}NH_4SO_4$.

The T_c of those AS were determined using the differential scanning calorimetry (DSC) measurement. The apparatus used was a Seiko model DSC 200. Firstly, we checked the resolution and repeatability of the DSC system, using normal AS and deuterated AS (DAS). The DAS was supplied by Cambridge Isotope Laboratories (Lot. No. F-1307). The enrichment degree of D was 98%. For DAS, we used heavy water (with 99.96% D_2O), supplied by ISOTEC Inc. (Lot No. NS0590), as the solvent in the recrystallization process. Also, we fabricated normal AS as a reference material using an aqueous-solution method, and using normal H_2O.

The DSC data of the four samples are shown in Fig. 1. The weights of the samples measured were all 1 mg, and the temperature rising rate was 1 °C/min, for all samples. We observed a clear difference of 0.6 °C between AS and DAS. From the line width of the DSC signals, it was estimated that the relative resolution of T_c, $\delta T_c / T_c$, was about 0.25% in the sulfates. However, no isotope shift was observed within experimental error between reference material and ^{15}N-enriched two samples.

In conclusion, AS does not show any N-isotope effect. It is consistent with the very weak deuteron isotope effect in DAS. In DAS, the change of the ND_4 mass is 4 (in a.u.) from NH_4. The mass change due to ^{15}N introduction is 1 (a.u.). The T_c shift due to ^{15}N introduction can be expected to be a fourth of that of DAS (about 0.15 °C), if the effects of D and N introductions give the same mass-change effect only. Also, a very weak N-isotope effect in AS is in fair agreement with that in $NaNO_2$. The mechanism responsible for the phase transition in AS is surely similar to that in $NaNO_2$ (ordering of permanent dipoles).

NH_4LiSO_4 (ALS) shows two transitions at 15 and 187 °C.[10,11] Between these two transition temperatures, it shows a ferrielectric phase, as well as a low-temperature phase, similar to AS. The N and Li isotope effects were studied for these two transitions. Firstly, we introduced ^{15}N. Stoichiometric powders of $(^{15}NH_4)_2SO_4$, noted above, and Li_2SO_4 (including natural Li; its atomic mass is 6.941 a.u.; hereafter it will be referred to as ^{7}Li) were resolved into normal water (H_2O) and recrystallized. Also, normal (with ^{14}N) ALS was fabricated as a reference, by the same method. For ^{6}Li introduction, ^{6}Li-enriched Li_2SO_4 was used as the starting Li sulfate. The ^{6}Li-enriched Li_2SO_4 was supplied by ISOTEC Inc. (Lot

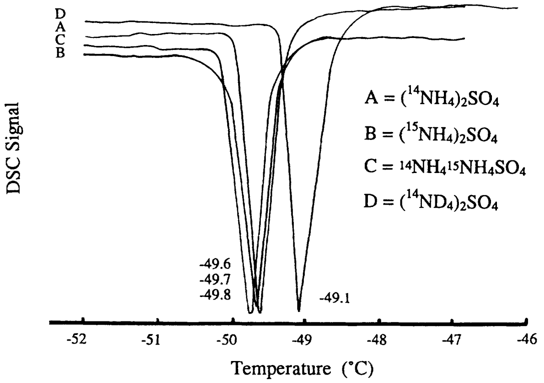

FIG. 1. DSC (differential scanning calorimetry) signals for $(^{14}NH_4)_2SO_4$ (reference), $(^{15}NH_4)_2SO_4$, $^{14}NH_4\,^{15}NH_4SO_4$, and $(^{14}ND_4)_2SO_4$. The apparatus was a Seiko model DSC-200. The weights of the samples were 1 mg and the temperature rising rate was 1 °C/min. Deuterated $(ND_4)_2SO_2$ showed a 0.6 °C higher DSC peak, than those of other samples, whereas there is no difference between ^{14}N- and ^{15}N-enriched samples. The relative resolution limit, $\delta T_c / T_c$, was 0.25%.

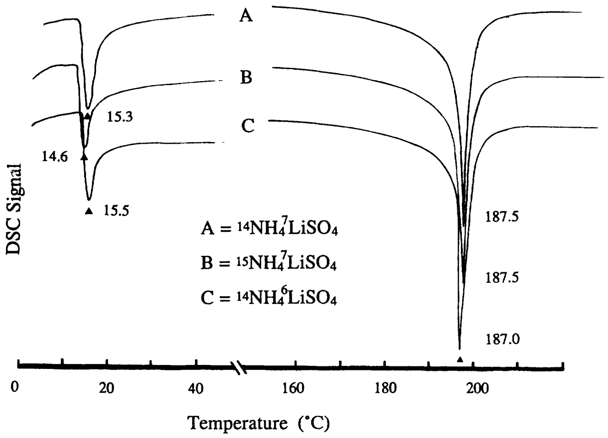

FIG. 2. DSC signals of $^{14}NH_4\,^7LiSO_4$, $^{15}NH_4\,^7LiSO_4$, and $^{14}NH_4\,^6LiSO_4$. No N- and Li-isotope effects were observed between them. The weights of the samples were 4 mg and the temperature rising rate was 10 °C/min.

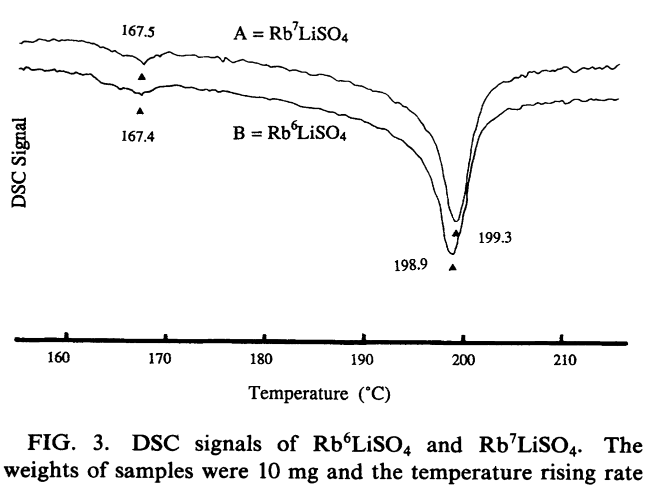

FIG. 3. DSC signals of Rb^6LiSO_4 and Rb^7LiSO_4. The weights of samples were 10 mg and the temperature rising rate was 10 °C/min. No Li-isotope effect was observed.

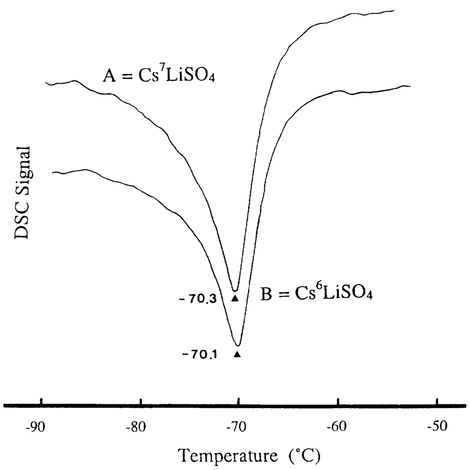

FIG. 4. DSC signals of Cs^{6}LiSO$_4$ and Cs^{7}LiSO$_4$. The weights of the samples were 10 mg and the temperature rising rate was 10 °C/min. ^{6}Li-enriched CLS shows about a 0.2 °C higher T_c than the ^{7}Li-enriched one.

No. MT 0695). The nominal value of ^{6}Li enrichment was 98.6%. Figure 2 shows the DSC signals for the three types of ALS. The weights of these samples were all 4 mg, and the temperature rising rate was 10 °C/min. As in the case of AS, isotope effects could not be observed within the experimental error, for either N or Li.

RbLiSO$_4$ (RLS) shows very interesting successive transitions from over 200 °C to about 165 °C (Refs. 12 and 13). ^{6}Li-enriched RLS was recrystallized from aqueous solution with stoichiometric Rb$_2$SO$_4$, and ^{6}Li$_2$SO$_4$ discussed above. Also, we fabricated natural RLS with ^{7}Li, similarly to the ^{6}Li-enriched sample. We observed mainly two DSC peaks, shown in Fig. 3. The weights of the samples were 10 mg and the temperature rising rate was 10 °C/min. No Li isotope effect was observed on either peak.

CsLiSO$_4$ (CLS) is one of the famous materials showning a *ferroelastic* phase transition (acoustic phonon freezing) at about -70 °C.[14,15] Similarly to RLS, ^{6}Li- and ^{7}Li-enriched CLS were fabricated, separately, from aqueous solutions. The samples were recrystallized with three-time repeats of the recrystallization procedure. For these materials, no difference was observed between the respective DSC data. Figure 4 shows the DSC data near T_c. The weight of each sample was 10 mg and the temperature rising rate was 10 °C/min. No isotope effect was observed (isotope shift, $\Delta T_c = 0.2$ °C, is a half of the experimental error). All the results are summarized in Table I.

TABLE I. N and Li isotope effects on phase-transition temperatures, T_c, of several sulfates. Naturally available ^{7}Li and ^{14}N are defined as the reference isotopes. 0 means the effect is very weak (within experimental errors). The isotope shift ΔT_c means those from the T_c of reference materials. The Li-isotope effect in LiTaO$_3$ was given in Ref. 5, which was extremely larger than Li sulfates in this Brief Report.

Materials	Introduced isotope (%)	T_c (°C)	Isotope shift ΔT_c (°C)	Relative shift $\Delta T_c/T_c$ (%)
$(^{14}NH_4)_2SO_4$	^{14}N	-49.7		
	(Ref.)			
$(^{14}ND_4)_2SO_4$	^{2}D 98	-49.1	$+0.6$	$+0.27$
$(^{15}NH_4)_2SO_4$	^{15}N 99.3	-49.6	$+0.1$	0
$^{14}NH_4{}^{15}NH_4SO_4$	1/2 ^{15}N	-49.8	-0.1	0
$^{14}NH_4{}^7LiSO_4$	^{7}Li 92.6	15.3		
	(Ref.)	187.5		
$^{15}NH_4{}^7LiSO_4$	^{15}N 99.3	14.6	-0.7	-0.24
		187.5	0	0
$^{14}NH_4{}^6LiSO_4$	^{6}Li 98.6	15.5	$+0.2$	0
		187.0	-0.5	-0.1
Rb^{7}LiSO$_4$	^{7}Li 92.6	167.5		
	(Ref.)	199.3		
Rb^{6}LiSO$_4$	^{6}Li 98.6	167.4	-0.1	0
		198.9	-0.4	0
Cs^{7}LiSO$_4$	^{7}Li 92.6	-70.3		
	(Ref.)			
Cs^{6}LiSO$_4$	^{6}Li 98.6	-70.1	$+0.2$	$+0.1$
^{7}LiTaO$_3$	^{7}Li 99.99	656		
^{6}LiTaO$_3$	^{6}Li 99.16	670	$+14$	$+1.5$

In conclusion, isotope effects were not observed for either N or Li in all the sulfates studied. The result is in good agreement with NaNO$_2$. Thus, it is concluded that the mechanism responsible for the phase transitions in sulfates is similar to that in NaNO$_2$. In Table I, the Li-isotope effect in LiTaO$_3$ reported earlier[5] is also shown. The Li-isotope effect in LiTaO$_3$ is stronger than in the sulfates. Thus, the mechanism responsible for the phase transition in LiTaO$_3$ is expected to be completely different from sulfates. It is also concluded that the short-range force constant, k_{SR}, in Eq. (1) does not change with isotope replacement. The isotope effect on T_c in displacive materials is due only to the effect on k_{LR} in Eq. (1).

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