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Phase Transitions in Ferroelectric $RbLiSO_4$

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The crystal of $RbLiSO_4$ belonging to the $(NH_4)_2SO_4$ family ferroelectrics undergoes successive phase transitions. It is known that one of the phases called the phase IV is typically ferrielectric. In this study we have found that $RbLiSO_4$ shows a triple *D-E* hysteresis loop in the phase II. The spontaneous polarization is very small but the phase II is at least ferroelectric and may be ferrielectric. The double *D-E* hysteresis loop can be observed in the whole temperature region of the phase III. We can say that the phase III is antiferroelectric. Additionally, the hysteresis loop of the crystal changes complexly just below the V-IV phase transition point.

§1. Introduction

The crystal of $RbLiSO_4$ belonging to the $(NH_4)_2SO_4$ family ferroelectrics undergoes successive phase transitions at about 166, 185, 202 and 204°C from the phase V to the phase IV, III, II and I on heating, respectively.[1] Specially, it is known that $RbLiSO_4$ is typically ferrielectric in the phase IV because the typical triple *D-E* hysteresis loop is observed and the phase VI induced by the electric field can be ascertained by the X-ray analysis in the phase IV.[1,2] The dielectric constant ε_a of the crystal along the *a*-axis shows a stepwise anomaly at the V-IV phase transition point and a sharp peak around the III-II phase transition point.[1] The former anomaly is caused by the ferrielectric phase transition. However, it has not been known what causes the latter anomaly.

§2. Experimental

In this study, our equipment observing the *D-E* hysteresis loop has been improved at many points especially in order to observe small polarization. We can observe the *D-E* hysteresis loop under a condition of noise less than 0.05 nC/cm^2 for a specimen with $2\sim3$ mm^2 electrode area.

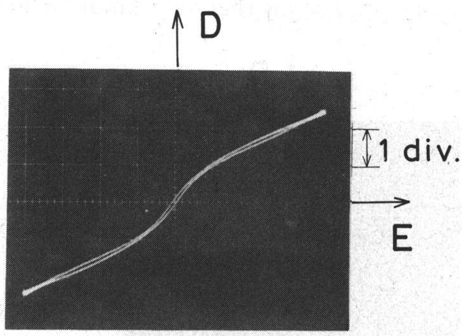

Fig. 1. *D-E* hysteresis loop just above the III-II transition point in the phase II. $E_{max} = 21$ kV/cm, D (1 div.) $= 0.64$ nC/cm^2.

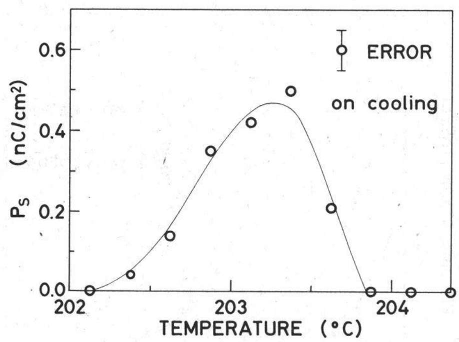

Fig. 2. Temperature dependence of spontaneous polarization in the phase II.

Figure 1 shows a triple *D-E* hysteresis loop observed at 60 Hz along the *a*-axis just above the III-II transition point in the phase II. The loop becomes a pseudotriple loop at the middle of the phase II and a single loop just below the II-I transition point. The temperature dependence of spontaneous polarization P_s in the phase II is shown in Fig. 2. Even the maximum value around the center of the phase II is very small (about 0.5 nC/cm^2) and about 1/200 of that in the phase IV.[1]

An antiferroelectric double *D-E* hysteresis loop could be observed only in a temperature range of a few degrees above the IV-III phase transition point.[1] However, in this study, the double loop can be observed in the whole temperature region of the phase III because of the improvement mentioned above. Figure 3 shows an example at 191°C on heating. The antiferroelectric polarization P_a is decreasing on heating and vanishes at the III-II phase transition point and the reverse process is seen on cooling, as is shown in Fig. 4. The hysteresis loop becomes exactly paraelectric at the III-II transition. There is a clear difference between the temperature dependence of the antiferroelectric polarization on heating and on cooling. On cooling P_a does not so change at 200∼190°C and it begins to increase below 188°C. Around this transient temperature region the *D-E* hysteresis loop looks like a quadruple one suggesting that two kinds of antiferroelectric loops are overlapping. Such a quadruple loop can be observed only on cooling.

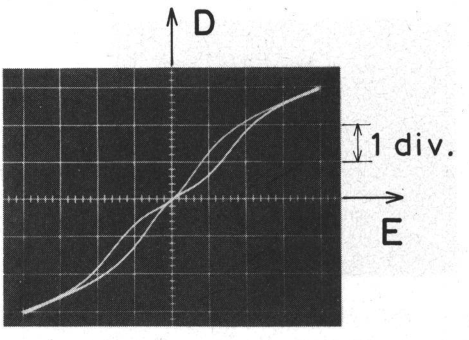

Fig. 3. *D-E* hysteresis loop at 191°C on heating. E_{max} = 21 kV/cm, D (1 div.) = 2.6 nC/cm^2.

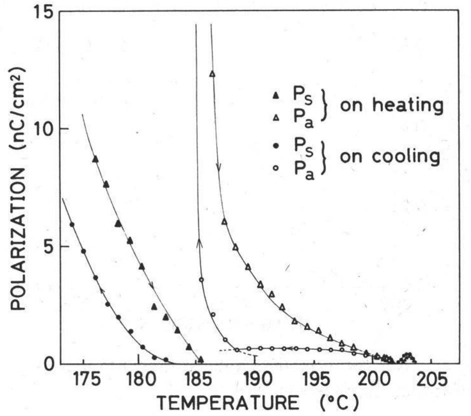

Fig. 4. Temperature dependence of spontaneous ploarization P_S and antiferroelectric polarization P_a determined by the *D-E* hysteresis loop method. E_{max} = 21 kV/cm.

The *D-E* hysteresis loop changes complexly just below the V-IV phase transition point. On increasing the applied field the loop changes from paraelectric first to antiferroelectric double, then triple and finally pseudotriple.

§3. Discussion

The X-ray crystal analyses[2,3] show that the structure of the phase II is similar with that of the ferrielectric phase IV. Combining this fact and the result of present observation of the hysteresis loop, we can say that the phase II is at least ferroelectric and may be ferrielectric. However, the phase II is incommensurate and the known incommensurate phases in the other ferroelectrics of the $(NH_4)_2SO_4$ family have been reported not ferroelectric. Some of those phases might be ferroelectric but even then the spontaneous polarization must be very small.

The fact that the double hysteresis loop can be observed throughout the phase III, combined also results of the X-ray analyses,[2,3] shows that the phase III is antiferroelectric.

The sharp peak of the dielectric constant along the *a*-axis at the III-II transition must be related to the ferroelectricity in the phase II and the antiferroelectricity in the phase III.

The quadruple loop observed around 188°C on cooling may correspond to the transition III →IV→VI induced by the electric field around this temperature.

The hysteresis loop complexly observed around the V-IV phase transition point may suggest the existence of some new phases around this transition but also the co-existence of the phases V and IV in the sample cannot be so easily denied as its cause.

References

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