

## Low-Temperature Specific Heat of KCl:OH<sup>†</sup>

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In KCl containing OH<sup>-</sup> ions with small concentration  $n_{\text{OH}}$ , a low-temperature specific-heat anomaly is observed which peaks at 0.3°K and whose entropy is close to  $n_{\text{OH}}k \ln 6$ . This anomaly is interpreted with the model in which the OH<sup>-</sup> ion in the Cl<sup>-</sup> cavity has six equilibrium positions among which it can tunnel. Assuming a Devonshire potential, a best fit to the data is obtained for a splitting between the  $A_{1g}$  and  $T_{1u}$  states of  $6.2 \times 10^{-5}$  eV (0.5 cm<sup>-1</sup>), and between the  $T_{1u}$  and  $E_g$  states of  $3.1 \times 10^{-5}$  eV. The observed anomaly is somewhat broader than the predicted one, which indicates that the potential of octahedral symmetry is only an approximation. From the rise of the anomaly at low temperatures, a splitting of  $4.1 \times 10^{-5}$  eV (0.33 cm<sup>-1</sup>)  $\pm 10\%$  is determined, in agreement with the value determined by paraelectric resonance. At concentrations exceeding  $10^{-4}$  mole ratio, the anomaly changes its shape in a way similar to that in KCl:Li. Our interpretation is that the tunneling states are perturbed by an electric interaction between the OH<sup>-</sup> ions. Specific evidence for an ordered state has not been found.

### I. INTRODUCTION

THIS paper deals with the study of the tunneling states of OH<sup>-</sup> ions in KCl crystals through the use of low-temperature specific-heat measurements. The reasons for our interest in this problem can be summarized as follows.

(a) It is known that OH<sup>-</sup> ions substituted into alkali-halide host lattices have quasirotational states similar to those known for other molecular impurities, such as CN<sup>-</sup>. The details of these states, however, are at present less well understood for OH<sup>-</sup> than for CN<sup>-</sup>.<sup>2</sup> The tunnel splitting of the motional ground state, for instance, has been observed in KCl:OH through paraelectric resonance experiments.<sup>3</sup> The interpretation of these measurements, however, has recently been questioned by Wolf and co-workers,<sup>4</sup> who claimed that part of the resonance signal in KCl:OH was actually caused by some spurious lithium impurities.<sup>5</sup> Also, high-resolution measurements of the electric-field-induced dichroism of the OH<sup>-</sup> stretching vibrations failed to reveal a tunnel splitting of the magnitude

derived from the resonance work.<sup>6</sup> Furthermore, it was recently shown<sup>7</sup> that the tunnel splitting of the OH<sup>-</sup> ion in KCl derived from the known relaxation rate<sup>8</sup> of the excited tunneling states was 10 times smaller than that observed in paraelectric resonance. Thus the different studies resulted in estimates of the tunnel splitting which differed by at least one order of magnitude in energy. This controversy can be settled through specific-heat measurements. This technique allows a determination of the tunnel splitting and also of the total number of tunneling states associated with the impurities in a very straightforward manner.

(b) Deviations from the Debye  $T^3$  behavior of the low-temperature specific heat of several nominally pure alkali-halide crystals<sup>9,10</sup> indicated the presence of some impurities with low-energy states. Since OH<sup>-</sup> is known to be a very common impurity in these materials, it was suggested that the anomalies were caused by tunneling OH<sup>-</sup> ions. The only way to test this is by measuring the specific heat of intentionally doped crystals.

(c) During the investigation of the tunneling states in KCl:Li, it had been found that for concentrations exceeding  $10^{-4}$  mole ratio of LiCl dissolved in KCl the shape of the excess specific heat  $C_{v, \text{KCl:Li}}(T) - C_{v, \text{KCl}}(T)$  became strongly concentration-dependent.<sup>11</sup> As a possible cause an electric dipole-dipole interaction had been considered. If this were the cause, a similar behavior ought to be expected also for other impurities with comparable dipole moments. The OH<sup>-</sup> ion has a dipole moment almost as large as Li<sup>+</sup>, 3.8 Debye<sup>12</sup>

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<sup>1</sup> For a recent review of this work, see B. Wedding and M. V. Klein, *Phys. Rev.* **177**, 1274 (1964).

<sup>2</sup> W. D. Seward and V. Narayanamurti, *Phys. Rev.* **148**, 463 (1966).

<sup>3</sup> W. E. Bron and R. W. Dreyfus, *Phys. Rev. Letters* **16**, 165 (1966); L. D. Scheerer and T. L. Estle, *Solid State Commun.* **4**, 639 (1966); G. Feher, I. W. Shepherd, and H. B. Shore, *Phys. Rev. Letters* **16**, 500 (1966).

<sup>4</sup> G. Höcherl, D. Blumenstock, and H. C. Wolf, *Phys. Letters* **24A**, 511 (1967); G. Höcherl and H. C. Wolf, *ibid.* **27A**, 133 (1968).

<sup>5</sup> See also T. L. Estle, *Phys. Rev.* **176**, 1056 (1968).

<sup>6</sup> H. Härtel and F. Lüty, in Proceedings of the International Color Center Conference, Rome, 1968 (unpublished).

<sup>7</sup> B. G. Dick, *Phys. Status Solidi* **29**, 587 (1968).

<sup>8</sup> K. F. Weinmann, Diplomarbeit, Stuttgart, Physikalisches Institut, 1966 (unpublished). See also the review paper by F. Lüty, *J. Phys. (Colloque C4)* **28**, C4-120 (1967).

<sup>9</sup> J. P. Harrison, *Rev. Sci. Instr.* **39**, 145 (1968).

<sup>10</sup> J. P. Harrison, P. P. Peressini, and G. Lombardo, *J. Phys. Chem. Solids* **19**, 557 (1968); see also P. P. Peressini, Ph.D. thesis, Cornell University, 1969 (unpublished).

<sup>11</sup> J. P. Harrison, P. P. Peressini, and R. O. Pohl, *Phys. Rev.* **171**, 1037 (1968).

<sup>12</sup> U. Kuhn and F. Lüty, *Solid State Commun.* **2**, 281 (1964).

TABLE I. KCl:OH samples used in this investigation.

Boule	Spec.-heat run	Label (this paper)	Amount KOH in melt (mole %)	ir samples			$K$ (cm <sup>-1</sup> ) 2045 Å	$C_v$ samples OH <sup>-</sup> concentration (10 <sup>17</sup> cm <sup>-3</sup> )		Entropy $\Delta S$ (erg/g °K)
				Absorption 2045 Å <sup>a</sup>	const. $K$ (cm <sup>-1</sup> ) 2.7 $\mu$	7.1 $\mu$ <sup>b</sup>		from uv absorp. <sup>c</sup>	from $\Delta S$ <sup>d</sup>	
SH2	31B <sup>e</sup>	A	"pure"	...	...	...	...	0.08 <sup>f</sup>	0.19	2.3
612141	PP12B	B	unknown	13.1	0.013	<10 <sup>-2</sup> g	12.7	4.9	4.3	54.5
611221	PP7A	C	0.1	35	0.034	0.036 <sup>h</sup>	32	12.3	11.0	135
806031W	PP13A	D	0.3	200	0.201	0.072	180	70	56	695
606211	PP9A	E	1.5	1750	1.24 <sup>i</sup>	0.12	1750	670	j	j

<sup>a</sup> Averaged over cross section of ir beam.

<sup>b</sup> Due to CO<sub>2</sub>.

<sup>c</sup> Averaged over  $C_v$  sample.

<sup>d</sup> Assuming  $\Delta S = nk \ln 6$ .

<sup>e</sup> This sample has been measured previously: Ref. 2, Fig. 21, curve D, and Ref. 9, Fig. 6, curve A.

<sup>f</sup> After Ref. 9. Because of the small absorption, this value is believed to be accurate to no better than a factor of 2.

<sup>g</sup> Also observed were two unidentified absorption bands, at  $\lambda^{-1} = 2920$  cm<sup>-1</sup>,  $K = 0.034$  cm<sup>-1</sup> and at  $\lambda^{-1} = 2840$  cm<sup>-1</sup>,  $K = 0.022$  cm<sup>-1</sup>.

<sup>h</sup> Unidentified absorption at  $\lambda^{-1} = 2920$  cm<sup>-1</sup>,  $K = 0.019$  cm<sup>-1</sup> and at  $\lambda^{-1} = 2840$  cm<sup>-1</sup>,  $K = 0.009$  cm<sup>-1</sup>.

<sup>i</sup> Superimposed on the broad band, peaking at 3647 cm<sup>-1</sup>, was a narrow band, at 3620 cm<sup>-1</sup>.

<sup>j</sup> Not enough high-temperature data to determine  $\Delta S$ .

compared to 6.0 Debye<sup>11</sup> (uncorrected for local field). Therefore, it should be interesting to compare the specific heat of KCl:OH and KCl:Li at higher concentrations.

## II. EXPERIMENTAL PROCEDURE

Specific heat was measured by the transient heat-pulse technique as previously described.<sup>9</sup> At high impurity concentrations, the sample mass was chosen as small as 1 g in order to achieve a proper thermal sample-to-bath time constant.

The OH<sup>-</sup> doped crystals were seed-pulled from chlorine-treated reagent-grade KCl using a Pt crucible in a high-vacuum quartz furnace with external heater under a protective atmosphere of purified argon. The dopant was heated under vacuum before adding it to the melt in order to minimize contamination by K<sub>2</sub>CO<sub>3</sub>.

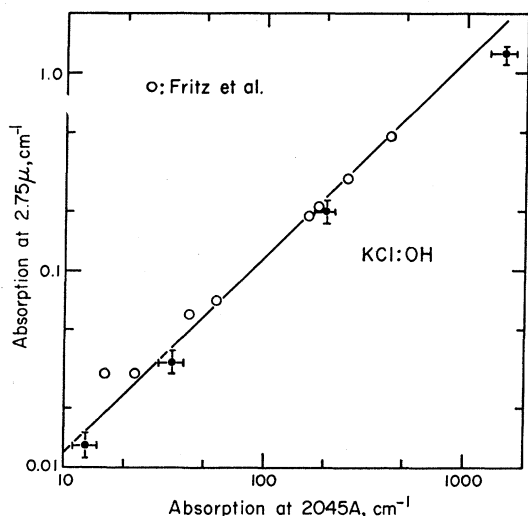


FIG. 1. Scaling of the absorption constants in the uv and the ir. Solid circles: this work. Open circles and straight line: Fritz *et al.* (Ref. 13).

The crystals used in this investigation are listed in Table I.

The OH<sup>-</sup> concentrations were determined by measuring the optical absorption caused by the electronic transition and by the stretching vibration at 205  $\mu$ m and at 2.75  $\mu$ m, respectively, using a Cary 14 and a Perkin-Elmer 521 recording spectrophotometer. The OH<sup>-</sup> concentration can fluctuate in a boule by as much as a factor of 2 over distances of 2–3 cm. Therefore, the absorption constants had to be carefully averaged over the entire sample. The scaling between the peak absorption constant of the uv and the infrared (ir) absorption, shown in Fig. 1, confirms the earlier result by Fritz *et al.*<sup>13</sup> within the experimental accuracy, and is taken as an indication of the proper doping of the crystals. Infrared absorption by unintentional impurities was found to be small. (See Table I.) From the peak-absorption constant of the uv band, the OH<sup>-</sup> concentration was determined with the conversion factor 2.4 ppm/cm<sup>-1</sup> given by Klein *et al.*<sup>14</sup>:

$$n_{\text{OH}} = \sigma K_{\text{max}}, \quad \sigma = 3.84 \times 10^{16} \text{ cm}^{-2}. \quad (1)$$

For high concentrations or thick samples, it is sometimes desirable to determine the OH<sup>-</sup> concentration by measuring the absorption on the wing of the band rather than at the peak. For this the exact band shape has to be known. The entire band was measured for concentrations of  $5 \times 10^{17}$  and  $6.7 \times 10^{18}$  cm<sup>-3</sup>. For  $n_{\text{OH}} = 5.7 \times 10^{19}$  cm<sup>-3</sup>, the band was measured up to  $K = 0.1 K_{\text{max}}$ . No influence of the concentration on the band shape was found. Some of the data are presented in Fig. 2 and in Table II. The peak position at 2045 Å agrees well with the accepted values (2.040 Å,<sup>13</sup> 2050 Å<sup>14</sup>); the half-width of the asymmetric band,  $H = 0.72$  eV, is also close to the previously published values (0.78 eV,<sup>13</sup> 0.75 eV<sup>14</sup>). In the long-wavelength

<sup>13</sup> B. Fritz, J. Anger, and F. Lüty, *Z. Physik* **174**, 240 (1963).

<sup>14</sup> M. V. Klein, S. O. Kennedy, Tan Ik Gie, and Brent Wedding, *Mater. Res. Bull.* **3**, 677 (1968).

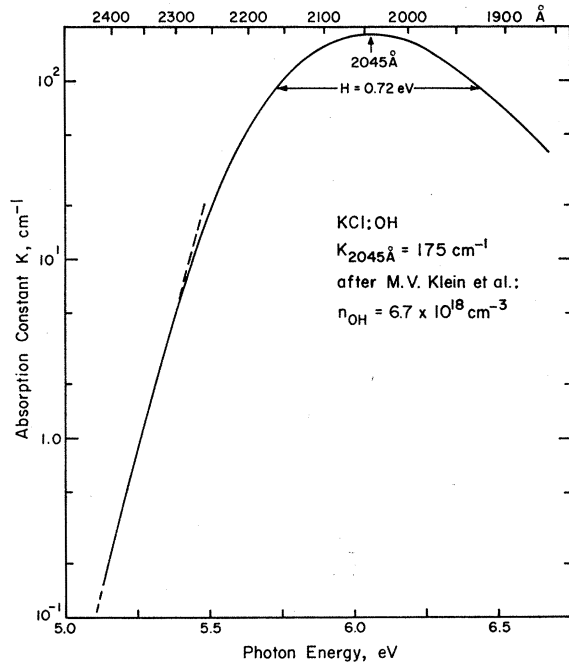


FIG. 2. Absorption constant  $K$ , defined through  $I = I_0 e^{-Kx}$ , where  $I$  and  $I_0$  are the transmitted and incident light intensities, respectively, and  $x$  is the sample thickness. For small  $K$ , the distance  $x$  has to be chosen large, and vice versa. Because of the concentration gradient along  $x$ , the absorption constants measured on different sections of the crystal must be carefully averaged.  $I_0/I$  was found to be independent of the spectrometer slit width; hence the shape of the band is probably not influenced by the instrumental resolution. Dashed line: Urbach's rule; see Eq. (2). Measurements at room temperature.

tail the absorption varies exponentially:

$$K = K_0 e^{-a(h\nu_0 - h\nu)/kT}, \quad a = 0.36. \quad (2)$$

We refer to the article by Dexter<sup>15</sup> for the discussion of this phenomenon, known as Urbach's rule.

TABLE II. Absorption constant  $K$  for KCl:OH, piece of sample D. Absorption measured on pieces with thicknesses ranging from  $x = 0.45$  cm to  $x = 0.024$  cm.  $n_{\text{OH}} = 6.7 \times 10^{18} \text{ cm}^{-3}$ , conversion factor  $\sigma$  from Eq. (1), and  $K_{\text{max}}$  (at  $2045 \text{ Å}$ ) =  $175 \text{ cm}^{-1}$ .

$\lambda$ (Å)	$K$ ( $\text{cm}^{-1}$ )
2400	0.25
2350	1.2
2300	5.7
2250	10
2200	52
2150	102
2100	152
2050	175
2000	159
1950	114
1900	68

<sup>15</sup> D. L. Dexter, Phys. Rev. Letters **19**, 1383 (1968); see also D. Dunn, Phys. Rev. **174**, 855 (1968).

### III. EXPERIMENTAL RESULTS

#### A. Low Concentrations

For concentrations up to  $1.2 \times 10^{18} \text{ cm}^{-3}$  the excess specific heat, Fig. 3, has the shape of a Schottky anomaly very similar to that found, for instance, in KCl:CN,<sup>2</sup> resulting from the tunnel splitting of the lowest oscillatory state of the molecular impurity. The OH<sup>-</sup> ion is known to have equilibrium orientations pointing in the six  $\langle 100 \rangle$  crystallographic directions of the host lattice,<sup>12</sup> and the lowest oscillatory state should therefore split into six tunneling states. This is confirmed by the total entropy  $\Delta S$  associated with the anomaly. We show this by comparing (in Fig. 4) the OH<sup>-</sup> concentration  $n_{\text{opt}}$  determined optically with that determined from  $\Delta S$ :

$$\Delta S = n_{\Delta S} k \ln 6. \quad (3)$$

Over three orders of magnitude,  $n_{\text{opt}}$  and  $n_{\Delta S}$  agree to within the experimental accuracy.

The solid curves in Fig. 3 are computed for a Devonshire potential.<sup>16,17</sup> By adjusting the tunnel splittings to make the computed anomaly peak at the same temperature as the experimental one, the splitting between the lowest ( $A_{1g}$ ) and the first excited ( $T_{1u}$ )

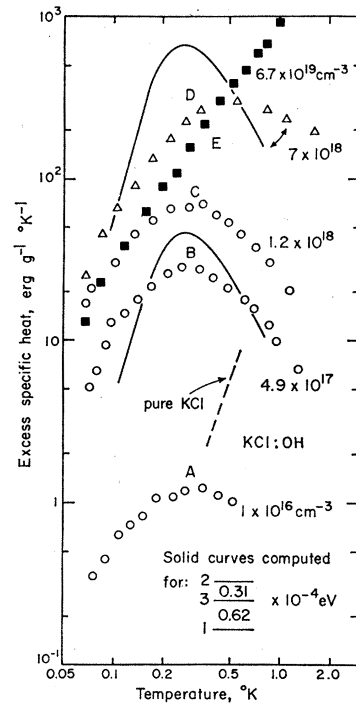


FIG. 3. Excess specific heat,  $C_{v, \text{KCl:OH}} - C_{v, \text{KCl}}$ , for crystals containing OH<sup>-</sup> ions. The solid curves are Schottky anomalies computed for a level system consisting of one  $A_{1g}$ , three  $T_{1u}$ , and two  $E_g$  states. The dashed line indicates  $C_{v, \text{KCl}}$  for pure KCl. Curve A is from Ref. 9.

<sup>16</sup> A. F. Devonshire, Proc. Roy. Soc. (London) **A153**, 601 (1936).

<sup>17</sup> V. Narayanamurti, Phys. Rev. Letters **13**, 693 (1964).

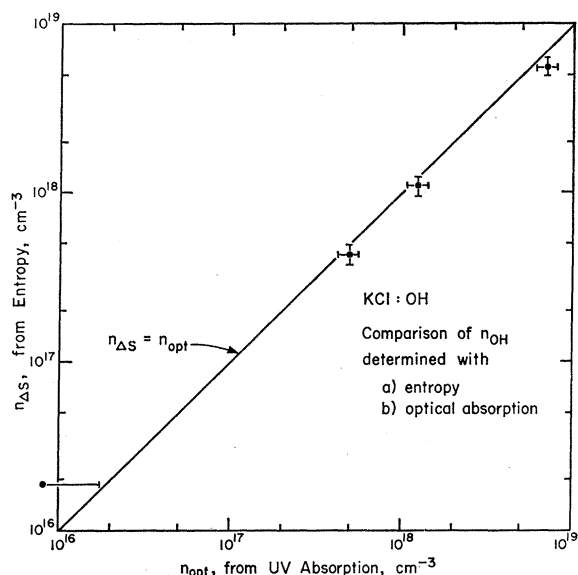


FIG. 4. Comparison of OH concentration  $n_{opt}$  determined from the uv absorption [using the scaling factor  $\sigma$  from Eq. (1), as given by Klein *et al.* (Ref. 14)] with the concentration  $n_{\Delta S}$  determined from the entropy [Eq. (3)]. The error bars indicate our experimental accuracy, and do not reflect possible errors in the titration (Ref. 14; see also Ref. 13) or in Eq. (3), if the number of tunneling states were different from 6.

state is determined to  $6.2 \times 10^{-5}$  eV ( $0.5 \text{ cm}^{-1}$ ) and the splitting between the  $T_{1u}$  and  $E_g$  state to  $3.1 \times 10^{-5}$  eV ( $0.25 \text{ cm}^{-1}$ ).

The measured anomaly is somewhat broader than the computed one. Such a broadening is also known for  $\text{CN}^-$ ,<sup>2,18,19</sup> where it has been explained through a

TABLE III. Comparison of elastic and electric data for  $\text{OH}^-$ ,  $\text{Li}^+$ , and  $\text{CN}^-$ . Solubility limit defined as maximum concentration dissolved in KCl without formation of precipitates. Stress dipole moment  $\alpha$  defined through  $\Delta E = \rho \lambda P$ , where  $\Delta E$  is the stress energy and  $P$  is the stress. One often finds  $\lambda_A - \lambda_B = \rho \lambda / v_0$  in the literature, where  $v_0$  is the atomic volume [ $v_0, \text{KCl} = (3.2 \times 10^{22})^{-1} \text{ cm}^3$ ], and  $\lambda_A$  and  $\lambda_B$  are the principal values of the stress tensor assumed to be an ellipsoid of revolution. This assumption is only a crude approximation in the case of  $\text{CN}^-$ ; see Byer and Sack (Ref. 24). The concentrations  $n_{\rho, e}$  and  $n_{\lambda, e}$  are defined in the text.

	Solubility limit ( $10^{19} \text{ cm}^{-3}$ )	Stress dipole moment ( $10^{-24} \text{ cm}^3$ )	Electric dipole moment (Debye)	$n_{\rho, e}$ ( $10^{19} \text{ cm}^{-3}$ )	$n_{\lambda, e}$ ( $10^{19} \text{ cm}^{-3}$ )
$\text{OH}^-$	16 <sup>a</sup>	5.9 <sup>b</sup>	3.8 <sup>c</sup>	1.9	11
$\text{Li}^+$	2.7 <sup>d</sup>	3.8 <sup>d</sup>	6.0 <sup>e</sup>	0.86	27 <sup>d</sup>
$\text{CN}^-$	5.9 <sup>f</sup>	9.4 <sup>e</sup>	0.5 <sup>h</sup>	120	4.4

<sup>a</sup> H. Paus and F. Lüty, Phys. Status Solidi 12, 341 (1965).

<sup>b</sup> Reference 22.

<sup>c</sup> Reference 12.

<sup>d</sup> Reference 23.

<sup>e</sup> Reference 11.

<sup>f</sup> Reference 2.

<sup>g</sup> Reference 24.

<sup>h</sup> H. S. Sack and M. C. Moriarty, Solid State Commun. 3, 93 (1965). The value quoted here is based on a more recent determination; H. S. Sack (private communication).

<sup>18</sup> P. P. Peressini, Ph.D. thesis, Cornell University, 1969 (unpublished).

<sup>19</sup> R. L. Pompei and V. Narayanamurti, Solid State Commun. 6, 645 (1968); R. L. Pompei, Ph.D. thesis, Cornell University, 1968, Cornell University Materials Science Center Report No. 942 (unpublished).

small tetragonal distortion of the Devonshire potential, probably caused by a distortion of the  $\text{Cl}^-$  cavity housing the  $\text{CN}^-$  ion. This results in a partial lifting of the degeneracies of the excited tunneling states, which broadens the specific-heat anomaly. A detailed discussion can be found elsewhere.<sup>19</sup> A similar change of the octahedral symmetry in the case of  $\text{KCl:OH}$  has been predicted by Shore,<sup>20</sup> and it is believed that the observed broadening of the anomaly results from just such a distortion. No attempt has been made to determine the distortion (the quantity  $K'$  used in Ref. 19). By fitting the low-temperature rise of the specific-heat anomaly with an exponential function, the splitting between the two lowest tunneling states is determined to  $4.1 \times 10^{-5}$  eV ( $0.33 \text{ cm}^{-1}$ )  $\pm 10\%$ .

Our results show that the specific-heat anomaly observed earlier in nominally pure  $\text{KCl}$ <sup>9</sup> is indeed caused by  $\text{OH}^-$  ions, and not by some hitherto unknown impurities in the crystals. The measurements also confirm the magnitude of the tunnel splittings derived from the paraelectric work<sup>3</sup> ( $A_{1g} - T_{1u}$ :  $0.4 \text{ cm}^{-1}$ ;  $T_{1u} - E_g$ :  $0.2 \text{ cm}^{-1}$ ).<sup>21</sup>

### B. High Concentrations—Comparison with $\text{KCl:Li}$ and $\text{KCl:CN}$

For OH concentrations  $n_{\text{OH}}$  greater than  $1.2 \times 10^{18} \text{ cm}^{-3}$ , the shape of the specific-heat anomaly changes; see curves *D* and *F* in Fig. 3. The entropy, however, continues to scale with  $n_{\text{OH}}$  as determined optically (see Fig. 4). This behavior is similar to that found earlier for  $\text{KCl:Li}$ .<sup>11</sup> Some of these data are reproduced in Fig. 5. The change in shape indicates that at these concentrations ( $n > 10^3$  ppm) the tunneling states of the individual ions are perturbed. In  $\text{KCl:CN}$ , too, a perturbation of the tunneling states has been observed (see Fig. 6).<sup>2,18</sup> In that case, however, it occurs at higher concentrations,  $n > 1000$  ppm. Furthermore, the shape of the anomaly changes differently; whereas in  $\text{KCl:OH}$  and  $\text{KCl:Li}$  the specific heat on the low-temperature side of the anomaly appears to saturate, it increases very rapidly in  $\text{KCl:CN}$  as the concentration increases.

What causes the perturbation, and why do  $\text{Li}^+$  and  $\text{OH}^-$  behave differently from  $\text{CN}^-$ ? With increasing concentration, random internal stress will build up in the crystal. This will ultimately limit the solubility. It is also known that the elastic properties of the doped crystals can be described through a stress dipole moment

<sup>20</sup> H. B. Shore, Phys. Rev. Letters 17, 1142 (1966). A rather similar effect would be expected if the c.m. of the  $\text{OH}^-$  ion were displaced from the center.

<sup>21</sup> For a comparison of the data obtained by Bron and Dreyfus and by Feher *et al.*, see W. E. Bron and R. W. Dreyfus, Phys. Rev. 163, 304 (1967).

associated with each impurity ion.<sup>22-25</sup> These moments are listed in Table III. A comparison of the solubility limits and the stress dipole moments for the three ions gives no indication why OH<sup>-</sup> and Li<sup>+</sup> should behave differently from CN<sup>-</sup>. A comparison of the electric dipole moments, however, shows a profound difference. The moment of CN<sup>-</sup> is about 10 times smaller than that of OH<sup>-</sup> and Li<sup>+</sup>. This suggests that the perturbation of the tunneling states may be caused by an electric dipole interaction.

A simple estimate for the energy  $W_p$  of this interaction can be made as follows: For two classical dipoles of moment  $p_0$  at the separation  $r$  ( $r \perp p_0$ ) the energy  $W_p$  is

$$W_p = p_0^2 / 2\pi\kappa\epsilon_0 r^3, \quad (4)$$

where the dielectric constant  $\kappa=4.5$  for KCl and  $\epsilon_0=8.85 \times 10^{-12}$  A sec/V m. The average separation of two dipoles  $r$  is related to the concentration  $n_{p_0}$  of the dipoles through  $r^{-3}=n_{p_0}$ . Hence

$$W_p = n_{p_0} p_0^2 / 2\pi\kappa\epsilon_0. \quad (5)$$

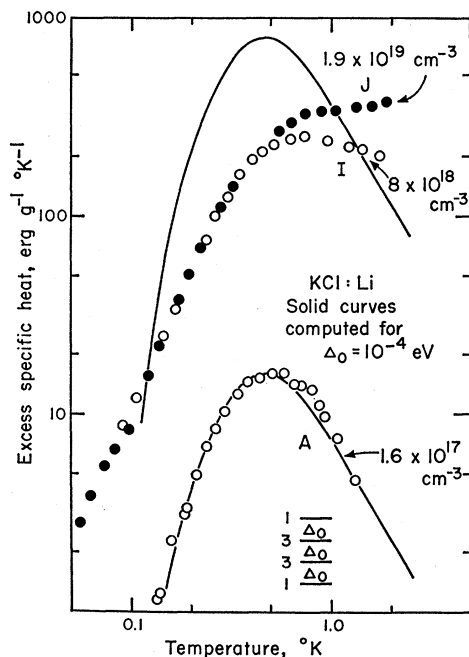


FIG. 5. Excess specific heat of KCl:Li, curves A and I after Ref. 11. Curve J was obtained on a sample into which Li<sup>+</sup> had been diffused [R. Hanson, Bull. Am. Phys. Soc. 13, 902 (1968)]. Diffusion allows one to dissolve about twice as much lithium as seed pulling does. The computed Schottky anomaly fits the experiment well at low concentrations (curve A). At high concentrations, the experimental curve broadens and shifts to higher temperatures. No theoretical curve is shown for sample J.

<sup>22</sup> H. Härtel and F. Lüty, Phys. Status Solidi 12, 347 (1965). For KCl:OH.

<sup>23</sup> N. E. Byer and H. S. Sack, J. Phys. Chem. Solids 29, 677 (1968). For KCl:Li.

<sup>24</sup> N. E. Byer and H. S. Sack, Phys. Status Solidi 30, 569 (1969); 30, 579 (1969). For KCl:CN.

<sup>25</sup> For a theoretical treatment of classical stress dipoles, see A. S. Nowick and W. R. Heller, Advan. Phys. 12, 251 (1963).

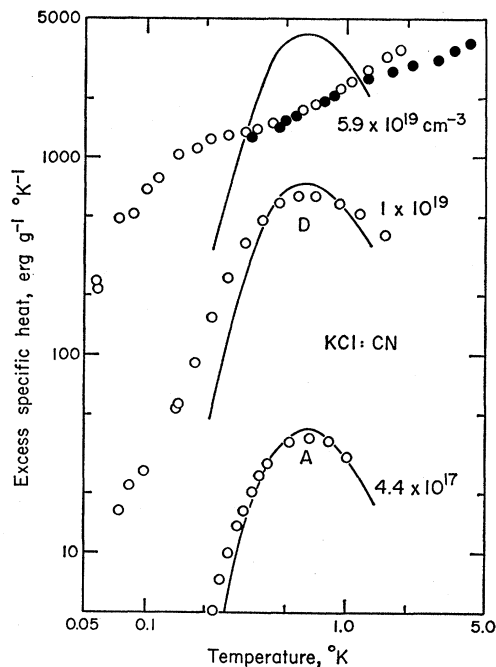


FIG. 6. Specific-heat anomaly in KCl:CN. Solid circles: Ref. 2. Open circles: this work. Data for top curve were obtained on samples cut from two different boules of equal CN<sup>-</sup> concentrations. For details of these measurements see Ref. 18. Curves computed for a Devonshire potential with the following splittings.  $A_{1g}-T_{1u}$ : 1.15 cm<sup>-1</sup> and  $T_{1u}-E_g$ : 0.85 cm<sup>-1</sup>. Possible reasons for the fact that the experimental curves are slightly broader than the theoretical ones even at low concentrations are discussed in the text and in Ref. 19.

At the temperature  $T_c$  defined by  $kT_c=W_p$ , a correlation between the two dipoles is expected to become noticeable. The concentrations  $n_{p_0,c}$  at which  $T_c=1^\circ\text{K}$  are listed in Table III. For OH<sup>-</sup> and Li<sup>+</sup> they are of the same order of magnitude as the concentrations at which the shapes of the specific-heat anomalies begin to change. This comparison demonstrates that the electric dipole interaction can indeed account for the observed effect in KCl:OH and KCl:Li.

Byer and Sack<sup>23</sup> determined the elastic dipole-dipole interaction energy  $W_\lambda$  for KCl:Li.<sup>25</sup> In Table III we list their critical concentration  $n_{\lambda,c}(T_c=1^\circ\text{K})$  and also estimates for OH<sup>-</sup> and CN<sup>-</sup>, based on the stress dipole moments given in Table III. For OH<sup>-</sup> and Li<sup>+</sup>, this interaction is weaker than the electric one, but for CN<sup>-</sup> the elastic interaction is stronger. The change in shape of the specific heat in KCl:CN may therefore be caused by elastic interaction.

In Ref. 11 the relative change of the specific heat of KCl:Li in an electric field, defined as

$$\Delta C/C = [C_v(E,T) - C_v(0,T)] / [C_v(0,T) - C_{v,KCl}(T)], \quad (6)$$

has been found to agree with the change predicted on the basis of the tunneling model<sup>26</sup> for concentrations

<sup>26</sup> M. Gomez, S. P. Bowen, and J. A. Krumhansl, Phys. Rev. 153, 1009 (1967).

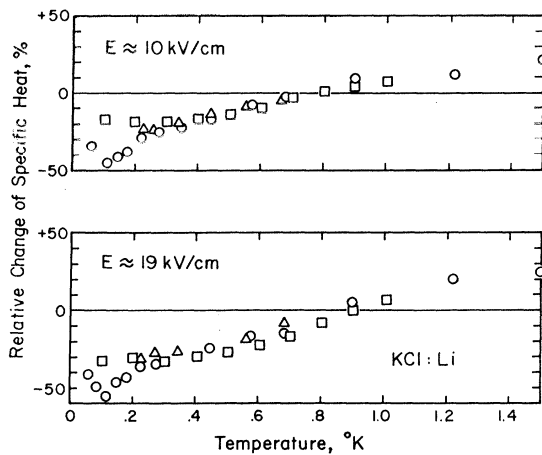


Fig. 7. KCl:Li. Relative change of the specific heat in an applied electric field  $E \parallel \langle 100 \rangle$ . Open triangles:  $n_{\text{Li}} = 2.3 \times 10^{17} \text{ cm}^{-3}$ ; open circles:  $n_{\text{Li}} = 3.3 \times 10^{18} \text{ cm}^{-3}$ , samples A and E, respectively, of Ref. 11. Open squares:  $n_{\text{Li}} = 1.9 \times 10^{19} \text{ cm}^{-3}$ , sample J of Fig. 5 of this work. Within the experimental accuracy  $\Delta C_v(E)/C_v(0)$  does not change with concentration and agrees with the change computed on the basis of the tunneling model. This indicates that this model is still adequate even at the highest concentration studied at least for the major fraction of the  $\text{Li}^+$  ions.

up to  $3 \times 10^{18} \text{ cm}^{-3}$ . In Fig. 7 these measurements are extended to the concentration  $n_{\text{Li}} = 1.9 \times 10^{19} \text{ cm}^{-3}$ . Although the shape of the zero-field specific-heat anomaly is distinctly different from that found at low concentrations,  $\Delta C/C$  remains unaltered to within the experimental accuracy, which is indicated by the scatter of the data in Fig. 7. Following the arguments presented in Ref. 11, it is concluded that most of the lithium ions are still tunneling even at a concentration close to the solubility limit. Interaction between the ions at higher concentrations changes the tunneling states perhaps in a way comparable to the tetragonal distortion mentioned above. Note, however, that the distortion in this case is concentration-dependent.

One has to be careful not to interpret our results as an indication that no dipole-dipole ordering occurs in these crystals. Fiory<sup>27</sup> has recently been able to observe a ferroelectric remnant polarization in KCl:Li through dc dielectric measurements. He found the concentration of lithium ions involved to be relatively small (<20%), and it is quite likely that their influence on the specific heat may not be large enough to show up above the background of the tunneling ions.

<sup>27</sup> A. T. Fiory, Bull. Am. Phys. Soc. **14**, 346 (1969).

The specific-heat anomaly in KCl:OH at zero field is similar to that of KCl:Li. Again, dielectric measurements have indicated some dipole-dipole ordering at high concentrations.<sup>28</sup> We suggest, therefore, that in this system, too, the specific-heat background caused by the tunneling ions is too large to detect the specific heat associated with the breakup of the ordered dipoles. Whether the situation for the radically different anomaly at  $n_{\text{OH}} = 6.7 \times 10^{19} \text{ cm}^{-3}$  is different cannot be decided. In any case, at this point measurements of the dielectric constant seem more likely to provide deeper insight into the question of electric dipole interaction than do specific-heat measurements, since the latter are not sufficiently specific with regard to the breaking up of dipoles.

#### IV. CONCLUSIONS

In contrast to the higher motional states of the  $\text{OH}^-$  ions, which appear to be rather complex, the tunneling states can be described with the same simple model that has been used successfully for other tunneling defects, such as the  $\text{CN}^-$  ion in various host lattices. The tunnel splitting agrees with the values derived from paraelectric resonance experiments,<sup>3,21</sup> although in view of the work by Wolf *et al.*<sup>4</sup> more detailed resonance experiments seem to be required. We do not attempt to explain why the different investigations mentioned in the Introduction lead to different tunnel splittings, but we hope that our results will contribute to a better understanding of the motional states of the  $\text{OH}^-$  ion.

The specific-heat anomaly at high concentration indicates an electric interaction between the  $\text{OH}^-$  ions, but the measurements fail to provide specific evidence for an ordered state. The reason is probably the large specific-heat background caused by the tunneling states of the  $\text{OH}^-$  ions.

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<sup>28</sup> W. Känzig, H. R. Hart, and S. Roberts, Phys. Rev. Letters **13**, 543 (1964). See also the theoretical discussions given in R. Brout, *ibid.* **14**, 175 (1965); W. Zernik, Phys. Rev. **139**, A1010 (1965); M. W. Klein, *ibid.* **141**, 489 (1966).