PHYSICAL REVIEW VOLUME 173, NUMBER 2 10 SEPTEMBER 1968

Pressure and Temperature Dependence of the Dielectric Properties of Hydrogen-Bonded Ferroelectrics: $LiH_3(SeO_3)_2$ and $LiD_3(SeO_3)_2$†

G. A. SAMARA

Sandia Laboratory, Albuquerque, New Mexico 87115

(Received 15 April 1968)

The dielectric properties of $LiH_3(SeO_3)_2$ (LHS) and $LiD_3(SeO_3)_2$ (LDS) were investigated as functions of hydrostatic pressure to 26 kbar and temperature 20–140°C. A ferroelectric-to-paraelectric transition can be induced in both crystals at high pressure, and their Curie points decrease linearly with pressure with slopes of -6.0 ± 0.2°K/kbar for LHS and -5.9 ± 0.4°K/kbar for LDS. The high-pressure results indicate that LHS and LDS would have Curie points of 147°C and 172°C, respectively, at 1 bar were it not for the fact that both melt at 110°C. The room-temperature phase of LDS may be antiferroelectric, but the experimental evidence is not conclusive. The experimental results on LHS are correlated by means of a phenomenological theory. The transition entropy calculated on the basis of this theory is 0.61 cal/mole °K as compared with a value of 0.69 cal/mole °K predicted from statistical mechanics for an order-disorder transition of the KH_2PO_4 type. The decrease of the Curie points of LHS and LDS with pressure are compared with the results on KH_2PO_4 and KD_2PO_4 recently reported elsewhere by the author and others. The similarities between LHS and KH_2PO_4 are discussed, and the point of view is taken that the ordering of the protons (which in turn leads to a distortion of the lattice) is the triggering mechanism for the ferroelectric transition in these crystals. The effects of pressure on their Curie points are discussed in terms of a model in which the proton moves in a double-minimum potential well along the length of the H bond. Increasing pressure decreases both the separation of the potential minima and the height of the potential barrier between them. Both effects lead to a lower Curie point.

I. INTRODUCTION

MUCH experimental and theoretical work has been reported on the dielectric properties of hydrogen-bonded ferroelectrics with particular emphasis devoted to the important role played by the hydrogen (H) bond.[1,2] Potassium dihydrogen phosphate, KH_2PO_4 (henceforth abbreviated KDP), is the classic H-bonded ferroelectric. Its ferroelectric properties are well known.[1] On the other hand, lithium trihydrogen selenite $LiH_3(SeO_3)_2$ (henceforth abbreviated LHS) is a relatively new H-bonded ferroelectric whose properties have not been studied in detail. Ferroelectricity in LHS was first reported by Pepinsky and Vedam.[3] It is a room-temperature ferroelectric that possesses a number of features which make it attractive for both experimental and theoretical studies. It exhibits by far the largest spontaneous polarization yet observed for an H-bonded ferroelectric, namely, 15 $\mu C/cm^2$. This value is to be compared with 5 $\mu C/cm^2$ for KDP and 0.25 $\mu C/cm^2$ for Rochelle salt. LHS also has the somewhat unusual property that it remains ferroelectric up to its melting point of 110°C. Both small-field dielectric-constant and specific-heat measurements over the temperature range $-175°$ to 110°C have failed to reveal any transitions below the melting point.[3]

Previous experimental studies on LHS have consisted of measurements of the dielectric and piezoelectric constants and the spontaneous polarization in the ferroelectric phase.[3–5] From the theoretical point of view, the most important properties of ferroelectrics are those observed in the vicinity of the Curie point. No such measurements have been made on LHS because it melts before reaching its Curie point.

We recently found that a ferroelectric-to-paraelectric transition can be induced in LHS by the application of hydrostatic pressure.[6] The transition is made possible by the simultaneous raising of the melting point and lowering of the Curie point with pressure. The present work consists of a detailed study of the dielectric properties of LHS, with emphasis on the behavior near the Curie point. The dielectric constant, spontaneous polarization, and coercive field were measured in the temperature range 20 to 140°C and hydrostatic pressure up to 26 kbar. The nonlinear effects of dc bias fields on the dielectric properties were also investigated. In addition, the volume compressibility of LHS was measured to 24 kbar at 22°C.

In view of the importance of the H bond in the onset of ferroelectric behavior in H-bonded ferroelectrics, some dielectric properties of the deuterated analog $LiD_3(SeO_3)_2$ (henceforth abbreviated LDS) were also

---

† This work was supported by the U.S. Atomic Energy Commission.

[1] See, for example, F. Jona and G. Shirane, *Ferroelectric Crystals* (The Macmillan Company, New York, 1962); W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4.

[2] R. Blinc and S. Svetina, Phys. Rev. **147**, 430 (1966); M. Tokunaga and T. Matsubara, Progr. Theoret. Phys. (Kyoto) **35**, 581 (1966), and references therein.

[3] R. Pepinsky and K. Vedam, Phys. Rev. **114**, 1217 (1959).

[4] V. P. Konstantinova, T. M. Sil'vestrova, L. A. Shuvalov, and V. A. Yurin, Izv. Akad. Nauk SSSR, Ser. Fiz. **24**, 1318 (1960) [English transl.: Bull. Acad. Sci. USSR, Phys. Ser. **24**, 1317 (1960)].

[5] D. Berlincourt, W. R. Cook, Jr., and M. E. Rander, Acta Cryst. **16**, 163 (1963).

[6] G. A. Samara and D. H. Anderson, Solid State Commun. **4**, 653 (1966).

investigated at high pressure. There appear to be no previously reported dielectric measurements on this compound.

The results are presented and discussed in the following sections. In particular, the present results will be compared with the hydrostatic-pressure measurements on KDP and KD_2PO_4 recently reported by the author and others.[7–9]

II. CRYSTALLOGRAPHIC CONSIDERATIONS

An x-ray crystal-structure study of LHS was carried out by Vedam *et al.*[10] The crystal is monoclinic (space group *Pn*) with two molecules per unit cell. In the usual choice of the orthogonal axes, the normal to the symmetry plane is taken as the y $(=b)$ axis and the normal to the (001) plane as z. Berlincourt *et al.*[5] found that at 25°C the ferroelectric moment ($15\ \mu C/cm^2$) is directed 3° from the normal to the (001) plane (i.e., 3° from $+z$ toward $+x$ in the xz plane) and shifts to an angle of 1.1° at 85°C, thus suggesting that it should lie very nearly along the normal to (001) at temperatures in the vicinity of the Curie point. Consequently, all the measurements reported in the present work were made with the electric field applied along the normal to the (001) plane.

III. EXPERIMENTAL TECHNIQUES

The experiments were performed in both a 30-kbar and a 14-kbar hydrostatic-pressure apparatus. A description of the apparatus and general experimental procedures including pressure calibration has been given elsewhere.[11] Pressure was measured with manganin gauges to an accuracy of $\pm 1\%$, and temperature changes were measured with Chromel-Alumel thermocouples to an accuracy ± 0.1°C.

The polarization and coercive field were measured from both low-frequency (manual) and 60-cycle hysteresis loops, using conventional circuitry. Capacitance and dissipation factor were measured at 10 and 100 kHz (field strength <10 V/cm) with a transformer ratio arm bridge having an accuracy $>\pm 0.1\%$.

The samples used were cut from large single crystals grown by evaporation from saturated H_2O and D_2O solutions.[12] In the case of LDS, the starting material was LHS which was then deuterated by successive exchanges with D_2O solutions. From the number of exchanges, the crystals were estimated to be over 90% deuterated. The crystal axes and faces were identified by geometry and x-ray diffraction techniques. The samples were in the form of thin plates (0.5–1.0) mm thick $\times$(0.3–0.7) cm^2, with the polar direction normal to the large faces. Silver electrodes were painted on the large faces of the samples.

The volume compressibility of polycrystalline LHS was measured to 25 kbar by a piston-displacement technique using an apparatus described earlier.[13] The accuracy of the method is better than $\pm 10\%$.

IV. EXPERIMENTAL RESULTS

A. $LiH_3(SeO_3)_2$

Measurements were made on several samples with good agreement among the results. At 1 bar both the dielectric constant ϵ and the dielectric loss $\tan\delta$ increase very rapidly for temperatures above 90°C because of the large increase in sample conductivity as conditions approach the melting point. At high pressures the temperature dependence of ϵ shows the behavior expected at a ferroelectric (FE)-to-paraelectric (PE) transition with ϵ reaching peak values often $>10^4$ at the Curie point (see Figs. 1 and 2 of Ref. 6). The main effect of pressure is to displace the isobars to lower temperatures.

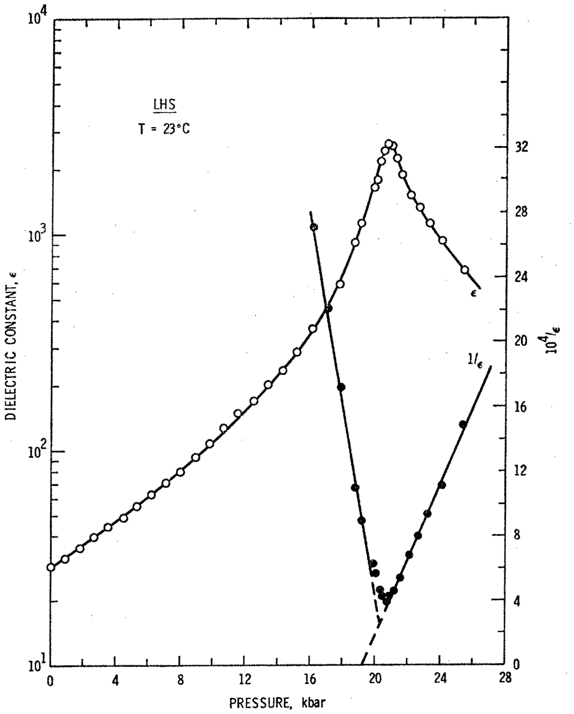


FIG. 1. Pressure dependence of the dielectric constant of $LiH_3(SeO_3)_2$ and its reciprocal measured along the polar axis at 10 kHz and 23°C.

---

[7] H. Umebayashi, B. C. Frazer, G. Shirane, and W. B. Daniels, Solid State Commun. **5**, 591 (1967).

[8] G. A. Samara, Phys. Letters **25A**, 264 (1967).

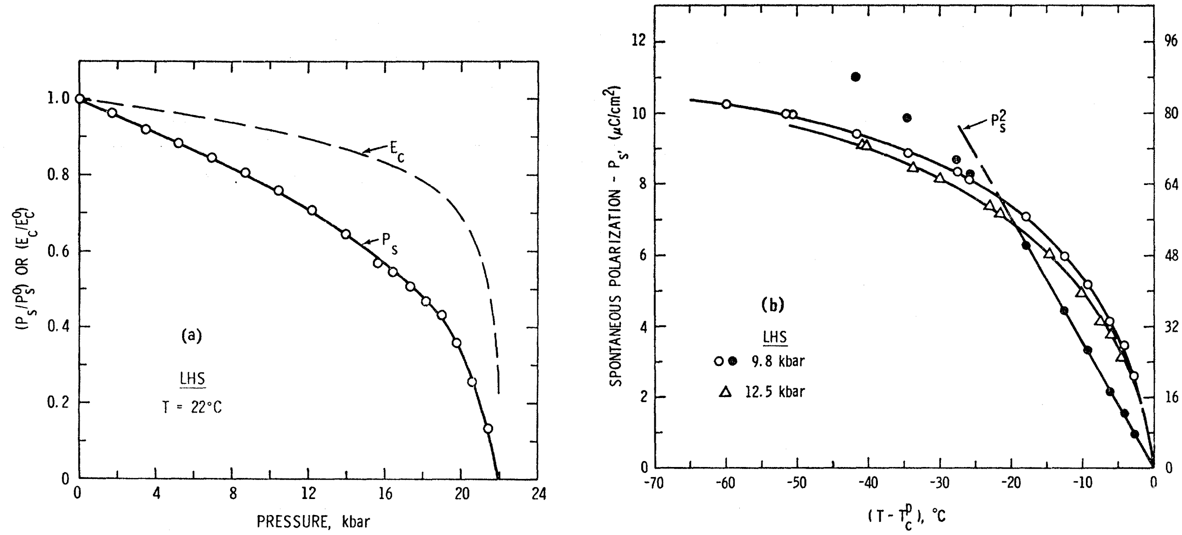
[9] H. Hegenbarth and S. Ullwer, Cryogenics **7**, 306 (1967).

[10] K. Vedam, Y. Okaya, and R. Pepinsky, Phys. Rev. **119**, 1252 (1960).

[11] G. A. Samara, J. Phys. Chem. Solids **26**, 121 (1965).

[12] The crystals were grown at this laboratory and were furnished by D. H. Anderson. The LDS crystals were taken from the same batch used by Anderson in his nuclear magnetic resonance studies [D. H. Anderson, in *Proceedings of the XIV Colloque Ampere, International Conference on Magnetic and Electrical Resonance and Relaxation, Ljublijana, Yugoslavia, 1966* (North-Holland Publishing Co., Amsterdam, 1967), p. 743].

[13] G. A. Samara, L. C. Walters, and D. Northrop, J. Phys. Chem. Solids **28**, 1875 (1967).



(a) (b)

FIG. 2. (a) Fractional changes of the spontaneous plarization and coercive field of $LiH_3(SeO_3)_2$ as functions of hydrostatic pressure at 22°C. $P_s^0 = 14.8\ \mu C/cm^2$ and $E_c^0 = 1010$ V/cm. (b) Spontaneous polarization of $LiH_3(SeO_3)_2$ as a function of the reduced temperature $(T - T_c^p)$ at two pressures. The lines represent a least-squares fit of the experimental data to Eq. (12). P_s^2 versus $(T - T_c^p)$ is also shown for the 9.8-kbar isobar.

Dielectric-constant versus frequency measurements in the PE phase did not indicate any piezoelectric resonances, thus suggesting that the crystal structure in this phase is centrosymmetric. As suggested by Vedam *et al.*,[10] this structure is most likely monoclinic space group $P2_1/n$.

Figure 1 shows a 23°C isotherm of ϵ as a function of pressure. These results clearly show that the FE–PE transition in LHS can be induced by pressure at room temperature. In analogy to the Curie point T_c, there is a transition pressure p_c corresponding to ϵ_{max}.

LHS exhibits well-saturated, square hysteresis loops. The spontaneous polarization P_s decreases with both increasing temperature and pressure. Figure 2(a) shows the fractional changes in P_s and the coercive field E_c as functions of pressure at 22°C. Here P_s^0 and E_c^0 are the values of P_s and E_c at 1 bar. Figure 2(b) shows two isobars of P_s versus the reduced temperature $(T - T_c)$.

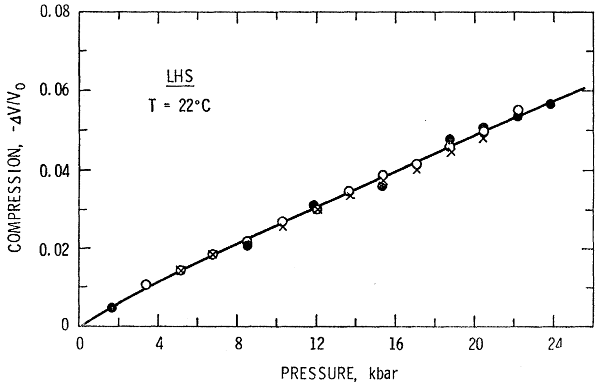


FIG. 3. Volume compression of $LiH_3(SeO_3)_2$ as a function of pressure. The data are from three different runs.

Figure 3 shows the volume compression of LHS up to 24 kbar. Results from three samples, one of which (marked ×) was encapsulated in a 0.025-cm-thick sleeve of silver chloride, are shown. Silver chloride is a soft material which helps in making the pressure across the sample more uniform. Correction for its compression was taken into account. The initial volume compressibility is $-(1/v_0)(dv/dp)_T = (2.7 \pm 0.2) \times 10^{-3}$ kbar^{-1}. For two of the samples the measurements were extended to 30 kbar. Small deviations from the curve in Fig. 3 in the direction of larger compression were noted above 22 kbar. These may be associated with the phase transition expected in this pressure range.

B. $LiD_3(SeO_3)_2$

The general features of the temperature and pressure dependence of ϵ of LDS are quite similar to those for LHS. Again the main effect of pressure is a lowering of the Curie point (Fig. 4).

Hysteresis-loop measurements at 1 bar and 22°C revealed features characteristic of antiferroelectric behavior; however, the evidence is not conclusive. The polarization-versus-field relation is linear up to a critical field of $\simeq 12$ kV/cm, above which field-induced loops appear in both the positive and negative field directions. These loops become well saturated at fields of 20–30 kV/cm, but they are often asymmetric. This is indicative of strong internal bias in the crystals. In some crystals the bias is so strong that loops are induced in only one direction of the applied field. Measurements

Table I. Comparison of the values of the spontaneous polarization, Curie point and its pressure coefficient, and the coefficients of the free-energy expansion for various ferroelectrics.

Compound	P_s^0 (μC/cm^2)	T_c^0 (°K)	dT_c^0/dp (°K/kbar)	C (°K)	ξ (esu/cm^2)$^{-2}$	ζ (esu/cm^2)$^{-4}$
$LiH_3(SeO_3)_2$	15	420	−6.0	4.1×10^4	1.22×10^{-11}	2.98×10^{-21}
$LiD_3(SeO_3)_2$	(AFE)[a]	446	−5.9	2.9×10^4	...	...
$NaD_3(SeO_3)_2$	(AFE)[a]	258	−3.3[b]	4.5×10^3	...	...
$BaTiO_3$	26	393	−5.5[c]	1.7×10^5	-2.77×10^{-12} [d]	5.40×10^{-22} [d]
KH_2PO_4	5	122 120	−4.5[e] −5.6[f]	3.3×10^3	... ...	... ...
KD_2PO_4	...	213 208	−2.6[e] −3.9[g]	4.0×10^3	... ...	... ...
TGS[h]	3.2	322	+2.6[i]	3.2×10^3	8.00×10^{-10} [i]	5.04×10^{-18} [i]

[a] Antiferroelectric.

[b] G. A. Samara (unpublished results).

[c] Reference 17.

[d] F. Jona and G. Shirane, Ref. 1, Chap. 4.

[e] Reference 7.

[f] Reference 9.

[g] Reference 8.

[h] Triglycine sulfate.

[i] F. Jona and G. Shirane, Ref. 1, Chap. 2.

on several crystals allow us to estimate for the saturation polarization a value of 15–20 μC/cm^2.

At high pressures, and for temperatures in the vicinity of the Curie point, the two loops coalesce into one with a kink at its center. The asymmetry in this loop made it difficult to accurately measure the variation of the polarization with temperature and pressure.

V. DISCUSSION

A. Transition Temperatures

Figure 4 shows the shifts of the Curie points T_c (taken as the temperatures corresponding to the peak values of ϵ) of LHS and LDS with pressure. T_c of each compound decreases linearly with increasing pressure over the range of the measurements. Extrapolating the results back to zero pressure shows that LHS and LDS would have Curie points of 147±1 and 172±3°C, respectively, at atmospheric pressure were it not for their melting before reaching these temperatures. The Curie point at any given pressure T_c^p can then be expressed as

$$T_c^p = T_c^0 - kp, \tag{1}$$

where T_c^0 is the value of T_c at atmospheric pressure. The coefficient k is (6.0±0.2)°C/kbar for LHS and (5.9±0.4)°C/kbar for LDS. Table I compares the present values of T_c^0 and k $(=-dT_c/dp)$ with those of other well-known ferroelectrics.

Very careful dielectric-constant versus temperature measurements in the vicinity of the Curie point showed that, to within 0.3°C, the transitions in LHS and LDS do not exhibit any temperature hysteresis between increasing and decreasing temperature cycles, thus suggesting that the transitions may be second order. This is supported in LHS by the observed continuous changes of the polarization and the dielectric constant as the Curie point is approached from below. But it is recognized that thermal gradients and inhomogeneities

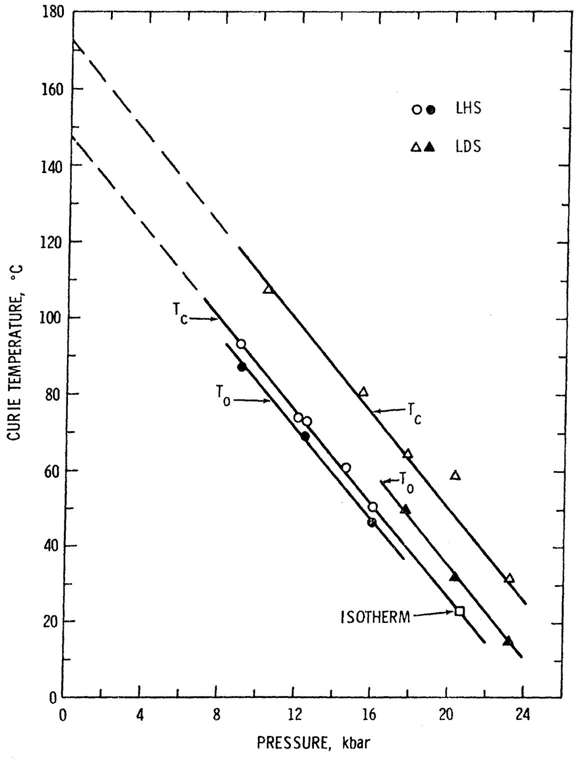


Fig. 4. Shifts of the Curie points T_c and Curie-Weiss temperatures T_0 of $LiH_3(SeO_3)_2$ and $LiD_3(SeO_3)_2$ with hydrostatic pressure.

TABLE II. Comparison of the crystallographic structures, transition temperatures at 1 bar, and Curie constants for the alkali trihydrogen selenites. Three dots indicate that the quantity is either not known or inappropriate.

Compound[a]	FE or AFE phase Symmetry class	Space group	PE Phase Symmetry class	Space group	T_c (°K)	T_0 (°K)	C (°K)
$LiH_3(SeO_3)_2$	m	Pn	$2/m$	$P2_1/n$?	420	417	4.1×10^4
$LiD_3(SeO_3)_2$	···	···	···	···	446	432	2.9×10^4
γ-$NaH_3(SeO_3)_2$ [b]	m	Pn	···	···	101	···	···
β-$NaH_3(SeO_3)_2$ [b]	1	···	$2/m$	$P2_1/n$	194	193	4.6×10^2
$NaD_3(SeO_3)_2$ [c]	···	···	···	···	270	245	7.0×10^3
$KH_3(SeO_3)_2$ [d]	1	$P1$	mmm	···	211	···	···
$CsH_3(SeO_3)_2$ [e]	$\bar{1}$	$P\bar{1}$	$\bar{1}$	$P\bar{1}$	145	65	1.1×10^3

[a] $NaH_3(SeO_3)_2$ exhibits two transitions. On cooling, the PE phase (α) transforms to a FE phase (β) at 194°K which then transforms to a second FE phase (γ) at 101°K.

[b] Reference 14.

[c] R. Blinc *et al.*, Ref. 14.

[d] Reference 15.

[e] Reference 16.

in the sample can smear a first-order transition and make it look like second order.

B. Comparison with other Alkali Trihydrogen Selenites

There has been considerable recent work on the dielectric properties of the alkali trihydrogen selenites.[14–16] Although chemically isomorphous, these compounds exhibit structural and dielectric peculiarities which make a comparison of the present results on LHS with those of the other selenites useful. Table II summarizes the available data. LHS and LDS are the only members that exhibit ferroelectric properties at room temperature, and they have the largest spontaneous polarizations. The low-temperature phases of the Na salts are ferroelectric, whereas that of the Cs salt is believed to be antiferroelectric.[16] The K salt exhibits a small anomaly in ϵ at its transition point, but no hysteresis loops have been observed.[15]

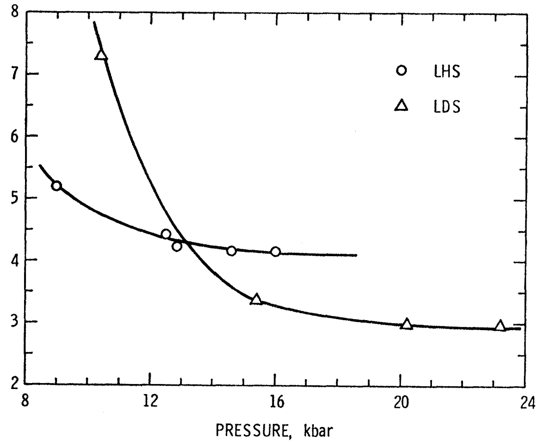


FIG. 5. Pressure effects on Curie-Weiss constants C of $LiH_3(SeO_3)_2$ and $LiD_3(SeO_3)_2$.

C. Curie-Weiss Behavior

In the paraelectric phase the dielectric constants of LHS and LDS obey the Curie-Weiss law

$$\epsilon = C^p/(T - T_0^p) \qquad (2)$$

over a wide temperature range (see Fig. 2 of Ref. 6). Here the superscript p is introduced to emphasize that C and T_0 are functions of pressure. At high pressure, T_0^p (defined as the temperature at which $1/\epsilon$ extrapolates to zero on a $1/\epsilon$ versus T plot) varies linearly with pressure (Fig. 4) and can be expressed as

$$T_0^p = T_0^0 - k'p. \qquad (3)$$

$T_0^0 = 143 \pm 3$°C for LHS and 159 ± 5°C for LDS. Within the accuracy of the data, the k''s have the same values as the k's in Eq. (1).

The Curie constants C^p decrease rapidly with increasing pressure at low pressures and approach limiting values at high pressures (Fig. 5). The decrease at low pressure is mostly due to the contribution of sample conductivity to ϵ and the dielectric loss at high temperatures (i.e., in the PE phase). The high-pressure limiting values of C^p are 4.1×10^4°K for LHS and 2.9×10^4°K for LDS. These values of C are compared with those of other ferroelectrics in Table I.

In the case of LHS, T_0^p is about 4°K lower than T_c^p. This is often taken as indicating a first-order transition; however, clamping and biasing effects can also be responsible for this deviation. In pressure experiments, this deviation is observed for ferroelectrics known to exhibit second-order transitions (e.g., triglycine sulfate) and is probably due to some mechanical clamping of the sample by the viscous pressure-transmitting fluid.

---

[14] R. Blinc, A. Jovanovic, A. Levstik, and A. Prelesnick, J. Phys. Chem. Solids **26**, 1359 (1965). See also L. A. Shuvalov and N. R. Ivanov, Phys. Status Solidi **22**, 279 (1967).

[15] L. A. Shuvalov, N. R. Ivanov, and T. K. Sitnik, Kristallografiya **12**, 366 (1967) [English transl.: Soviet Phys.—Cryst. **12**, 315 (1967)].

[16] Y. Makita, J. Phys. Soc. Japan **20**, 1567 (1965).

For LDS, T_0^p is some 15°K lower than T_c^p (Fig. 4), and this is consistent with the behavior usually observed at an antiferroelectric transition.

As noted earlier for other ferroelectrics,[11,17] the pressure dependence of ϵ of LHS in the PE phase obeys a relationship similar to Eq. (2) expressed in terms of pressure, i.e.,

$$\epsilon = C^*/(p-p_0), \tag{4}$$

where, at a given temperature, C^* and p_0 are constants corresponding to C and T_0, respectively. At 23°C, $C^* = 4.4\times 10^3$ kbar and $p_0 = 19.2$ kbar (see Fig. 1).

D. Phenomenological Theory

It is now well established that many of the physical properties of ferroelectrics, especially those in the transition region, can be successfully correlated and explained in terms of the phenomenological theory originally developed by Devonshire.[18] The theory is discussed in many reviews and texts.[1] We shall present here only those elements of the theory pertinent to the present discussion and check their applicability for the case of LHS. The theory is particularly useful in the present case, for it allows us to calculate certain quantities that cannot be measured directly, e.g., the changes in entropy and specific heat at the transition, both of which provide important information concerning the nature of the transition. The treatment differs slightly from the usual one in that pressure is introduced as a variable. It should be recalled here that the experimental results indicate that the FE–PE transition in LHS can be treated as a second-order transition.

In the theory, the free energy A of the crystal is expanded as a function of polarization P and strain x (or stress X). For the present case, the free energy expressed in terms of hydrostatic pressure p, polarization P, and temperature T is given by[19]

$$A(p,P,T) = \Lambda p^2 + \tfrac{1}{2}(\gamma+\Omega p)P^2 + \tfrac{1}{4}\xi P^4 + \tfrac{1}{6}\zeta P^6 + \cdots. \tag{5}$$

Here Λ and Ω are functions of the elastic and electrostrictive constants, and the coefficients γ, ξ, and ζ (especially γ) are, in general, functions of temperature.

1. *Dielectric Constant*

From Eq. (5) and the defining relations

$$(\partial A/\partial P) = E, \tag{6}$$

$$(\partial E/\partial P) = 1/\chi, \tag{7}$$

and

$$\epsilon = 1 + 4\pi\chi \simeq 4\pi\chi \qquad (\text{for } \epsilon \gg 1), \tag{8}$$

where E is the electric field and χ the dielectric susceptibility, it is easily shown that, in the PE phase,

$$\begin{aligned}(1/\epsilon)_{T>T_0^p} &= (1/4\pi)(\gamma+\Omega p)\\ &= (T-T_0^p)/C^p\\ &= [T-(T_0^0-k'p)]/C^p.\end{aligned} \tag{9}$$

Here the last two equalities follow from the observed Curie-Weiss temperature dependence of ϵ [Eq. (2)], and the linear dependence of T_0^p on pressure, Eq. (3).

At high pressures, where C^p is independent of pressure (see Fig. 5), it is seen from Eq. (9) that

$$\gamma = 4\pi(T-T_0^0)/C \quad\text{and}\quad \Omega = 4\pi(k'/C). \tag{10}$$

In this case, Eq. (9) also predicts that, at any given temperature T, $1/\epsilon$ is a linear function of pressure with slope $= k'/C$. Comparison with Eq. (4) shows that

$$k'/C = 1/C^*. \tag{11}$$

Using the values $k' = 6.0$°K/kbar and $C = 4.1\times 10^4$°K for LHS, we obtain the theoretical slope $k'/C = 1.46\times 10^{-4}$ kbar^{-1} compared with the experimental value $1/C^* = 2.27\times 10^{-4}$ kbar^{-1} measured at 23°C (see Fig. 1). The agreement is reasonable, considering that the experimental results were obtained from two different samples.

2. *Spontaneous Polarization*

From Eqs. (5) and (6), and noting that $P = P_s$ for $E = 0$ (P_s = spontaneous polarization), it is easily shown that close to the transition, where P_s is small,

$$P_s^2 = (4\pi/C^p\xi)(T_0^p-T) - (4\pi/C^p)^2(\zeta/\xi^3)(T_0^p-T)^2, \tag{12}$$

where it has been assumed that ξ and ζ are independent of temperature. Near the Curie point, Eq. (12) predicts a linear dependence of P_s^2 on T at constant pressure. From Fig. 2(b) it is seen that this dependence is well obeyed over a 15–20°C range, thus indicating that the coefficient of the $(T_0^p-T)^2$ term is small, as is assumed in the derivation of Eq. (12).

The coefficients ξ and ζ were evaluated from a least-squares fit of the experimental data to Eq. (12). The values obtained from the 12.5-kbar data are listed and compared with the corresponding values for other ferroelectrics (at 1 bar) in Table I.

The results in Fig. 2(b) show that the major part of the change of P_s with pressure shown in Fig. 1(b) is caused by the shift of the Curie point to lower temperatures. There is only a small intrinsic decrease of P_s with pressure amounting to $\simeq$1%/kbar at temperatures far removed from the Curie point [see Fig. 2(b)]. Similar behavior has been observed for other ferroelectrics.[17]

3. *Thermal Properties*

An accurate study of the thermal properties of LHS through its transition point is rather difficult, if not impossible, at the high-pressure conditions required. However, estimates of the changes in entropy and specific heat at the transition can be obtained from the phenomenological theory.

The entropy S is defined by

$$S = -(\partial A/\partial T)_P. \tag{13}$$

---

[17] G. A. Samara, Phys. Rev. **151**, 378 (1966).

[18] A. F. Devonshire, Phil. Mag. Suppl. **3**, 85 (1954).

[19] F. Jona and G. Shirane, Ref. 1, Chap. 2.

At constant pressure, and assuming that ξ and ζ are independent of temperature, Eq. (5) yields for the change in entropy

$$\Delta S = S_0 - S = (2\pi/C^p)P_s^2, \qquad (14)$$

where S_0 and S are the entropies of the PE and FE phases, respectively, and P_s^2 is given by Eq. (12) and the experimental data. Using the saturation values of P_s and C^p, namely, 15 $\mu C/cm^2$ and 4.1×10^{4}°K, respectively, and the values 3.185 g/cm^3 for the density[4] and 264 g/mole for the molecular weight, we calculate, for LHS, $\Delta S = 0.61$ cal/mole °K. This value is in close agreement with that predicted from statistical mechanics for an order-disorder transition of the KDP type. In the latter case, for a system of N molecules per mole, in which the transition is from the completely polarized or ordered state (corresponding to + and − polarization) to the completely unpolarized or disordered state, the increase in entropy is[20]

$$\Delta S = \tfrac{1}{2}Nk\ln 2 = 0.69 \text{ cal/mole °K}, \qquad (15)$$

where k is Boltzmann's constant. It should be remembered that Eq. (15) represents only the entropy change associated with the ordering of dipoles and does not include vibrational and specific-heat contributions.

From Eq. (14) and the relationship $c = T(\partial S/\partial T)$, the excess specific heat due to the temperature variation of the polarization is given by

$$\Delta c_P = c_P - c_{P_0} = -(2\pi T/C^p)(\partial P_s^2/\partial T), \qquad (16)$$

where c_P and c_{P_0} are the specific heat (at constant polarization) per unit volume of the FE and PE phases, respectively. Thus at each pressure the temperature dependence of Δc_P can be calculated from the known value of C^p and the P_s^2 versus T data. From Eqs. (12) and (16) it is seen that, at the Curie point ($T = T_0^p$), Δc_P is given by

$$\Delta c_P = \tfrac{1}{2}(4\pi/C^p)^2(T_0^p/\xi). \qquad (17)$$

At 12.5 kbar, the known values of the parameters yield $\Delta c_P = 2.36$ cal/mole °K.

4. *Effects of dc Bias*

The superimposition of a large dc bias field on the small-amplitude ac measuring field causes nonlinearities in the dielectric response of a ferroelectric, especially in the vicinity of the Curie point. Figure 6 shows the effects of dc bias on the dielectric constant of LHS at 12.2 kbar. The peak value of ϵ decreases with increasing dc field and the temperature at which the peak occurs is displaced to higher values. This shift in temperature, ΔT, can be calculated from the phenomenological theory. It can be shown that[21]

$$E_b = \tfrac{4}{3}[(1/3\xi)(4\pi/C^p)^3]^{1/2}\Delta T^{3/2}, \qquad (18)$$

where E_b is the bias field. Figure 6 (insert) compares the measured values of ΔT (experimental points) with those calculated from Eq. (18) (solid line). The agreement is quite good.

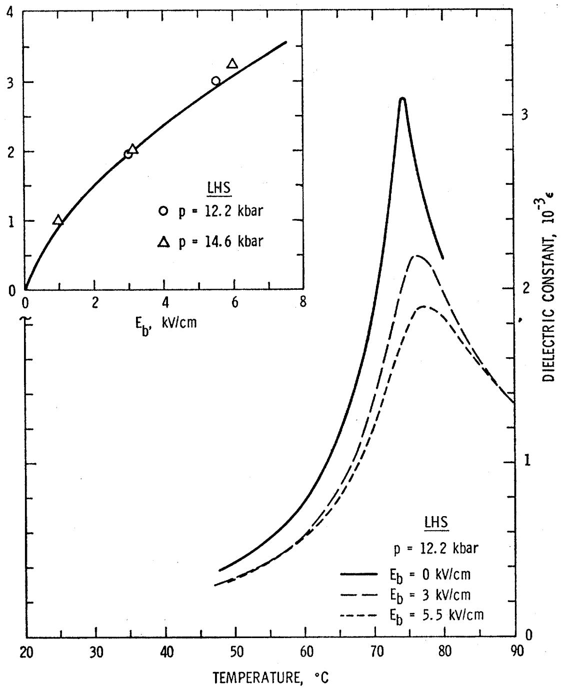


FIG. 6. Effects of dc biasing field on the temperature dependence of the dielectric constant of $LiH_3(SeO_3)_2$ measured at 100 kHz. Insert shows the shift of the transition temperature (T at ϵ_{max}) as a function of biasing field, where the points are experimental values and the curve is calculated from Eq. (18).

E. Nature of the Transition and the Effect of Pressure on the Potential Field of the Proton

Although the isotope shift in LHS is not as large as in KDP, there is a body of evidence suggesting that the mechanisms for the FE transitions in the two materials are similar. Room-temperature x-ray[10] and neutron[22] diffraction studies have shown that the LHS structure consists of pyramidal SeO_3^{2-} ions joined together by a system of strong O–H···O hydrogen (H) bonds and Li ions. The H bonds lie nearly in the planes normal to the polar axis, and there is evidence[22–24] that, in the FE phase, the protons are ordered in double-minimum potential wells between pairs of oxygen ions. These features are very similar to those found in KDP.[1,2] In addition, as mentioned earlier, the transition entropies of the two materials are comparable. Also important from the point of view of the present work is the fact

---

[20] J. C. Slater, J. Chem. Phys. **9**, 16 (1941).

[21] H. H. Wieder, J. Appl. Phys. **30**, 1010 (1959).

[22] J. H. van den Hende and H. P. Boutin, Acta Cryst. **16**, A184 (1963).

[23] R. Blinc and M. Pintar, J. Chem. Phys. **35**, 1140 (1961); G. V. Gavrilova-Podol'skaya, S. P. Gabuda, and A. G. Lundin, Fiz. Tverd. Tela **9**, 1166 (1967) [English transl.: Soviet Phys.—Solid State **9**, 911 (1967)].

[24] R. K. Khanna, J. C. Decius, and E. R. Lippincott, J. Chem. Phys. **43**, 2974 (1965).

that the Curie points of both compounds are similarly affected by pressure.

From the thermodynamic point of view, the decrease of the Curie point of KDP (and probably LHS[25]) with pressure can be accounted for on the basis of the sign of the volume change[26] ΔV and latent heat[27] L of the transition (which is first-order). In fact, use of the Clapeyron equation $(dT_c/dp)=T_c\Delta V/L$ with the observed values of ΔV and L yields values of dT_c/dp comparable to those observed experimentally for both KDP and KD_2PO_4. However, if we accept the ordering of the protons in the potential minima as the triggering mechanism for the ferroelectric transition (and this ordering in turn leads to the deformation of the lattice), then at least part of the explanation for the decrease of the Curie points of KDP and LHS must be sought in the effect of pressure on the potential field of the proton in the O–H···O bond.

Detailed theoretical treatments of the total energy of the H bond are not possible[28]; however, a number of reasonably successful semiempirical models, dealing mostly with the interpretation of infrared and Raman spectra of H-bonded crystals at 1 bar, have been proposed. One such model is due to Lippincott and Schroeder.[29] In this model the potential function for the motion of the proton in the H bond is written as the sum of two diatomic-molecule potentials, one (V_1) for O–H and the other (V_2) for H···O, plus an oxygen-oxygen interaction term (W). Thus,

$$V(r,R)=V_1(r)+V_2(R-r)+W(R). \qquad (19)$$

Here r is the O–H distance and R the O···O distance. W is considered a function of R only and is taken to be the sum of a van der Waals respulsion term and an electrostatic attraction term.

A simple potential such as Eq. (19) cannot completely describe the situation in ferroelectrics such as LHS and KDP; however, its use leads to two pertinent results. With decreasing R ($\equiv$increasing pressure), (1) r increases, and (2) the height of the energy barrier between the two potential minima decreases.

The relationship between r and R, obtained on the basis of the results of Lippincott and Schroeder,[29] is shown in Fig. 7. For the ferroelectric case of interest to us here, the results show that the separation of the two potential minima along the H bond should decrease as R decreases. Particularly important, the results suggest that if R becomes sufficiently short, then the proton will move to the center of the bond and the ferroelectric ordering should vanish. The critical distance for this to occur appears to be $R\simeq 2.40$ Å. Ideally, the test of this prediction would require dielectric and crystallographic (both x-ray and neutron diffraction) measurements at high pressures and low temperatures. Unfortunately, there are at present no data on the variation of R with pressure for any of the H-bonded ferroelectrics of interest.

On the above model, the decrease of the Curie points of LHS and KDP with pressure can result from either a thermal activation of the protons across a lower barrier or an increase in the tunneling probability of the protons through the lower and narrower barrier, or both. At present, the experimental situation,[2] including the pressure results,[7] favors a tunneling model for KDP, whereas the case of LHS is not as well understood. Because of its much higher Curie point (420 versus 122°K), tunneling should be less important in LHS than in KDP.

The above model can also provide a part of the explanation for the isotope shift. It has been observed[30] that deuteration causes a marked expansion (up to 0.04 Å) of the O–H···O bond length for short ($R<2.6$ Å) H bonds with a negligibly small effect for long ($R\simeq 2.65$–2.8 Å) bonds. For short bonds this effect is then the opposite of the pressure effect. On the basis of the experimental results, then, the isotope shift should be larger for the shorter bonds, and this appears to be consistent with experiment. For example, the O–H···O bond lengths in KDP are 2.49 Å and those in LHS are 2.52 and 2.57 Å.[22] KDP exhibits a much larger isotope shift.

At least two other factors are important in the explanation of the isotope effect. Both are quantum effects which are consequences of the larger mass of the deuteron. The larger mass leads to (1) a lower zero-point energy and (2) a lower tunneling probability through the barrier for the deuteron. Both effects lead to a higher Curie temperature. These effects can be expected to become less important the higher the transition temperature. This is also consistent with the experimental observations—e.g., compare LHS and KDP.

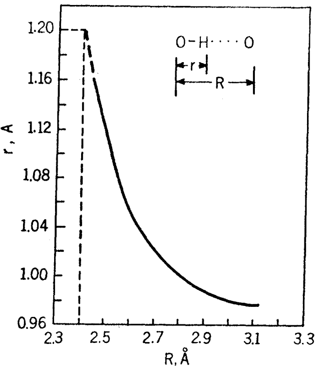


FIG. 7. The relation between the O–H distance r and the O···O bond length R for the O–H···O bond obtained on the basis of the model and parameters given in Ref. 29.

---

[25] It should be recalled that the compression data (see Sec. III) on LHS suggested the existence of a volume change in the transition region, but the experimental technique used is not suited for detecting small volume changes.

[26] W. R. Cook, Jr., J. Appl. Phys. **38**, 1637 (1967).

[27] W. Reese (to be published).

[28] C. A. Coulson, Research (London) **10**, 149 (1957).

[29] E. R. Lippincott and R. Schroeder, J. Chem. Phys. **23**, 1099 (1955).

[30] A. R. Ubbelohde and K. J. Gallagher, Acta Cryst. **8**, 71 (1955).

F. Model Calculation of the Effects of Pressure on T_c

The above conclusions concerning the effects of pressure on the Curie point are qualitatively consistent (at least in the case of KDP) with the more elaborate theoretical treatments[2] of the problem. It is then of interest to inquire as to whether it is possible to predict quantitatively the observed results from the theoretical models.

In both the Tokunaga and Matsubara and the Blinc and Svetina theories[2] the transition temperature is expressed in terms of (1) the configuration energies of the protons around a given PO_4 group, (2) the kinetic energy of the protons, and (3) the proton-lattice interaction energy. Thus, for example, in terms of the Blinc and Svetina theory[2] the transition temperature can be written as

$$T_c = T_c(\epsilon_0, \Gamma, \gamma', \omega), \qquad (20)$$

where ϵ_0 is the Slater short-range configuration energy, Γ is the tunneling matrix element, γ' is the long-range dipole-dipole interaction energy, and ω is the energy of an H_3PO_4 defect. The functional dependences of ϵ_0, Γ, γ', and ω involve a large number of parameters and their pressure derivatives cannot be evaluated without many assumptions and approximations.

On the basis of the Blinc and Svetina model and several assumptions, Blinc and Žekš[31] have recently calculated dT_c/dp and compared their results with experimental values. They obtained values of -4.70°K/kbar for KDP and -3.36°K/kbar for KD_2PO_4, both in surprisingly good agreement with the experimental results given in Table I. Interestingly enough, it turns out that it is the larger value of the tunneling matrix element which is responsible for the larger (dT_c/dp) in KDP than in KD_2PO_4.

Blinc and Žekš also calculated the pressure dependence of the Curie-Weiss constant C. For KD_2PO_4 they find $(1/C)(dC/dp) = -0.91\%$/kbar, again in reasonably good agreement with our experimental value[8] $1.5\pm0.3\%$/kbar.

VI. SUMMARY AND CONCLUSIONS

The results of this work can be summarized as follows:

(1) A ferroelectric-paraelectric transition can be induced in LHS and LDS by the application of high hydrostatic pressure. This results from the simultaneous increase of the melting points and decrease of the Curie points with increasing pressure.

(2) The Curie points of both compounds decrease linearly with slopes -6.0 ± 0.2°K/kbar for LHS and -5.9 ± 0.4°K/kbar for LDS. Extrapolating the high-pressure results back to zero pressure indicates that LHS and LDS would have Curie points of 147 ± 1°C and 172 ± 3°C, respectively, if it were not for their melting (melting point 110°C) before reaching these temperatures.

(3) The spontaneous polarization P_s of LHS decreases continuously to zero at the Curie point with both increasing temperature and pressure. The decrease of P_s with pressure at constant temperature is mostly due to the shift of the Curie point at lower temperatures; however, a small intrinsic decrease ($\approx 1\%$/kbar) in the magnitude of P_s is indicated by the data.

(4) The experimental results on LHS were correlated by means of a phenomenological theory of the Devonshire type. The theoretical value of the transition entropy is 0.61 cal/mole °K which is in close agreement with the value of 0.69 cal/mole °K predicted from statistical mechanics for an order-disorder transition of the KDP type.

(5) The similarities between LHS and KDP, namely, the existence of strong O–H···O bonds in planes normal to the polar axes, the ordering of the protons in the FE phases, the magnitude of the transition entropies, and the pressure dependence of the Curie points were discussed. Taking the point of view that the ordering of the protons (which in turn leads to a deformation of the lattice) is the triggering mechanism for the ferroelectric transition in these crystals, the shift of the Curie point with pressure was explained in terms of a model in which the proton moves in a double-minimum potential well along the length of the O–H···O bond. Increasing pressure decreases both the separation of the two potential minima and the height of the potential barrier between them. Both effects lead to a lower Curie point.

ACKNOWLEDGMENTS

The author expresses his thanks to Dr. D. H. Anderson for many useful discussions concerning the properties of the alkali trihydrogen selenites, to W. L. Chrisman for technical assistance, and to R. J. Baughman and J. Matsko for growing some of the LHS and LDS samples.

---

[31] R. Blinc and B. Žekš, Phys. Letters **26A**, 468 (1968); and (to be published).