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Double-well potential of SO_4 in NH_4LiSO_4, $LiRbSO_4$, and mixed-crystal $LiRb_{1-x}Cs_xSO_4$ ($x = 0.097$) studied by x-ray diffraction

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The double-well potential of SO_4 in NH_4LiSO_4 was estimated at 465 K in its highest-temperature phase on the assumption that each rigid SO_4 ion executes independent anharmonic oscillation in an effective single-particle potential about the mean position determined in the displacive-type model. The values of potential parameters for the librational motion were estimated by the method of structural analysis using numerical integration of structure factors. The height of the potential barrier is 0.754×10^{-13} erg, about 1.2 times that of the thermal energy $k_B T$ at 465 K. An effective asymmetric potential was also estimated at 457 K in the ferroelectric phase; the stable configuration of the SO_4 lies near one of two configurations in the disordered phase. NH_4LiSO_4 was confirmed to undergo an order-disorder phase transition. The potential of SO_4 in $LiRbSO_4$ at 493 K turned out to be also a double-minimum one with barrier height 0.512×10^{-13} erg, about 0.75 times that of $k_B T$ at 493 K. The substitution of Cs for Rb by 9.7 at. % made the potential a shallow broad one. Satisfactory correspondence of the estimated potential with the observed distribution of electron density of oxygen atoms was obtained.

I. INTRODUCTION

Anharmonicity of potential plays an important role near the transition temperature irrespective of the mechanism of the structural phase transition. Let the electron density of an oscillating atom and that at rest be denoted as ρ and ρ_0, then the ρ is expressed by the convolution product as follows:

$$\rho(\mathbf{u}) = \rho_0(\mathbf{u}) * p(\mathbf{u}) , \qquad (1)$$

where $p(\mathbf{u})$ represent the probability function of the atom whose displacement from the equilibrium position is represented by $\mathbf{u}$. After the report of the anharmonic potential term in fluorite structure,[1] it has been usually assumed that each atom oscillates independently in an effective one particle potential in order to take into account the anharmonicity in the diffraction problem. To calculate the temperature factor $\langle \exp(2\pi i \mathbf{Q}\cdot\mathbf{u}) \rangle$ for the analysis of x-ray or neutron diffraction data, the method of Taylor expansion of anharmonic terms of potential energy[1-4] was conventionally used. Another method of the cumulant expansion[5,6] was formulated and applied successfully when the anharmonic vibration became so large.[7,8] In order to estimate anharmonic potential parameters, a direct method to deconvolute Eq. (1) was also reported.[9] Application of these methods, however, was limited to the potential of a single atom.

In some phase transitions in ionic crystals consisting of polyatomic ions, orientational order of polyatomic ions grows. In discussing the mechanism of the phase transitions in these crystals, it is reasonable to neglect the degree of internal vibration in ionic groups provided that they are hard against deformation. For these rigid ions, quite anisotropic anharmonic effective potential of ions can be well defined, and the estimation of them gives the intuitive picture on the mechanism of the structural phase transitions. Although an exact calculation of the dynamical susceptibility of interacting classical oscillators moving in the double-well potential was made as early as 1970,[10] no estimation of such anharmonic potential has been made experimentally yet.

This paper deals concretely with three compounds, NH_4LiSO_4, $LiRbSO_4$, and mixed-crystal $LiRb_{1-x}Cs_xSO_4$ ($x = 0.097$) (abbreviated hereafter as ALS, LRS, and LRCS, respectively), in order to estimate such double-well potential. The crystal structures of ALS (Refs. 11–13) and LRS (Refs. 14 and 15) have been well established; it has been concluded that the SO_4 tetrahedron occupies two configurations in equal probability in their highest-temperature phase (phase I).[13,14] In Sec. II, the procedure of experiments and results of computer calculations of the structure analysis are briefly described. Section III deals with the numerical estimation of the parameters of anharmonic potentials. Finally, Sec. IV contains a discussion of the present results.

II. PROCEDURE OF EXPERIMENT AND CRYSTAL-STRUCTURE ANALYSIS

Single crystals of ALS, LRS, and $LiCsSO_4$ (LCS), were grown by the slow evaporation method described in Ref. 16. Mixed-crystals LRCS were grown also by the slow evaporation method from aqueous solutions of LRS and LCS at 33 °C. Content of Rb and Cs in LRCS were measured by the atomic absorption spectrophotometry. Spherical specimens of ALS and LRCS with radius 0.285 and 0.132 mm were prepared. The collection of reflection data was made on a four-circle diffractometer (Rigaku

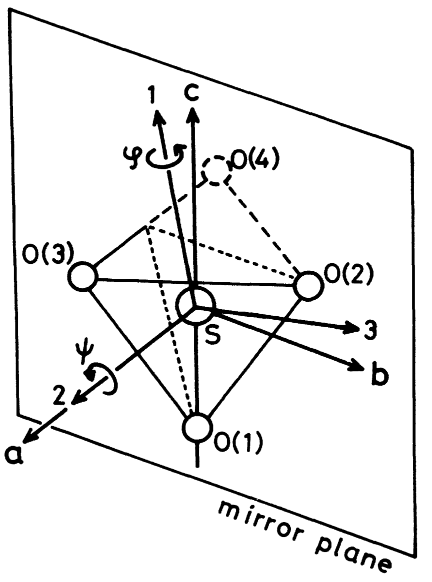

FIG. 1. A view of SO_4 ion in the displacive-type model with atomic numbering. Three principal axes of libration 1, 2, and 3 are shown by arrows.

AFC-5) with graphite-monochromated Mo $K\alpha$ radiation: for ALS it was made at 465 K in phase I and at 457 K in the ferroelectric phase ($T_c = 460$ K; transition temperature), while for LRCS, at 503 K in phase I ($T_c = 465$ K). Reflection data of LRS at 493 K in phase I which had been used for a structural study[14] were kindly supplied by Dr. Mashiyama.

The phase I's of three compounds have the orthorhombic *Pmcn* symmetry. In this phase, positional parameters determined on the basis of the structural model of the displacive-type phase transitions have not been reported yet: In this model Li, Rb, and Cs are confined in the mirror plane and tetrahedral ion (NH_4,SO_4) is related with itself by the mirror operation. It is necessary to use these positional parameters in this study, then the above model was refined at first.[17] The block-diagonal least-squares program of UNICS3 (Ref. 18) was used. A view of the SO_4 ion in this model, with atomic numbering in ALS, is shown in Fig. 1. The arrangement of SO_4 in LRS or LRCS is similar to that in ALS. Next, the structures of ALS and LRCS were refined on the basis of the disordered model: In this model the SO_4 occupies in equal probability two configurations which are related to each other by the mirror operation. The converged values of parameters in ALS agreed well with those reported by Itoh *et al.*[13] According to the significance test,[19] the disordered model turned out to be more probable than the displacive one with 99.5% significance level.

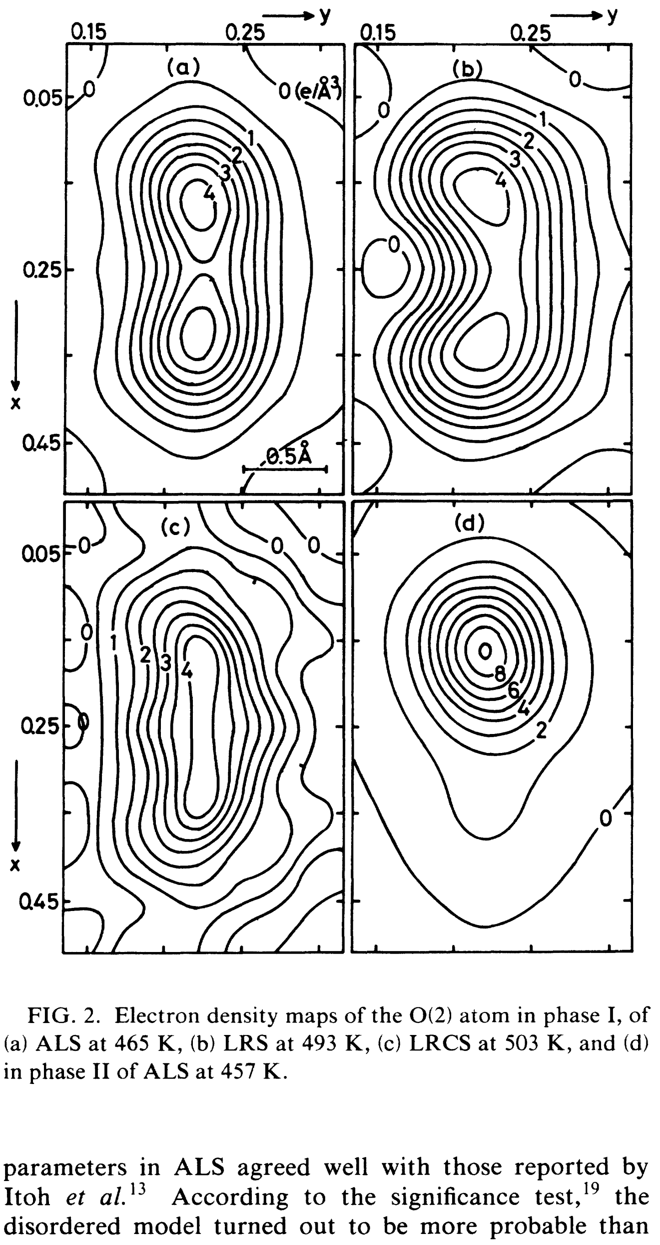

FIG. 2. Electron density maps of the O(2) atom in phase I, of (a) ALS at 465 K, (b) LRS at 493 K, (c) LRCS at 503 K, and (d) in phase II of ALS at 457 K.

In order to analyze the structure of ALS in the ferroelectric phase, the program was rewritten to include the occupation probability of SO_4 also as a parameter. Starting with the parameters of the disordered model in phase I, the refinement converged. The occupation probability of SO_4 with larger occupancy was 0.900(5).

TABLE I. The angle and the axis of rotation to relate the displacive-type model with the disordered model in phase I. The last line gives those to relate the displacive-type model of phase I with the ordered model of phase II in ALS. Values of direction cosines are determined in reference to the axes a, b, and c. The e.s.d's are given in parentheses.

	Rotational angle	l	m	$n=(1-l^2-m^2)^{1/2}$
ALS	16.3(14)°	−0.032(86)	0.019(82)	0.999
LRS	17.6(15)°	−0.030(9)	0.032(82)	0.999
LRCS	16.9(10)°	0.046(57)	−0.124(56)	0.991
ALS	15.7(10)°	0.061(11)	−0.152(61)	0.987

III. ESTIMATION OF POTENTIAL PARAMETERS

A. Disordered phase in ALS

Bond lengths and bond angles in SO_4 tetrahedron were calculated. These values range from 1.352(8) to 1.425(6) Å and from 104.0(3)° to 112.4(3)° for the displacive-type model, while 1.426(4)–1.444(6) Å and 105.6(3)°–113.8(9)° for the disordered model: The distortion of SO_4 is relatively small. Then the configuration of SO_4 in the disordered model of phase I can be derived from that of the displacive-type model by a rotation of the tetrahedron. The angle and the axis of the rotation are listed in Table I. The axis lies quite nearly along [001]. The anisotropic rigid-body vibration of SO_4 was analyzed[20] by using parameters of the displacive-type model of phase I as shown in Table II. Three principal axes of libration are shown in Fig. 1. It is noticed that the amplitude of libration is large on axes 1 and 2 and that axis 1 is quite near to the axis given in Table I.

On the basis of these structural characteristics, SO_4 ions were assumed to execute independent anharmonic oscillations rigidly in an effective single-particle potential about the equilibrium positions determined in the displacive-type model. If we neglect the coupling between translational motion and librational motion, then an effective single-particle potential of SO_4 can be expressed as follows:

$$U=U_t+U_r\ . \tag{2}$$

where U_t and U_r represent contributions from translational and librational motions. The amplitude of libration on axis 3 is 7.6° (Table II) and the corresponding amplitude in the ferroelectric phase is 6.4°: The difference is small. This motion is irrelevant to the phase transition and may well be assumed to be harmonic. The degree of libration on axis 3 was neglected also. Then the potential U_r can be expanded in terms of the rotational angles φ and ψ on axes 1 and 2, respectively, as

$$\begin{aligned} &U_r(\varphi,\psi)=U_1(\varphi)+U_2(\psi)\ ,\\ &U_1(\varphi)=\frac{\alpha}{2}\varphi^2+\frac{\beta}{4}\varphi^4+\frac{\gamma}{6}\varphi^6\ ,\\ &U_2(\psi)=\frac{\xi}{2}\psi^2+\frac{\eta}{4}\psi^4\ , \end{aligned} \tag{3}$$

in accordance with the site symmetry of SO_4. Here it is also assumed that the SO_4 librates independently on axes 1 and 2. The structure factor can be expressed as

$$F(\mathbf{h})=\sum_{j=\mathrm{N,Li,S}} f_j(\mathbf{h})T_j(\mathbf{h})\cos(2\pi\mathbf{h}\cdot\mathbf{r}_j) + \sum_{j=\mathrm{O(1)}\sim\mathrm{O(4)}} f_{\mathrm{O}}(\mathbf{h})T_{\mathrm{O}}(\mathbf{h})\int\cos[2\pi\mathbf{h}\cdot\mathbf{r}_j(\varphi,\psi)]p(\varphi,\psi)d\varphi\, d\psi\ , \tag{4}$$

where

$$p(\varphi,\psi)=\exp[-U_r(\varphi,\psi)/k_BT]\Big/\int\exp[-U_r(\varphi,\psi)/k_BT]d\varphi\, d\psi\ , \tag{5}$$

TABLE II. Parameters characterizing the principal directions 1, 2, and 3 of the thermal vibration of SO_4: root-mean-square displacements (rms) and direction cosines.

	Translational					Librational			
Axis	rms	l	m	n	Axis	rms	l	m	n
[NH_4LiSO_4 at 465 K]									
1	0.198 Å	0[a]	−0.731	0.682	1	22.6°	0[a]	−0.080	0.997
2	0.191 Å	1[a]	0[a]	0[a]	2	17.1°	1[a]	0[a]	0[a]
3	0.116 Å	0[a]	0.682	0.731	3	7.6°	0[a]	0.997	0.080
[$LiRbSO_4$ at 493 K]									
1	0.170 Å	1[a]	0[a]	0[a]	1	21.9°	0[a]	−0.156	0.988
2	0.161 Å	0[a]	0.744	−0.668	2	15.6°	1[a]	0[a]	0[a]
3	0.095 Å	0[a]	0.668	0.744	3	7.5°	0[a]	0.997	0.080
[$LiRb_{1-x}Cs_xSO_4(x=0.097)$ at 503 K]									
1	0.183 Å	0[a]	−0.591	0.807	1	21.7°	0[a]	−0.080	0.997
2	0.178 Å	1[a]	0[a]	0[a]	2	16.1°	1[a]	0[a]	0[a]
3	0.068 Å	0[a]	0.807	0.591	3	6.7°	0[a]	0.997	0.080

[a] Required by symmetry to be the values.

and $T(\mathbf{h})$ represents the temperature factor. The contribution of the translational motion to temperature factors of oxygen atoms, which is represented by $T_O(\mathbf{h})$, is equal to the temperature factor of the central atom, sulfur, in this model calculation.

In order to estimate the potential $U_r(\varphi,\psi)$, reflections whose structure factors are largely or considerably contributed by oxygen atoms were selected. There were only 36 reflections in the range of $8.8° < 2\theta < 60.9°$. Positional and thermal parameters determined by the displacive-type model were used.[21] The Gauss method was used for numerical integration. Only the coefficients of the potential were refined in the least-squares calculations:

$$\sum_{\mathbf{h}}[|F_O(\mathbf{h})|-|F_c(\mathbf{h})|]^2$$

was minimized and the R factor was used as a measure of the correctness of the refinements just as in the standard structural analysis, where F_O and F_c denote the observed and calculated structure factors, and R is defined as

$$\sum_{\mathbf{h}}||F_O(\mathbf{h})|-|F_c(\mathbf{h})||\Big/\sum_{\mathbf{h}}|F_O(\mathbf{h})|$$

In the course of calculations, the value of γ turned out to be very small, so it was put to be zero. Converged values are listed in Table III (Ref. 22) which give the R factor of 0.086.[23] It is noted that the final R of the displacive-type model and that of the disordered model are 0.105 and 0.067, respectively, in phase I.

B. Ferroelectric phase in ALS

In this phase, odd order terms of φ were also taken into account:

$$U_1(\varphi)=\frac{\alpha}{2}\varphi^2+\frac{\beta}{4}\varphi^4+\frac{\gamma}{6}\varphi^6+\lambda\varphi+\frac{\mu}{3}\varphi^3\ . \qquad (6)$$

Thirty-six reflections with the same indices as in phase I were used in the least-squares calculations. For N, Li, and S atoms, positional and thermal parameters determined in the ferroelectric phase were used; the temperature factor of S was substituted for $T_S(\mathbf{h})$, and positional parameters of oxygen atoms relative to S were set as the same ones used in phase I. Only the coefficients in the single-particle potential were refined. The value of γ was again put to be zero because of its small value. Converged values are also included in Table III. The R factor of the present calculation and that of the structure analysis in the ferroelectric phase are 0.076 and 0.054, respectively.

C. Disordered phase in LRS and LRCS

Estimation of potentials of SO_4 tetrahedra in these compounds was made in the same way as in ALS in phase I. Table I includes the axis of rotation and the angle to relate the configuration of SO_4 in the displacive-type model with that of the disordered one. Table II shows the characteristics of the anisotropic rigid-body vibration of SO_4 analyzed by using parameters of the displacive-type model. As well as the case in the disordered ALS, the amplitude of libration is large on axes 1 and 2 and

TABLE III. The values of potential parameters and $U_1(\varphi)_{\min}$ in ALS, LRS, and LRCS in 10^{-13} erg together with $\varphi_{\min}$, $\langle\varphi^2\rangle^{1/2}$ and $\langle\psi^2\rangle^{1/2}$ in degree.

Compound	α	β	ξ	η	$U_1(\varphi)_{\min}$	$\varphi_{\min}$	$\langle\varphi^2\rangle^{1/2}$	$\langle\psi^2\rangle^{1/2}$	λ	μ
ALS (465 K)	−22.0	160	−2.86	44.1	−0.754	21.2	19.3	18.3		
ALS (457 K)	−8.89	76.4	4.99	12.5	−1.247	21.1	a	a	−3.68	21.6
LRS (493 K)	−17.3	146	4.55	7.60	−0.512	19.7	18.2	18.4		
LRCS (503 K)	−4.74	52.9	2.73	36.9	−0.106	17.2	18.8	15.7		

[a] Values were not calculated.

axis 1 is quite near to the axis given in Table I. Thirty-five reflections in LRS and 33 in LRCS were selected with the same criterion as in Sec. III A. Converged values of least-squares calculations are also listed in Table III. The R factors were 0.043 for LRS and 0.042 for LRCS, respectively,[22] while R factors of the structure analysis are 0.046 for LRS and 0.039 for LRCS.

IV. DISCUSSION

It has been shown that characteristics of the disordered nature of the SO_4 ion in ALS and LRS are most clearly visualized in the electron density map near the O(2) or O(3) atom[13–15] (see Fig. 1). Figure 2 shows electron density maps near O(2).[24] Double-peaked contours in ALS and LRS, and an unusually elongated contour in LRCS, are seen. The asymmetric electron density map near O(2) in the ferroelectric phase of ALS is also shown in Fig. 2(d).

Figures 3(a) and 3(b) show the estimated potential and the probability density function of SO_4 in ALS in phase I. The value $\varphi_{\min}$ and corresponding minimum value of $U_1(\varphi)$, calculated root-mean-square amplitudes $\langle \varphi^2 \rangle^{1/2}$ and $\langle \psi^2 \rangle^{1/2}$, are listed in Table III. The value of $\varphi_{\min}$ agrees fairly well with the rotational angle given in Table I, $\langle \varphi^2 \rangle^{1/2}$ and $\langle \psi^2 \rangle^{1/2}$ agree with the mean-square amplitude of libration on axis 1 and that on axis 2 given in Table II. The height of the potential barrier is 7.54×10^{-14} erg, about $1.18 k_B T$ at 465 K in ALS. A broad shallow section of the potential shown in Fig. 3(b) corresponds to the large amplitude of librational motion on axis 2 parallel to the a axis (see Table II): This motion is irrelevant to the phase transition.

At 497 K, 3 K below the transition temperature, ordering of SO_4 took place with the occupation probability in the ratio 0.900(5):0.100(5). Figures 4(a) and 4(b) show the estimated asymmetric potential and the probability density function of SO_4 in ALS in the ferroelectric phase. The minimum value of $U_1(\varphi)$ and corresponding $\varphi_{\min}$ are listed in Table III. The value of $U_1(\varphi)_{\min}$ is -1.25×10^{-13} erg, about 1.66 times that in phase I. It is also noted that

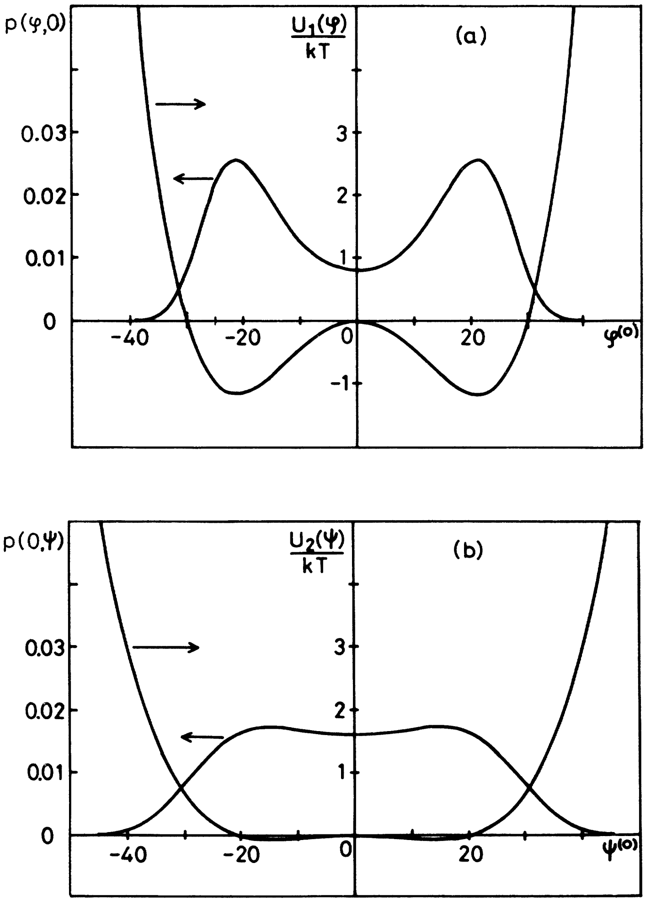

FIG. 3. The estimated potential and probability density function of the SO_4 ion in ALS at 465 K (phase I) as a function of rotational angle from the position determined by the displacive-type model. (a) $U_1(\varphi)$ and $p(\varphi,0)$. (b) $U_2(\psi)$ and $p(0,\psi)$.

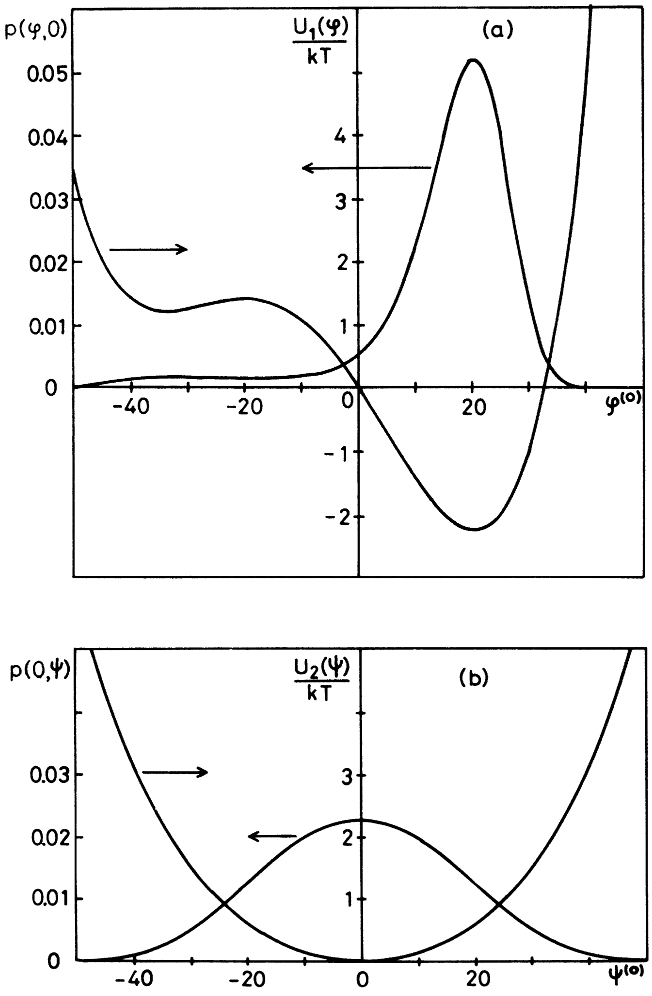

FIG. 4. The estimated potential and probability density function of the SO_4 ion in ALS at 457 K (phase II) as a function of rotational angle from the position determined by the displacive-type model. (a) $U_1(\varphi)$ and $p(\varphi,0)$, (b) $U_2(\psi)$ and $p(0,\psi)$.

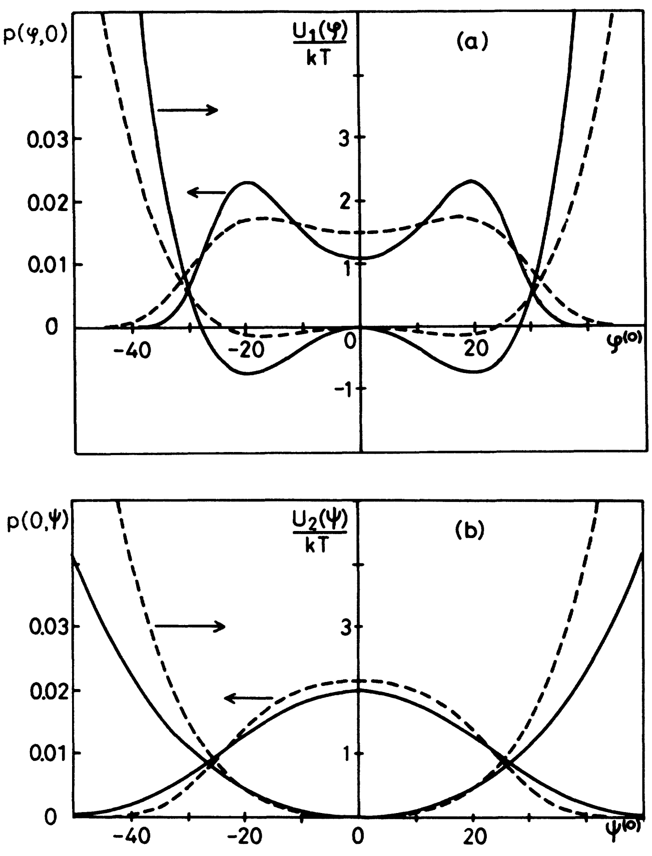

FIG. 5. The estimated potential and probability density function of the SO_4 ion in phase I as a function of rotational angle from the position determined by the displacive-type model. (a) $U_1(\varphi)$ and $p(\varphi,0)$ in LRS at 493 K (solid curves) and in LRCS at 503 K (dashed curves). (b) $U_2(\psi)$ and $p(0,\psi)$ in LRS at 493 K (solid curves) and in LRCS at 503 K (dashed curves).

the integration of the probability function,

$$\int_0^\infty d\varphi \int_{-\infty}^\infty p(\varphi,\psi)d\psi = 0.89 \ , \qquad (7)$$

which is consistent with the occupation probability of 0.90 determined by the structural analysis.

The estimated potentials and probability density functions of SO_4 in LRS and LRCS in phase I are shown in Figs. 5(a), 5(b), 5(c), and 5(d), respectively. The values of $U_1(\varphi)_{\min}$, $\varphi_{\min}$, $\langle \varphi^2 \rangle^{1/2}$, and $\langle \psi^2 \rangle^{1/2}$ are also listed in Table III. Agreement of the values with the observed ones given in Tables I and II are rather satisfactory. The height of the potential barrier in LRS is 0.512×10^{-13} erg, about $0.75k_BT$ at 493 K, which is smaller than that in ALS in phase I.

It is reasonable to classify the mechanism of structural phase transition into two categories, the order-disorder one and the displacive-type one, according to whether the height of potential barrier is higher than k_BT_c or not. In ALS, the height of the potential barrier is about $1.2k_BT_c$, which manifests an order-disorder character of SO_4. On the other hand, the height of the barrier is about $0.79k_BT_c$ in LRS, which suggests that LRS lies on the displacive-type side. A mention is needed on the precision of estimated parameters. The ratio of standard deviation to the value of α is less than 0.09 for ALS and LRS in phase I, while those for other parameters are rather large; for LRCS they are of the same order. However, the ratio of maximum least-squares shift to error in the final refinement cycle is less than 0.006. Large standard deviations seem due mainly to the relatively small number of reflections whose intensities are largely contributed by oxygen atoms. In addition, because of the large x-ray scattering factor of Rb compared with that of the NH_4 ion, the neutron scattering measurements will be needed to obtain more convincing values of the potential parameters of LRS. It should be noted, however, that the estimated potential parameters reproduce quite well the characteristic feature of the observed electron density maps shown in Fig. 2.

It has been well known that LRS undergoes successive phase transitions among six phases including incommensurate and commensurate ones.[25,26] The main lock-in phase is the antiferroelectric phase with twofold superstructure along the c direction. A stepwise substitution of Rb by Cs results in an increase of the temperature range of the disordered and twofold phases and in a reduction of the range of the incommensurate and the sevenfold and fivefold commensurate phases.[27,28] The effect of substitution has been clarified in a microscopic scale; the potential of the SO_4 ion changes from a double-well to a shallow single-well type. As the ionic radius of Cs, 1.65 Å, is larger than that of Rb, 1.48 Å, the substitution may work to suppress the disordering of SO_4.

If the anharmonic motion relevant to the phase transition carries a dipole moment, there is another possibility to estimate anharmonic potential parameters experimentally; they can be determined from the measurements of the frequency dispersion of the susceptibility in different temperatures.[10] However, the method cannot be applied to the present materials, because the distortion of the SO_4 is very small.

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[21] In the displacive-type model, the distortion becomes apparently larger because of large thermal motion. When the positional parameters were corrected for the thermal motion, the tetrahedra became less distorted; bond lengths and angles range from 1.382 to 1.444 Å and from 104.4° to 112.4°, respectively.

[22] Lists of structure factors will be sent on request.

[23] Positional parameters corrected for thermal motion were used for oxygen atoms. Otherwise R factor is 0.101.

[24] The difference between the electron density calculated by using F_O and F_c are drawn. The contribution of O(2) is artifically removed in F_c.

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