Superionic Phase Transition of (NH4)3H(SeO4)2 Studied by ESR of SeO3-

Superionic Phase Transition of $(NH_4)_3H(SeO_4)_2$ Studied by ESR of SeO_3^-

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Abstract

The superionic phase transition of $(NH_4)_3H(SeO_4)_2$ is studied by X band ESR within the phases II and III. On X-ray irradiation the unstable SeO_3^- radical is observed with $g_{//}$ = 2.004, $g_\perp$ = 2.015, $A_{//}$ = 624 œ, $A_\perp$ = 430 œ at 293 K (phase III) and $g_{//}$ = 2.0034, $g_\perp$ = 2.0144, $A_{//}$ = 614 œ, $A_\perp$ = 437 œ, at 308 K (phase II). The principal axis of hyperfine which tilts from a^* in the monoclinic phase III, aligns parallel to a^* in the trigonal phase II. This means all the SeO_4 tetrahedrons align parallel to a^* in the superionic phase. This structural rearrangement is responsible for the higher electrical conductivity in the phase II, because expanded and weakened O-H-O hydrogen bond helps the proton transfer more easily.

Key words: Superionic conduction, Triammonium hydrogen diselenate, ESR, Phase transition, Proton conduction

§ 1. Introduction

Triamonium hydrogen diselenate, $(NH_4)_3H(SeO_4)_2$ (abbreviated as TAHSe) undergoes a successive phase transition with five phases[1,2,3] as shown in Table I. Transition temperatures listed are determined by ESR and electrical conductivity. Each phase is denoted as I, II, III, IV and V by descending temperature after Osaka et al.[3] TAHSe is also a member of $A_3H(XO_4)_2$ type crystals which are often compared with each other to discuss the mechanism of structural phase transition, where A is alkali metal or NH_4

Table I. Phase transition of TAHSe.
F: ferroelectric. SI: superionic.

PHASE	V	IV	III	II	I
STATE	F				SI	SI
SYSTEM			monoclinic	trigonal	
SPACE G.			C2/c		
heating (℃)	−84.0	4.9	34.4	58.8	
cooling	−84.3	1.5	32.2	58.1	

and X is S or Se.   The phase V exhibits ferroelectric properties and M. Kamoun et al.[4] have shown that the ordering of HH_4^+ ions is the main origin of poralization occurence as well as the case in sulphate isomorph $(NH_4)_3H(SO_4)_2$ (abbreviated as TAHS).   Among $A_3H(XO_4)_2$ type crystals only the crystals which contain NH_4^+ exhibit the ferroelectric phase so far.

Recently the phases I and II have been characterized as the superionic proton conductor by Furukawa et al.[5,6]   Therefore it is also interesting in the viewpoint of proton semiconductor.   Among selenate crystals NH_4HSeO_4 and $(NH_4)_4H_2(SeO_4)_3$ are also known to exhibit the superionic phase and have drawn special attention.   In order to study the successive phase transition of THASe especially the superionic phase transition we conducted ESR measurement by X irradiation method.

As for TAHS and deuterated isomorph, ESR studies have already been reported[7-11].   Although ESR study often goes with the ambiguity which always makes a weak point, J. Minge and S. Waplak[8] have reported SeO_3^- redical sensitively probes the structural phase transition.   We briefly report the result of SeO_3^- radical especially within the phases II and III of TAHSe.   In comparison with the case in TAHS, TAHSe has more simple phase sequence with lower transition temperature which is convenient for the radical ESR and has an advantage of no need for introduction of impurity or mixed crystal.

§ 2.   Experimental

Single crystals of TAHSe were grown in an electric refrigerator (about 6°C) by slow evapolation from aqueous solution containing a 3:1 mole fraction of $(NH_4)_2SeO_4$ and H_2SeO_4.

Crystals obtained were plates of elongated hexagonal shape with predominant face (100) and highly deliquescent.   Single crystals were identified by their crystal habit, X-ray photograph and their transition temperatures which agree well with the values reported.   The unique axis is chosen to b hence the polarization axis is a^* as P. A. Leclaire et al.[12] determined for TAHS.   Therefore a^* corresponds to c chosen by Suzuki et al.[13] and others.

On irradiation of X-ray (40 kV, 20 mA, about 1 hour) at room temperature the small crystal coloured in brown and faded away gradually in about a week at room temperature.   In accordance with the fading colour ESR signal intensity diminished.   At 30°C it was dificult to observe the signal approximately more than a day.   It was almost impossible to observe the signal in the phase I.   The spectrometer was a conventional X-band ESR with 100 kHz modulation.   The temperature was varied by blowing a controlled nitrogen gas.

§ 3.   Spectra in the phese II and III

The typical spectra at 300 K with a magnetic field approximately along (010) is
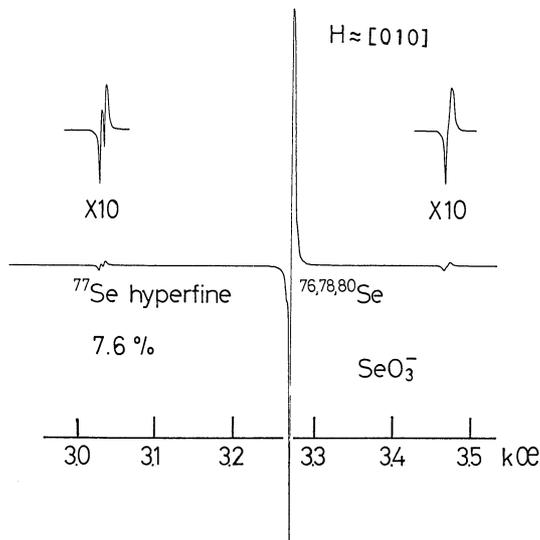
phase III (20 °C)

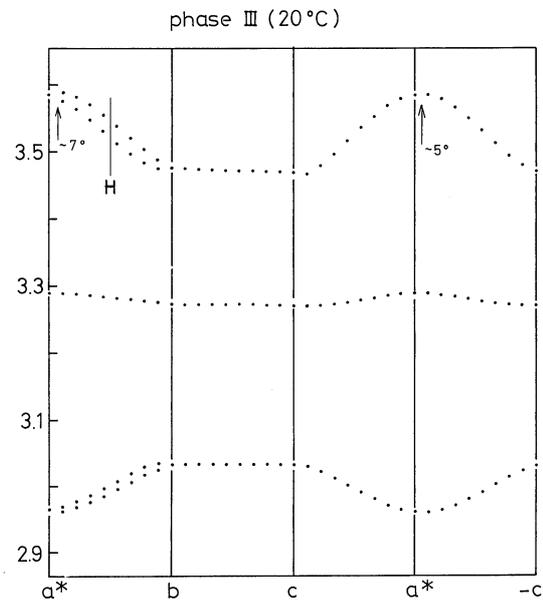Fig. 1. ESR Spectra at 300K with a magnetic field approximately along (010).

Fig. 2. The angular dependence of resonance field at 293K.

shown in Fig. 1. There exist two small doublets by hyperfine from ^{77}Se which has a spin 1/2 and a natural abundance of only 7.6%, and a overlapped strong center line of the other zero-spin nucleuses. The radical is assigned as SeO_3^- which is almost identical to the case of TAHS/SeO_4 by J. Minge and S. Waplak[8]. The spectra can be simply described by the following spin Hamiltonian

$$\mathscr{H} = \beta \cdot \boldsymbol{H} \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \boldsymbol{I} \cdot \boldsymbol{A} \cdot \boldsymbol{S}$$

phase II (35°C)

Fig. 3. The angular dependence of resonance field at 308K.

where $S=1/2$, $I=1/2$, β is a Bohr magneton, g is a spectroscopic splitting factor, A is a ^{77}Se hyperfine tensor and H is a magnetic field. The g-factor is calculated from the angular pattern of the center line, and the hyperfine tensor is easily estimated by the first order approximation. The parameters at 293 K (phase III) are $g_{//}=2.004$ $g_{\perp}=2.015$ $A_{//}=624$ œ $A_{\perp}=430$ œ. Fig. 2 shows the angular dependence of resonance field at the phase III (293 K). This pattern satisfies the point group 2/m (space group C2/c). The principal axis tilts from a^* by about 7° toward b and about 5° toward $-c$. Comparing this principal axis with bond axis in TAHS instead of TAHSe, because the
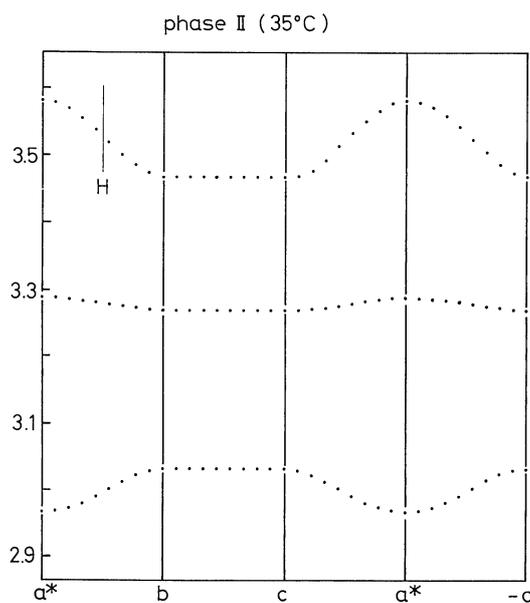
structure of TAHSe has not yet been reported, this direction coincides well with the direction of distorted SO_4 tetrahedron, namely the direction of bond axis from S to the longest O in TAHS. Although the radical SeO_3^- is a radiation damage center, this fact manifests that the principal axis of the radical well represents the direction of SeO_4.

Fig. 3 is the angular pattern in the phase II (308 K) which shows the principal axis coincide with a^* axis. The parameters are $g_{//} = 2.0034$, $g_{\perp} = 2.0144$, $A_{//} = 614$ œ, $A_{\perp} = 437$ œ. This means all the distorted SeO_4 tetrahedrons align their axis paralel to a^*.

§ 4. Temperature dependence

Fig. 4 shows the temperature dependence of spectra of higher hyperfine component where the magnetic field along H designated in Fig. 2. The temperature dependence of resonance field is plotted in Fig. 5. Reflecting the phase trnasition on heating from the phase V to II, the number of lines varied from 4 to 2 at IV-III transition and 2 to 1 at II-III transition. And at the transition V-IV there was no change of number. Corresponding to the first order transition, the coexistence of signal from both phases is
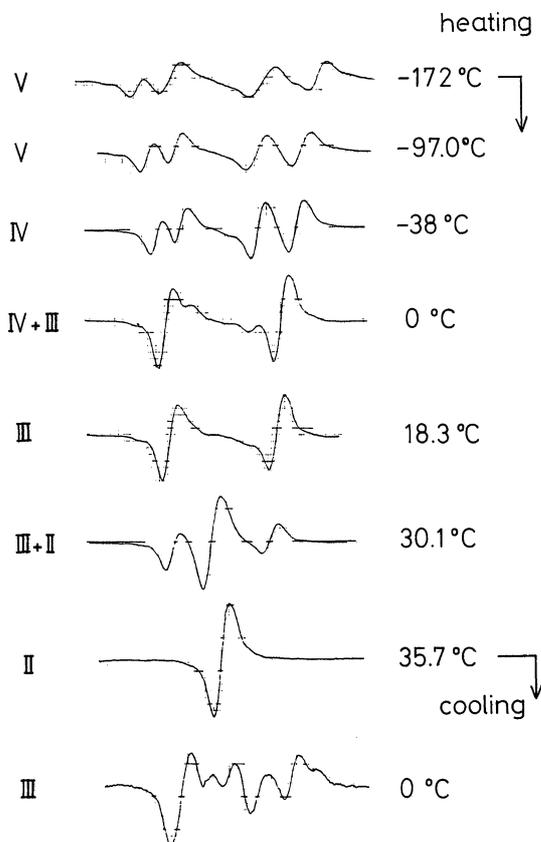

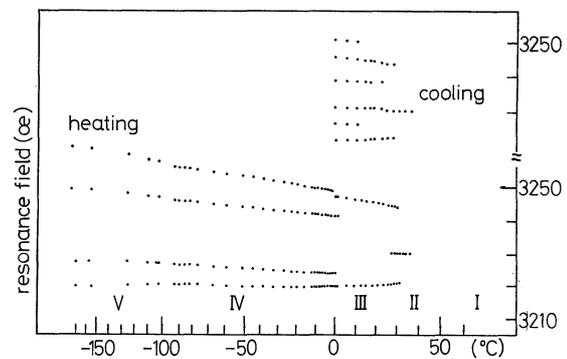Fig. 4. The temperature dependence of spectra of higher hyperfine component.

Fig. 5. The temperature dependence of resonance field of Fig. 4.

observed. Once the sample was heated up to the hase II then cooled down to the phase III, the number of lines tripled. This means the existence of three domains which appeared by cooling. This irreversibility due to domain generation also occured in the case of $TAHSe/VO^{2+}$ ESR as well as the case of $TAHS/VO^{2+}$. The domain generation is also confirmed by polarized microscope.

§ 5. Discussion

Although we have already determined the lattice parameters and the space group of TAHSe as C2/c in the phase III, the atomic coordinates have not yet been reported. So in order to discuss the result we adopt the structure data of TAHS by P. A. Leclaire et al.[12] at room temperature which corresponds to the phase III in TAHSe. The unit cell of TAHSe in the phase III is depicted schematically in Fig. 6. The longest bond axis Se-O(1) which corresponds to Se-O(2) by Suzuki tilts from a^* by 7.44° toward b and 4.74° toward $-c$. The direction agrees well the observed principal axis of the radical hence this radical well represents the orientation of SeO_4 terahedron. In the phase II, ESR signal manifests all the SeO_4 align parallel to a^* which makes a threefold axis in the trigonal system. As a result it is reasonable to think that O-H-O bond expands by a small amount through the rotation of SeO_4 tetrahedron and that the atomic distance generally expands in higher temperature, hence the intermedeate proton which links SeO_4 unit ends up to be easy to be releaed. Of course this rearrangement will affect the other proton on NH_4^+. But the spectroscopic data[4] on NH_4^+ have shown no distinguishable change at the trnasition between II and III. Therefore the proton in O-H-O bond is considered to be the most probable candidate for electric carrier in the phase II.

On the other hand according to A. D. Reddy et al.[14], the electrical conduction in TAHS is due to proton trasfer along the chains of N-H-O bond because $Na_3H(SO_4)_2$ which contains no NH_4^+ ion shows no proton conduction. As Leclaire et al.[12] discussed too, the proton conduction through N-H-O bond chain
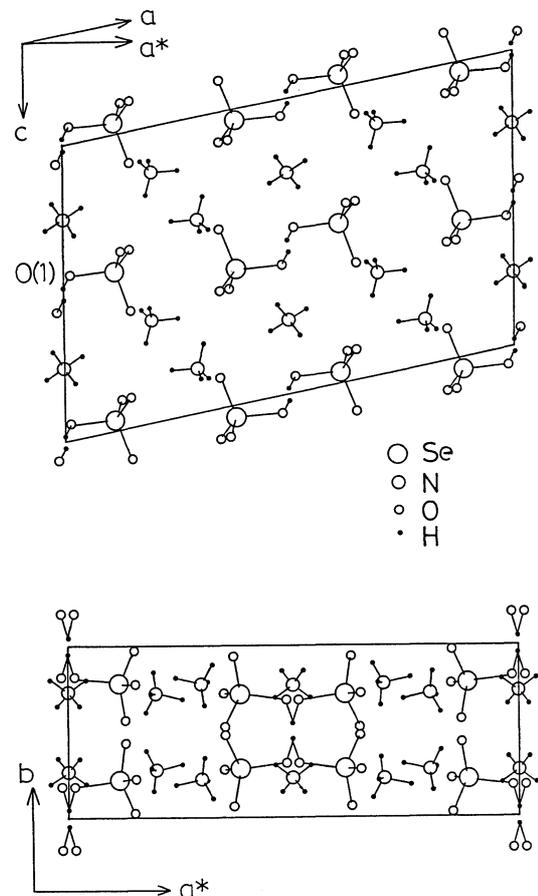

Fig. 6. The unit cell of TAHSe. The double minimum positions of proton are depicted. P. A. Leclaire's data are used.

may exist in every temperature region.   But taking account the fact that the drastic change of electrical conductivity and the rearrangement of tetrahedron SeO_4 at the transition II - III, it is natural to conclude the proton on O-H-O bond must be the most dominant electric carrier.

Next the ambiguity which is always accompanied by in ESR still remaines.   As for the radical assignment we followed the result by Minge and Waplak[8] though, the possibility of SeO_4^{3-} cannot be denied.   And that the probe itself is a damaged center hence the question whether the radical probes the environment honestely the undanaged crystal still remains.   But as far as the radical represents the orientation of SeO_4 tetrahedron in question, assignment is not necesarily important to discuss the mechanism of superionic phase trnasition.

In conclusion ESR study of X irradiated TAHSe crystal revealed the structural phase transition between the phases II and III, and explained the superionic conductivity.   To confirm the mechanism more extensive study such as NMR might be helpful.

§ 6.   Acknowledgement

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