PHYSICAL REVIEW B VOLUME 21, NUMBER 7 1 APRIL 1980

Phase-transition-induced dipolar relaxation, a new method for the investigation of phase transformations in dielectric materials, applied to K_2SnCl_6

J. Winter* and K. Rössler

Institut für Chemie 1 (Nuklearchemie), Kernforschungsanlage Jülich GmbH,
D-5170 Jülich, Federal Republic of Germany

(Received 21 March 1979)

A new method for the investigation of lattice dynamics at structural phase transformations is presented, TIDR (transition-induced dipolar relaxation). It relies on the fact that the relative positions of molecules and likewise of dipolar units within a crystal are determined by the minima in lattice potential. As a consequence of phase transformations, the lattice potential may change, thus changing the orientation of the dipoles and leading to polarization or depolarization currents. If intrinsic dipolar molecules are not present in the sample, a small concentration of dipolar defects which can act as indicators can easily be introduced via a mild neutron irradiation and subsequent recoil processes of the activated atoms. This technique has been applied to K_2SnCl_6, which exhibits two structural phase transitions at $T_1 = 262$ K and $T_2 = 253$ K. ppm-amounts of $SnCl_5^-$ dipoles were created by neutron-capture-induced ligand recoil. From the measurements a libration of the $SnCl_5^-$ units about two cubic main axes by $(6 \pm 2)^\circ$ below T_2 could be deduced. This result is in good agreement with recent neutron scattering data on the tilting of the intact $SnCl_6^{2-}$ octahedra. On the other hand, the data supply indications of 90° jumps of the $SnCl_5^-$ dipoles at $T \geq T_1$.

I. INTRODUCTION

Phase transformations in ionic or molecular crystals can often be determined via changes of the dielectric properties such as dielectric constant, conductivity, or spontaneous polarization, cf., e.g., Refs. 1–4. Many phase transitions are connected with orientational changes of larger units within the matrix, e.g., the NH_4^+ ion in ammonium halides.[5–8] A very sensitive tool for the determination of rotational relaxation of groups of atoms is the ITC method (ionic thermo current). This technique requires permanent intrinsic electric dipoles which, however, are not always present in the pure single-crystalline systems. This may be the reason that relatively few applications of the method to phase-transition problems have been reported.[8–15]

It now seems very promising to introduce a small concentration of dipolar defects by irradiation supposed that the damaged molecular units are not too different from the undamaged ones and occupy identical positions in the lattice. In the case of K_2SnCl_6, NH_4Cl, and NH_4Br use has already been made of the increased dipole mobility at phase transformations and the consequent anomalies in dc conductivity and ITC to study thermal- and radiation-induced defects such as the ligand-deficient complex $SnCl_5^-$.[8,15] Defects of this type are easily created by mild thermal-neutron irradiation and the nuclear-recoil processes following the neutron capture. They can serve as probes for the phase-transition dynamics. Information on minima in the lattice potential for these indicators can be obtained from changes in the orientation of their dipole moments. They are directly related to crystal symmetry and, thus, to changes of structure.

In this work the new method which will be called TIDR (transition-induced dipolar relaxation) is applied to the structural transitions at $T_1 = 262$ K and $T_2 = 253$ K in K_2SnCl_6, a prototype of the family of hexahalometallates IV (A_2BX_6), cf. Ref. 16. The transformation at T_1 from a cubic ($Fm3m$) high temperature to a less symmetric structure has been observed by several independent methods, such as heat capacity and differential thermal analysis,[16–18] nuclear quadrupole resonance (NQR),[19,20] x-ray or neutron-diffraction,[21–27] Raman[15,29–31] and Mössbauer spectroscopy,[15,29] dielectric measurements,[8,15] and photoacoustic effect.[32] The intermediate phase has been described to be tetragonal ($P4/mnc$).[27] Recent experimental results, however, suggest an orthorhombic symmetry.[28] The transition at T_2, most probably leading to a monoclinic structure ($P2_1/n$), has been observed by NQR,[19,20] dielectric measurements,[8,15] x-ray and neutron diffraction.[24,27,28]

It has been emphasized that structural transformations in A_2BX_6 compounds are associated with the softening of rotary phonons.[20,21,29–36] In K_2SnCl_6, anomalies of the rotational modes of the $SnCl_6^{2-}$ octahedra occur at the two transitions.[29–31] From the temperature dependence of the ^{35,37}Cl-NQR frequency, a hindered 90° rotation about one of the cubic axes has been suggested, whereas in the distorted phases ($T < T_1$) small angle relaxation of the octahedra seems to be dominant.[20,37] Since lattice dynamics influences the rotational motions of the regular $SnCl_6^{2-}$ octahedra, changes in the rotational freedom of the $SnCl_5^-$ dipoles can also be expected at the phase transitions.

II. EXPERIMENTAL

K_2SnCl_6 was synthesized by conventional methods from $SnCl_4$ and KCl.[38] Single crystals of about 2 cm^3 were grown from concentrated 0.1 N HCl solution and cut into plates of 0.5 mm thickness along their natural (1,1,1) faces. They were polished and provided with contacts of colloidal graphite. Dipolar indicators were introduced via recoil of the halogen ligands after thermal-neutron capture (Szilard-Chalmers process). The samples were irradiated in the thermal column BE-14 of the Jülich research reactor FRJ-1 (Merlin). At a typical thermal-neutron dose of $D_n = 4.5 \times 10^{15}$ cm^{-2} about 4×10^{14} ligand-deficient $SnCl_5^-$ species (cf. Fig. 1) were created in the zone between the contacts.[39,40] Since these defects were present in a concentration of 1.4×10^{-6} per molecule K_2SnCl_6, they could hardly influence the dynamics of the host lattice but act as probes due to their permanent dipole moment.

The experimental set up used for the dielectric measurements has been described elsewhere.[8,15] dc-conductivity measurements were performed after cooling the short-circuited crystals to 77 K. A constant voltage ranging from 5 to 40 V was applied. The crystal was heated at a constant rate of 3.2 K min^{-1}. For the TIDR measurements the samples were polarized with 500 V for 5 min at various polarization temperatures T_p ranging from 140 to 350 K, and cooled to 77 K with the electric field still applied. When 77 K was reached, the electric field was removed, and the sample short-circuited for 5 min. Then the crystal was heated at the same rate as in the conductivity measurements.

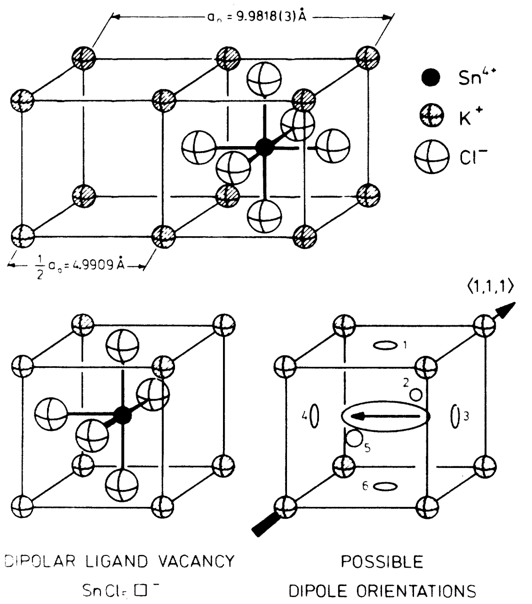

FIG. 1. Primitive cell of cubic K_2SnCl_6 (*Fm*3*m*) (upper part): dipolar, pentacoordinated complex with ligand vacancy (lower part).

III. RESULTS

The specific dc conductivity of a K_2SnCl_6 single crystal before and after thermal-neutron irradiation is shown in Fig. 2 as function of temperature in the range near the phase transformations. The irradiation causes sharp and intense minima and maxima of the electric current at T_1 and T_2, which in the nonirradiated samples can just barely be seen. These peaks are superimposed on an ionic background current which gently increases with the temperature and does not show significant changes upon irradiation, at least in the temperature range considered here. The anomaly at T_1 is of higher intensity than that at T_2 and exhibits a slightly variable substructure. The two anomalies can be located at $T_1 = (262.4 \pm 1.1)$ K and $T_2 = (253.2 \pm 1.2)$ K. These values are determined for the more symmetrical peaks from the cross zero and for the less symmetrical ones from the peak maximum.

The intensity of both peaks (sum over areas above and below the line of background current) is a linear function of the voltage applied, U_{ext}, as shown in Fig. 3. However, at higher U_{ext} the intensity might reach a certain saturation, which is already suggested by the experimental values for $U_{ext} \geqslant 30$ V. The dc experiments have not been performed at higher voltages, in order to avoid electrolysis of the samples at elevated temperatures and long measuring periods, whereas in the TIDR experiments reported below, the high-

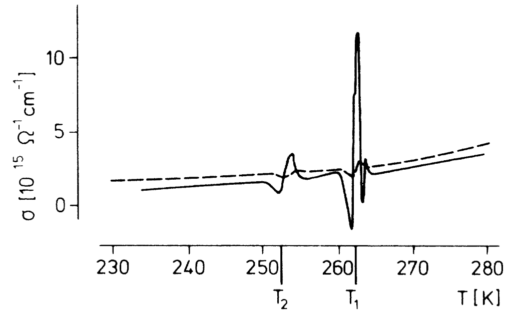

FIG. 2. dc conductivity of K_2SnCl_6 single crystals in ⟨111⟩ direction before (dashed line) and after (solid line) thermal-neutron irradiation ($D_{n(th)} = 4.5 \times 10^{15}$ cm^{-2}).

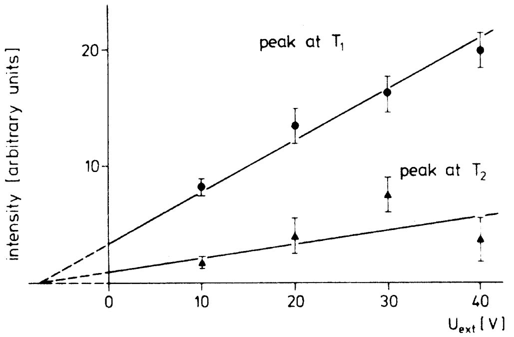

FIG. 3. Relative intensities of dc-conductivity anomalies at T_1 and T_2 in K_2SnCl_6 single crystals as depending on the voltage applied.

voltage region has deliberately been chosen in order to reach saturation of polarization. According to Fig. 3, the intensity ratio of the peaks at T_1 and T_2 amounts to (5 ± 1.5):1. Both curves do not meet the origin. Zero intensity is first reached at a negative voltage of about −8 V. The ionic background current at T_1 and T_2 shows strictly ohmic behavior, however.

The TIDR spectra of irradiated K_2SnCl_6 single crystals in Fig. 4 show intense peaks at the phase transitions, similar in shape and intensity ratio to those observed in dc conductivity. The absolute intensities of these TIDR peaks are independent of the polarization voltage beyond 100 V and on the polarization temperature $T_p > T_1$ since the number of dipoles is determined by the irradiation dose. The variation of the concentration of dipoles by thermal annealing of the irradiated samples results always in the same intensity ratio of (5 ± 1.5):1 between the peaks of T_1 and T_2, irrespective of the absolute number of dipoles involved in the TIDR process.[15]

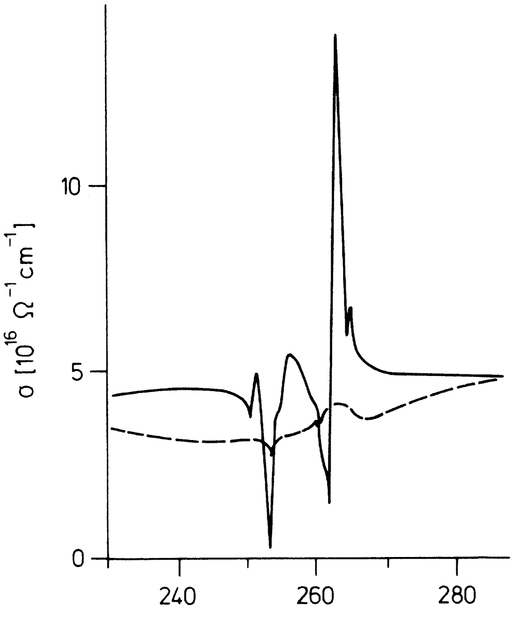

FIG. 4. TIDR spectra of K_2SnCl_6 single crystals in the region of the phase transitions at T_1 and T_2 before (dashed line) and after (solid line) irradiation with thermal neutrons ($D_{n(\mathrm{th})} = 4.5 \times 10^{15}$ cm^{-2}; $T_p = 296$ K; $U_p = 500$ V; $t_p = 5$ min).

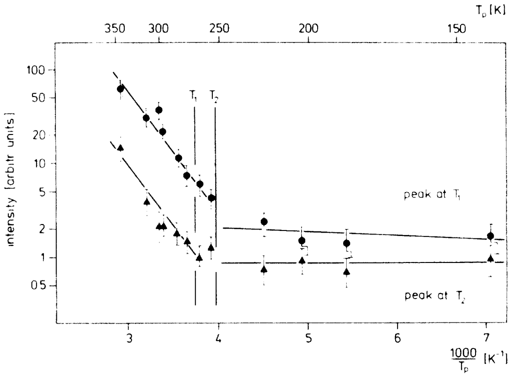

FIG. 5. Intensity of the TIDR peaks at T_1 and T_2 in K_2SnCl_6 single crystals without neutron irradiation as a function of the reciprocal polarization temperature T_p ($U_p = 500$ V; $t_p = 5$ min).

Since the sensitivity of the TIDR method is much higher than that of dc conductivity, weak depolarization anomalies due to ligand vacancies created by thermal dissociation can be observed in nonirradiated samples. The intensity of these peaks is shown in Fig. 5 as a function of the reciprocal polarization temperature. For temperatures $T_p > T_2$ the intensities of both peaks increase exponentially showing the same constant ratio as in the case of the radiation-induced dipoles. For $T_p < T_2$ the intensities become very small and seem to be unaffected by T_p.

IV. DISCUSSION

Since the observed anomalies occur exactly at the phase-transformation temperatures of K_2SnCl_6, they must be due to transition-induced polarization or depolarization currents. The different behavior of ionic background current and peak intensities as a function of the applied voltage in dc conductivity and the parallel occurrence of these peaks in TIDR shows that the peaks cannot be due to the free migration of charge carriers. Likewise, they cannot be produced by classical spontaneous polarization, as observed, e.g., for $NaNO_2$,[4] since this effect should be independent of the irradiation. Another reason for the electric anomalies could be a sudden expansion or contraction of the sample at the phase transformation causing a change of the capacitance. A calculation using the lattice parameter changes observed by x-ray diffraction[22] shows that the effect is by several orders of magnitude too small.[15] Dipolar impurities such as OH^- or H_2O are certainly present in the samples and could cause the signals as well. However, since the observed effect scales linearly with the irradiation dose and the current anomalies anneal in a way typical for $SnCl_5{}^-$ species ,[15] impurities cannot be responsible for the peaks. It thus is concluded, that the observed current anomalies are due to the orientation or reorientation of the irradiation-induced $SnCl_5{}^-$ dipoles.

A change in the orientation of these dipolar species may occur via several processes (i) intramolecular exchange between vacancy and adjacent ligands (cf. also "intramolecular twisting" of ligands,[41–45] (ii) intramolecular exchange between vacancy and a ligand of a neighboring anion,[46,47] (iii) rotation of the whole pentacoordinated complex.

The first two mechanisms require a considerable and sudden weakening of the covalent bonds within the molecule at both phase transitions, which cannot totally be excluded because of the vibrational fluctuations near T_1 and T_2. Nevertheless, a rotation of $SnCl_5{}^-$ as a whole seems to be more likely.

The peaks in the TIDR experiments are due to a depolarization of the $SnCl_5{}^-$ dipoles, whereas in dc conductivity one is dealing with the inverse procedure, i.e., the sudden alignment of the dipoles in the external field. Space charges built up by the external electric field are responsible for the fact that the peak intensities do not extrapolate to zero with decreasing voltage (cf. Fig. 3) or polarization temperatures below T_2 (cf. Fig. 5). These space charges have been observed and identified by ionic thermocurrent (ITC) experiments[15] and can be removed by heating the crystal at temperatures above 300 K. The nearly exponential increase of the TIDR-peak intensities at $T_p > T_2$ (cf. Fig. 5) may be due to ligand vacancies formed via thermal dissociation.

In a model for the rotation of the $SnCl_5{}^-$ dipoles, it is assumed that the vicinity of the defect is not too much distorted. Recently it has been shown by optical spectroscopy of K_2ReCl_6 and K_2ReBr_6, compounds isostructural with K_2SnCl_6, that radiation-induced pentacoordinated species may take a square pyramidal configuration by a slight relaxation of the ligands adjacent to the vacancy.[48]

The relative position of the dipole is determined by the lattice potential. Its dipole moment will point to one of the face centers of the surrounding K^+ cube (positions 1 to 6 in Fig. 1, lower part). In TIDR experiments with $T_p > T_1$, one group of these positions will be energetically favored by the interaction of dipole moment and electric field, in the case of a $\langle 111 \rangle$ field, the positions 1, 2, 3. The dipoles will preferentially occupy these positions. Within the model, this requires 90° jumps of the ligand vacancies around one cubic main axis. Below the phase-transition temperature these jumps are strongly hindered, possibly due to an abrupt change of the activation energy for rotation as a consequence of the first-order transition. At low temperatures the orientation is frozen in. Only when the crystal is heated again to the phase-transition temperature can a rapid reorientation occur. Thus, the anomaly at T_1 both in TIDR and dc conductivity is tentatively ascribed to a 90° hindered rotation of the $SnCl_5{}^-$ dipoles.

The question remains whether the intact octahedra can perform similar rotations. Small-angle lattice rotary vibrations of the anions around the equilibrium position do not change the gross orientation. Jumps by 90° can only proceed via the cooperative motion of four ligands. They should be much less frequent than the vibrations and more difficult to detect. X-ray scattering measurements are not sensitive, since the symmetry is not changed. The results of previous NQR experiments are less conclusive for a rotation of the anions by 90°, as discussed before.[20] On the other hand, since the damaged pentacoordinated unit is not too different from the undamaged octahedron regarding size and steric arrangement, a similar type of motion should not be impossible for both species. Very recently, evidence for a 90° rotation of $SnCl_6^{2-}$ octahedra at $T \geqslant T_1$ has been obtained from ^{35}Cl-NQR measurements in $[(NH_4)_xK_{1-x}]_2SnCl_6$-mixed crystals.[49,50]

For the signals at T_2, a similar process is discussed, namely small-angle orientations of the dipoles, as it is already known from the rotation of octahedra in the distorted phases of isostructural A_2BX_6 compounds.[20,21,27,33–35,37]

Figure 6 shows a schematic model for the lattice potential of K_2SnCl_6 at temperatures above and below T_1. For the 90° jumps at $T \geqslant T_1$, the minima in lattice potential are at the face centers of the K^+ cube [Fig. 6(b)]. For $T_1 > T > T_2$ a tetragonal or orthorhombic distortion of the lattice and the octahedron may take place,[20,27,28] leading to two equivalent potential minima, symmetrically arranged around the face-center positions of the cubic phase.

At $T > T_2$, a random distribution of the octahedra among these secondary minima seems to account for the observed NQR relaxation behavior.[20] At lower temperatures an antiferrodistortive ordering of the octahedra occurs, the structure being monoclinic.[27]

The TIDR peak at T_2 can now be explained via the side minima in the lattice potential. Similar to the transition at T_1 a preferential occupation of one of these secondary minima by $SnCl_5{}^-$ dipoles may take place in an electric field at $T > T_2$. Below T_2, jumps of the dipoles between the side minima are hindered.

It can be assumed that an equal number of dipoles takes part in the orientation-reorientation processes at both phase transformations. Obviously this is true

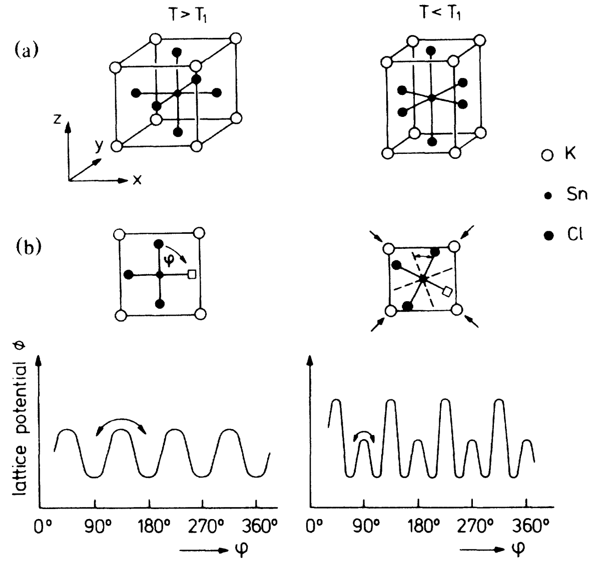

FIG. 6. Influence of lattice distortion (a) on the lattice potential as seen by the $SnCl_5^-$ units (b), projection on *xy* plane.

for the irradiation-induced dipoles and approximately also for those in thermal equilibrium, since T_1 and T_2 differ by 9 K only. By means of the observed intensity ratio of the anomalies at T_1 and T_2 the location of the side minima can be estimated.

Figure 7 shows the K^+ cube with the face-center positons 1–6, the face-diagonal directions $\overline{AB}$ and $\overline{CD}$ and the $\langle 111\rangle$ direction of the electric field (unit vector $=\vec{e}_{\langle 111\rangle}$).

For the sake of simplicity, it is assumed that the 90° rotations of the dipoles at T_1 occur in the 3,5,4,2 plane (the 1,3,6,4 plane is equivalent). The field applied, positions 2 and 3 are energetically favored over 4 and 5. If on depolarization the dipole jumps from 3 to 5 (90° jump), this gives rise to a net polarization change Δp_1 ($\vec{p}$ is the dipole moment)

$$\Delta p_1 = (\vec{p}_{3\text{-position}}\cdot\vec{e}_{\langle 111\rangle}) - (\vec{p}_{5\text{-position}}\cdot\vec{e}_{\langle 111\rangle}) \ ,$$

$$= 1.1\cdot|\vec{p}| \ .$$

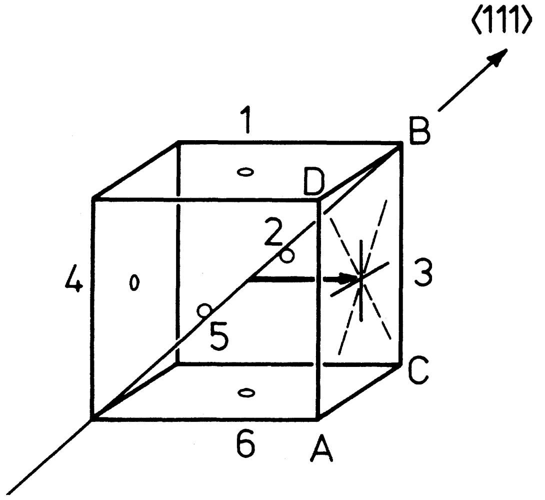

FIG. 7. Possible small-angle motion of $SnCl_5^-$ dipoles in the cubic subcell of K_2SnCl_6.

Since the intensity ratio of the TIDR peaks at T_1 and T_2 is about 5:1, the contribution Δp_2 of one dipole to the polarization change at T_2 is

$$\Delta p_2 = \tfrac{1}{5}\Delta p_1 = 0.22|\vec{p}| \ .$$

Under the assumption of a monoclinic distortion of the lattice at low temperatures ($T < T_2$), a small-angle rotation of an oriented dipole at T_2 from a site in $\overline{AB}$ or $\overline{CD}$ direction (cf. Fig. 7) into a position in the 3,5,4,2 plane near the face center has to be considered. The experimentally observed amount of Δp_2 is achieved when the minimum in lattice potential is located at about 7.5° from the face center into direction of the face diagonals. This corresponds to two consecutive rotations about the cubic main axes of $(6\pm 2)°$ each.

This value for the location of potential minima at T_2 is in excellent agreement with those obtained from neutron scattering[27] for the rotation of the intact octahedra at or below T_2 ranging from 4 to 7.5° according to the temperature. Since the value of 6° reported above was deduced on the basic hypothesis of 90°-reorientation jumps of the $SnCl_5^-$ dipoles at $T \geqslant T_1$, the agreement with the data from an independent experiment may, on the other hand, serve as a strong evidence for the latter assumption.

V. CONCLUSION

It has been shown that the technique of phase-transition-induced dipolar relaxation (TIDR) can render quantitative information on the orientational change of molecules in crystals at phase transformations, and thus on changes in lattice potential. As deduced from the experiments a rotation of the ligand-deficient $SnCl_5^-$ units in K_2SnCl_6 about two cubic main axes of about $(6\pm 2)°$ each, just below $T_2 = 253$ K, seems to be most likely. From a comparison with the results of neutron scattering experiments in K_2SnCl_6, it can be concluded that the damaged units follow the motion of the undamaged octahedra. The basic assumption of jumps of the $SnCl_5^-$ dipoles at T_1 by 90°, which underlies the discussion of the results, seems to be justified. According to this, a rotation of the intact $SnCl_6^{2-}$ octahedra by 90° at $T \geqslant T_1$ does not seem to be unlikely.

Since the types of motion described above should occur in a series of similarly structured compounds, TIDR could potentially be applied to a variety of dielectric materials in which dipolar indicators might be introduced via a mild thermal-neutron irradiation. The low concentration of these defects (10^{-6} per molecule) has the advantage not to influence the phase transition themselves. Besides the determination of changes in lattice potential, this technique may also yield interesting results on the dynamics of the transformation if a careful investigation on the shape and fine structure of the polarization and depolarization current signals is carried out.

ACKNOWLEDGMENTS

The authors with to thank Professor W. Schilling and Professor G. Stöcklin (Jülich) for their interest and stimulating discussion. Likewise they are obliged to Professor F. Fischer and Dr. C. Kokott (Münster) for the introduction into the measuring techniques.

---

[*] Present address: Institut für Plasmaphysik der Kernforschungsanlage Jülich GmbH, D-5170 Jülich, FRG.

[1] W. J. Merz, Phys. Rev. 76, 1221 (1949).

[2] W. Cochran, Adv. Phys. 9, 387 (1960).

[3] G. A. Samara, Ferroelectrics 2, 277 (1971).

[4] K. Hamano, J. Phys. Soc. Jpn. 35, 157 (1973).

[5] W. B. Yelon, D. E. Cox, and P. J. Kortmann, Phys. Rev. B 9, 4843 (1974).

[6] F. Boettcher and J. M. Spaeth, Phys. Status Solidi B 61, 465 (1974); B 62, 65 (1974).

[7] W. Press, J. Eckert, D. E. Cox, C. Rotter, and W. Kamitakahara, Phys. Rev. B 14, 1983 (1976).

[8] J. Winter and K. Rössler, J. Phys. (Paris) 37, C7-265 (1976).

[9] S. Bini and R. Cappelletti, in *Proceedings of the Electrochemical Society Fall Meeting* (Electrochemical Society, New York, 1972), p. 66.

[10] R. Cappelletti, A. Gainotti, and L. Pareti, *Electrochemical Society Fall Meeting*, edited by M. Smith (Electrochemical Society, New York, 1975), p. 277.

[11] A. Kessler, in Ref. 10, p. 270.

[12] A. Kessler, J. Electrochem. Soc. 123, 1239 (1976).

[13] T. Hino and Y. Kitamura, Trans. Inst. Electr. Eng. Jpn. 95, No. 1 (1975).

[14] L. Onsager, D. L. Staebler, and S. Mascarenhas, J. Chem. Phys. 68, 3823 (1978).

[15] J. Winter, Report Jül-1419 May 1977, (Thesis, Rheinisch-Westfälisch-Technische Hochschule Aachen, 1977).

[16] K. Rössler and J. Winter, Chem. Phys. Lett. 46, 566 (1977).

[17] R. G. S. Morfee, L. A. K. Staveley, S. T. Walters, and D. L. Wigley, J. Phys. Chem. Solids 13, 132 (1960).

[18] K. Rössler and T. Tessin (unpublished).

[19] A. Sasane, D. Nakamura, and D. Kubo, J. Magn. Reson. 3, 76 (1970).

[20] K. R. Jeffrey, J. Magn. Reson. 7, 184 (1972).

[21] G. P. O'Leary and R. G. Wheeler, Phys. Rev. B 1, 4409 (1970).

[22] H. Boysen, J. Ihringer, and W. Prandl, Acta Crystallogr. Sect. A 31, 189 (1975).

[23] H. Boysen, Z. Krist. 144, 426 (1976).

[24] H. Boysen, J. Ihringer, W. Prandl, and W. Yelon, Solid State Commun. 20, 1019 (1976).

[25] H. Boysen, thesis (Ludwig-Maximilians-Universität München, 1976) (unpublished).

[26] J. Ihringer, thesis (Ludwig-Maximilians-Universität München, 1976) (unpublished).

[27] H. Boysen and A. W. Hewat, Acta Crystallogr. Sect. B 34, 1412 (1978).

[28] J. Ihringer and W. Prandl, in *Abstract, DGF-Rundgespräch, Gitterdynamik und Phasenübergänge in Kristallen vom K_2PtCl_6-Typ*, 30. Aug./1. Sept. 1978, Bad Honnef, Germany, edited by K. Rössler (Institut für Chemie der KFA Jülich GmbH, FRG, 1978).

[29] J. Winter, K. Rössler, J. Bolz, and J. Pelzl, Phys. Status Solidi B 74, 193 (1976).

[30] J. Pelzl, W. Henkel, J. Winter, and K. Rössler, in *Proceedings of the 5th International Raman Conference, Freiburg, September 1976*, edited by E. Schmid (Verlag Schulz, Freiburg, 1976), p. 621.

[31] J. Pelzl, P. Engels, and R. Florian, Phys. Status Solidi B 82, 145 (1977).

[32] R. Florian, J. Pelzl, M. Rosenberg, H. Vargas, and R. Wernhardt, Phys. Status Solidi A 48, K35 (1978).

[33] K. R. Jeffrey, R. L. Armstrong, and K. E. Kisman, Phys. Rev. B 1, 3770 (1970).

[34] R. L. Armstrong and H. M. van Driel, in *Advances in NQR-spectroscopy*, edited by J. A. S. Smith, (Heyden, London, 1975), Vol. II, p. 179.

[35] Y. Furukawa, H. Kiriyama, and R. Ikeda, Bull. Chem. Soc. Jpn. 50, 1927 (1977).

[36] J. W. Lynn, H. H. Patterson, G. Shirane, and R. G. Wheeler, Solid State Commun. 27, 859 (1978).

[37] H. D. Grundy and I. D. Brown, Can. J. Chem. 48, 1151 (1970).

[38] G. Brauer, in *Handbuch der präparativen anorganischen Chemie* (Verlag, Stuttgart, 1960), Vol. I, p. 649.

[39] M. T. Robinson, K. Rössler, and I. M. Torrens, J. Chem. Phys. 60, 680 (1974).

[40] K. Rössler and M. T. Robinson, in *Atomic Collisions in Solids*, edited by S. Datz, B. R. Appleton, and C. D. Moak (Plenum, New York, 1975), Vol. I, p. 237.

[41] J. C. Bailar, Jr., J. Inorg. Nucl. Chem. 8, 165 (1958).

[42] C. S. Springer and R. E. Sievers, Inorg. Chem. 6, 852 (1967).

[43] J. E. Brady, Inorg. Chem. 8, 1208 (1969).

[44] H. E. LeMay, Jr., in *Coordination Chemistry*, edited by S. Kirschner (Plenum, New York, 1969), p. 303.

[45] W. Preetz and J. P. Nadler, Z. Anorg. Allg. Chem. 410, 48 (1974).

[46] R. Bell, K. Rössler, G. Stöcklin, and S. R. Upadhyay, Report Jül-625-RC (Nov. 1969) and J. Inorg. Nucl. Chem. 34, 461 (1972).

[47] W. Preetz and J. P. Nadler, Z. Anorg. Allg. Chem. 410, 59 (1974).

[48] L. Pross, Report Jül-1511 — June 1978 (Thesis, Universität zu Köln 1978).

[49] C. Dimitropoulos, J. J. van der Klink, J. Pelzl, M. Regelsberger, and K. Rössler, Proc. Farad. Soc. (to be published).

[50] J. J. van der Klink, and C. Dimitropoulos, J. Mol. Struct. (to be published).