DIELECTRIC AND OPTICAL PROPERTIES OF $NaCl:OH^-$ CRYSTALS ANNEALED IN HYDROGEN CHLORIDE GAS

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M.Sc. Degree

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It is also shown that the hypothesis of OH^- dissociation can be used to solve some apparent contradictions arising from various measurements that have been made on alkali halides doped with OH^- during the last few years.

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ASSAF

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by

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ABSTRACT

A semi quantitative work has been carried out to investigate the effect of annealing in HCl gas on the optical and dielectric properties of NaCl crystals containing OH^- impurities.

From infrared spectra measurements it appears that there is some dissociation of the OH^- ions into hydrogen and oxygen ions. Dielectric constant measurements showed that H^+ ions in NaCl crystals contribute to the polarization and show paraelectric effect. The H^+ ion should occupy an off-center position which would give rise to a dipole moment.

It is also shown that the hypothesis of OH^- dissociation can be used to solve some apparent contradictions arising from various measurements that have been made on alkali halides doped with OH^- during the last few years.

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CHAPTER I

INTRODUCTION

In this thesis we are concerned with the problem of the infrared spectra and the low temperature static dielectric constant (ε) of NaCl crystals doped with small concentrations of NaOH and HCl.

The electric and optical behavior of alkali halides containing polar impurities has been a subject of extensive research for the past few years. In 1958, Rolfe and independently Etzel and Patterson measured the ultraviolet (u.v.) absorption of OH^- dipoles in NaCl, KCl, and KBr and found bands at 185, 204, and 214 mμ. Fritz, Luty, and Anger (1963) observed that the infrared (i.r.) absorption at 2.8 μ was proportional to the u.v. absorption at 204 mμ in KCl:OH^-. They found however that both bands were very weak; in particular, the oscillator strength of the i.r. band was only about 1% of the expected value. Similar results were reported by J. Rolfe (1963) for KBr:OH^-. Kuhn and Luty (1964) showed that OH^- dipoles could be aligned by an applied electric field. Kanzig, Hart, and Robert (1964) measured the dielectric constant of KCl:OH^- crystals and found a paraelectric effect at low temperatures apparently due to OH^- dipoles. This means that at low temperatures ε is given by an equation of the form

$$\varepsilon = \varepsilon_o + \frac{\varepsilon'}{T - T_c}$$

for temperatures greater than the critical temperature T_c.

Independently, Robinson and Hollis Hallet (1965, 1966) found similar dielectric properties in nominally pure NaCl Harshaw crystals. In an attempt to explain this dielectric behavior they examined the infrared spectra of NaCl crystals but they could not find any trace of OH^-. Assuming the oscillator strength to be the same in NaCl as in KCl, they found the OH^- concentration to be at least one order of magnitude less than that required to explain the increase in the dielectric constant in NaCl crystals at low temperatures. They therefore felt that the effect was intrinsic. However, Lowndes (1966) found no anomalous behavior in ultra-pure alkali halides, and Wedding (1967) showed that the oscillator strength of OH^- in NaCl is about 12 times weaker than the oscillator strength of KCl:OH^- at room temperatures. In addition the infrared absorption of OH^- in NaCl becomes so broad at room temperatures as to be almost unobservable.

Sack and Moriarty (1965) measured the dielectric constant of KCl crystals doped with Li^+ ions and found that this system shows paraelectric effect at low temperatures similar to the one found for OH^- in KCl. Although Li^+ ion itself does not have a dipole moment, it does, because of its small size, sit off-center of the vacancy left by the K^+ ion. Such a configuration in an ionic crystal, is electrically equivalent to a positive monopole at the center plus a dipole (Lombardo and Pohl, 1965).

Paraelectric resonance in KCl:OH^- was investigated by Feher, Shepherd, and Shore (1966), and also by Bron and Dreyfus (1966). Hocherl, Blumenstock, and Wolf (1967) observed the paraelectric resonance spectrum of KCl crystals doped with HCl. It would seem plausible that H^+ replacing K^+ in a KCl lattice would behave in much the same way as Li^+ in KCl. Surprisingly the resonance line observed by Hocherl et. al. was the same as one of the lines found in KCl:OH^-, suggesting that this latter crystal contained H^+ ions.

No model has been found which could explain all the phenomena associated with OH^- dipoles in NaCl crystals. We note the following difficulties.

(i) The infrared and ultraviolet absorption of OH^- in the alkali halides, especially in NaCl are very weak. They are much less than one would expect on the basis of a simple theory of oscillator strength; and also weaker than bands, at almost the same frequency, observed in other compounds containing OH or $(OH)^-$.

(ii) According to Kuhn and Luty (1964), the equilibrium directions of OH^- in KCl are < 100 >. However on the basis of elementary electrostatics if the dipole is at the center of vacancy left by the Cl^-, then it should be pointing in the < 110 > direction. If on the other hand the dipole sits off center its equilibrium direction should be between < 100 > and < 110>.

(iii) As noted above Hocherl et. al. (1967) observed the same resonance line in paraelectric measurements of KCl:OH^- and KCl:H^+.

(iv) Robinson and Hollis Hallett (1966) mentioned observing a "doublet", which they did not identify, at 3.5 and 3.6 μ in the infrared spectra of nominally pure alkali halides (Harshaw). This absorption coincides almost exactly with that observed for free HCl (Herzberg, 1950), and for HCl in solid argon (Bowers and Flygare, 1966).

(v) Chandra and Agrawal (1967) have shown that there is a considerable discrepancy between the measured and the calculated value of the dipole moment of OH. Accurate measurements of the dipole moment of free OH give $p = 1.65$ D (1 D = 10^{-18} e.s.u.). Due to the polarization by the NaCl lattice, the OH dipole moment should be no more than 2.16 D. However, estimates of p_{OH^-} in KCl from dielectric measurements and paraelectric cooling experiments give value of p from 3 - 5 D.

As will be shown in Chapter V, these discrepancies can be largely explained by assuming that part of the OH^- introduced into alkali halide crystals is decomposed into O^{--} and H^+, with the H^+ ion becoming attached to a Cl^- to form an HCl molecule.

The main purpose of this thesis has been to test this hypothesis in the special case of NaCl:OH^-.

CHAPTER II

THEORY

A. Energy Levels of Diatomic Molecules

1) Free Diatomic Molecule

The Schrodinger equation for a 2-particle system with an internal potential energy V = V(r) can be written as

$$-\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$

$$+ V(r) = E\psi \qquad (1)$$

where μ is the reduced mass of the system. In general the potential energy can be expanded in a Taylor series

$$V(r) = \frac{1}{2}k\rho^2 + k_1\rho^3 + k_2\rho^4$$

where $\rho = r - r_o$ is the displacement from equilibrium. For our purposes, it is sufficient to drop all terms except the first. We now substitute a solution of the form

$$\psi = \frac{R(\rho)}{\rho}\,Y(\theta,\phi)$$

into Schrodinger's equation to obtain

$$-\frac{\hbar^2}{2\mu}\frac{d^2R}{d\rho^2} + \frac{1}{2}k\rho^2 R = E_v R \tag{2}$$

$$-\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dY}{d\theta}\right) + \frac{1}{\sin^2\theta}\frac{d^2}{d\phi^2}Y\right] = E_j Y \tag{3}$$

where $E = E_v + E_j$, and $I = \mu r^2$ is the moment of inertia. The customary approximation at this stage is to take I to be constant. Then (2) and (3) are the equations of an harmonic oscillator and rigid rotator, respectively. The solutions are well known. The energy levels are

$$E_{v,j} = E_v + E_j = h\left(\frac{k}{\mu}\right)^{\frac{1}{2}}\left(v + \frac{1}{2}\right) + \frac{\hbar^2}{2I}j(j+1) \tag{4}$$

E_v are the vibrational energy levels which are equally spaced, and E_j are the rotational energy levels whose spacings are proportional to j. The energy levels are degenerate with a multiplicity of $(2j + 1)$. As will be shown in the next section this degeneracy is partially lifted in a crystalline field, or in an external electric field. Equation (4) can be written in cm^{-1} units as

$$E_{v,j} = \bar{\nu}_o\left(v + \frac{1}{2}\right) + \bar{B}\,j(j+1) \tag{5}$$

where

$$\bar{\nu}_o = \frac{1}{2\pi c} \left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

$$\bar{B} = \frac{\bar{h}}{4\pi I c}$$

Transitions which involve both v, and j give rise to the vibration-rotation spectrum. The transition probabilities among the various states depend upon the matrix elements of the electric dipole moment. For a molecule with a permanent dipole, the transitions are given by

$$\Delta v = +1 \qquad \Delta j = \pm 1 \qquad \text{(absorption)}$$

$$\Delta v = -1 \qquad \Delta j = \pm 1 \qquad \text{(emission)}$$

Using the selection rules in eq. (4) and solving for $\bar{\nu} = \Delta\bar{E}$, we get for the absorption spectra

$$\bar{\nu}_R = \bar{\nu}_o + 2\bar{B}\,(j + 1) \tag{7a}$$

$$\bar{\nu}_p = \bar{\nu}_o - 2\,\bar{B}\,j \tag{7b}$$

The spectrum is shown in fig. 1. It consists of two series of lines spaced equally above (R-branch) and below (p-branch), $\bar{\nu}_o$. The lines are separated from each other by $2\bar{B}$, and a gap exists at the vibrational frequency $\bar{\nu}_o$.

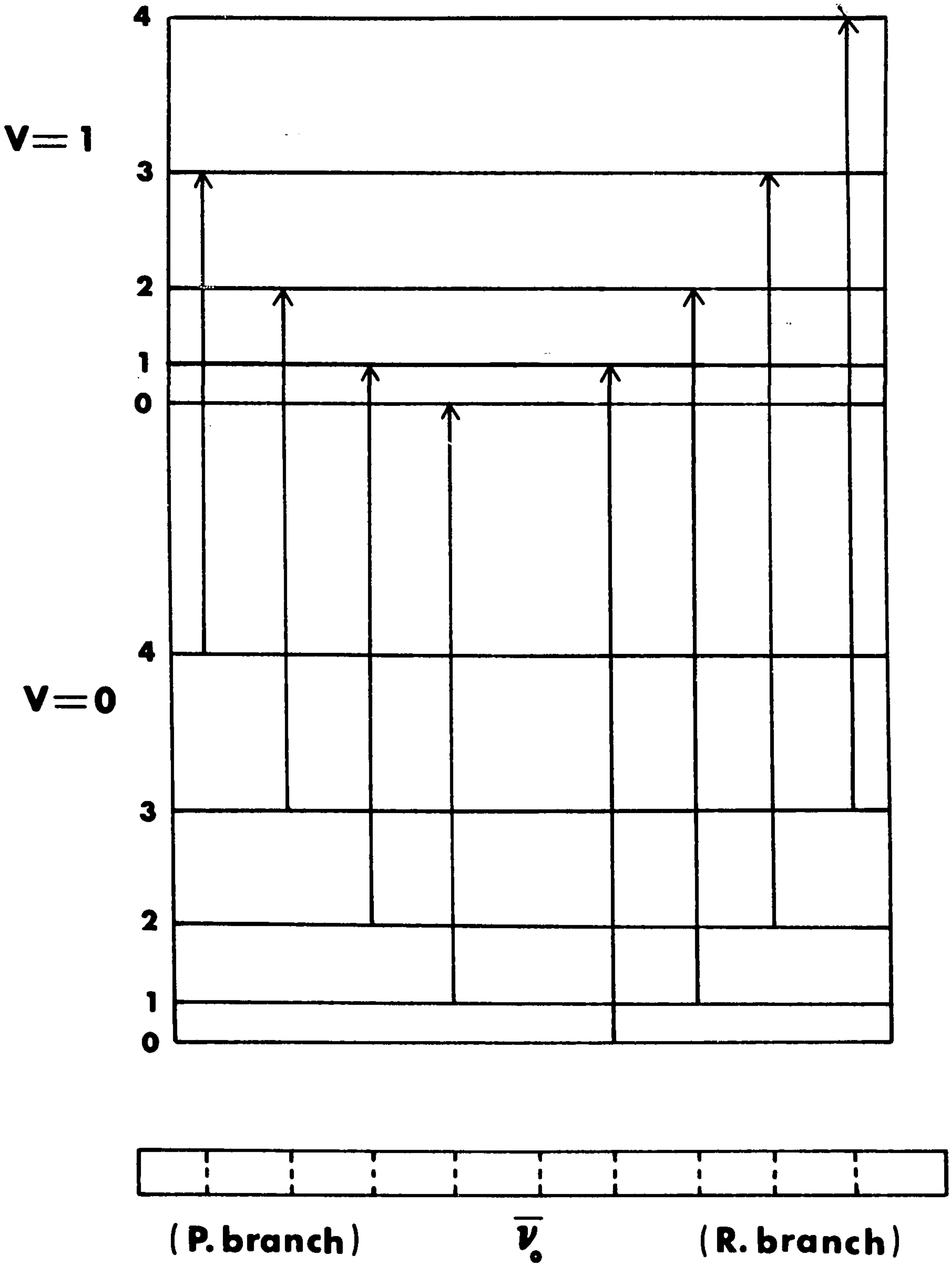

Fig. 1 Rotation-vibration spectrum of free diatomic molecule.

Eq. (7b) is not valid for $J = 0$ since J cannot be negative.

It should be mentioned that the spacing of the lines in the R and p branches will no longer be constant if the vibrational-rotational coupling is taken into account (Herzberg 1950). In fact, it can be shown that the spacing of the lines would be slightly different from $2\overline{B}$, being larger for the p branch and smaller for the R branch.

2) Diatomic Molecule in a Crystalline Field (Devonshire, 1936).

So far we have only considered the energy levels of free molecule. In this section we are going to discuss the energy levels of a molecule in a cubic crystal.

Devonshire calculated the energy levels of a diatomic molecule in a field of octahedral symmetry. He solved the angular part of Schrodinger's equation in the presence of a potential barrier with the simplest octahedral symmetry

$$v = -K \left[\frac{1}{8}\left(3 - 30\cos^2\theta + 35\cos^4\theta + 5\sin^4\theta\cos^4\phi\right)\right]$$

where K is a constant.

When K is positive $v(\theta,\phi)$ has six minima corresponding to the six (100) directions in the crystal (which is the case for OH^- in KCl) and eight maxima corresponding to the eight (III) directions. Devonshire calculated the energy eigenvalues as a function of K. A plot for the energy levels per unit $\overline{B}$ as a function of $K/\overline{B}$ is shown in fig. 2. For $K = 0$,

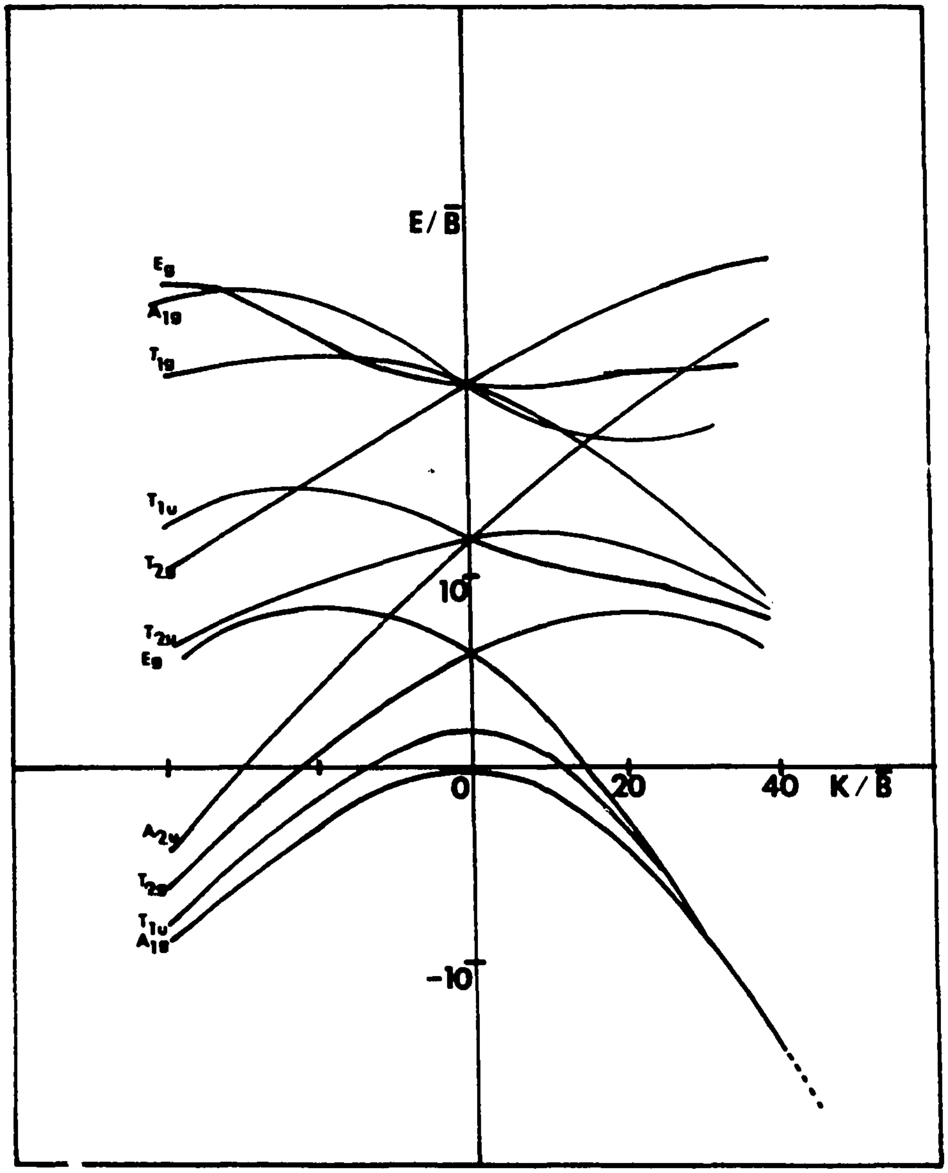

Fig. 2 Devonshire energy levels.

$v(\theta,\phi) = 0$, the levels are those of the free rotator as discussed in the previous section. The degeneracy of the levels is partially removed when $K \neq 0$. As $K/\bar{B}$ approaches infinity then, as can be seen from fig. 2, the ground state becomes six-fold degenerate due to the equality of the singlet $A_{1g}(J = 0)$, the triplet $T_{1u}(J = 1)$, and the doublet $E_g(J = 2)$. Such a result is to be expected on physical grounds since if the potential energy barrier is infinite, the rotator would become frozen in one of the six < 100 > directions and the energy levels corresponding to these directions would be equal. Starting from $K = \propto$ and going to large but finite K, we can consider the splitting of this six-fold degenerate state into three states (A_{1g}, T_{1u}, and E_g) as being due to tunneling between the energy levels.

While the Devonshire model explained fairly well the infrared absorption spectra of CN^- in KCl (Narayanamurti, 1964) and HCl in Ar (Bowers and Flygare, 1966) it could not account for all the absorption lines of OH^- in alkali halides. Some absorption lines which were not predicted by the Devonshire model were observed by Chau, Klein, and Wedding (1966) and also by Bosomworth (1967).

3) Small Ions in a Crystalline Field

The problem of an off center ion in a cubic crystal is mathematically equivalent to the hindered rotator. The first example of this is Li^+ in KCl, where due to the smaller size of Li^+ compared to K^+ ion the minimum energy configuration for

Li^+ is not at the center of the vacancy (Dienes et. al., 1966).

For this ion the potential minima lie along the eight (III) directions (Byer and Sack, 1966). The macroscopic phenomena associated with the hindered rotator and the off-center ion are very similar, as will be shown later on.

B. Absorption of Radiation and the Oscillator Strength

The absorption dI, of a monochromatic beam of frequency ν, and intensity I, is given by Beer's law

$$dI = - \alpha_\nu \ CI \ dx$$

where dx is an element of path length; C, the concentration of absorbing particles usually in mole per unit volume; and α_ν, a constant called the absorption coefficient. α_ν is, of course, frequency dependent and is characteristic of the absorbing material. The quantity,

$$A = \int \alpha_\nu \, d\nu$$

where the integration is over the entire absorption band, is called the integrated absorption coefficient.

Knowledge of α_ν and A enables the deduction of certain physical properties of the absorbing particles. For example in the case of the rotational-vibrational absorption of diatomic molecules or ions we shall show that A is determined by dp/dr, the variation of the dipole moment with inter-nuclear separation. The microscopic derivation of A proceeds as follows.

The probability of a transition from vibrational state v' to a higher state v" of a randomly oriented molecule is given by

$$\frac{8\pi^3}{3h^2} \mid p_{v',v''} \mid^2 \quad \rho(v',v'')$$

where $p_{v',v''}$ is the dipole matrix element and ρ is the radiation density at the corresponding frequency $\nu_{v',v''}$. If there are N' and N" molecules per unit volume in the lower and upper states respectively then the net absorption per unit volume will be

$$h \, \nu_{v',v''} \qquad \times \qquad \frac{8\pi^3}{3h^2} \mid p_{v',v''} \mid^2 \quad \rho(N' - N'')$$

$$= \frac{8\pi^3}{3h} \; \nu_{v',v''} \quad \mid p_{v',v''} \mid^2 \quad \rho(N' - N'')$$

The radiation flux is related to the density by

$$I = c\rho$$

where c is the velocity of light. Therefore

$$dI = -\frac{8\pi^3}{3hc} \mid p_{v',v''} \mid^2 \nu_{v',v''} \quad (N' - N'') \quad I\,dx \qquad (8)$$

If the system is in thermal equilibrium

$$\frac{N''}{N'} = e^{-h\nu_{v',v''}/kT}$$

Now the cases that we have in mind are the fundamental vibration absorption bands ($v'' - v' = 1$) of OH and HCl centered at 3600 cm^{-1} and 2880 cm^{-1} respectively. For these two oscillators at room temperature, $h\nu/kT$ equals 17 and 14 respectively. Therefore from eq. (8) we can write with negligible error

$$N' - N'' = N' = NC$$

where N' is the number of molecules per unit volume and C is the molar concentration. Hence

$$dI = -\frac{8\pi^3}{3hc} \mid p_{o,1} \mid^2 \nu\, NCI\, dx \qquad (9)$$

where ν is the fundamental absorption frequency. Now ν is not a single precise frequency since the vibrational line will be broadened by the rotational transitions and by perturbations from the neighbours of the absorbing molecule. We therefore identify the coefficient of CI dx in (9) with A, and not with α_ν. Therefore, the integrated absorption coefficient

$$A = \frac{8\pi^3 N}{3hc} \mid p_{o,1} \mid^2 \quad \nu$$

$p_{o,1}$, and hence A, are readily evaluated for the ideal harmonic oscillator. We have that

$$\psi_o = \left(\frac{\alpha}{\pi}\right)^{1/4} \quad e^{-\alpha r^2/2}$$

$$\psi_1 = \left(\frac{\alpha}{\pi}\right)^{1/4} \quad \sqrt{2\alpha} \quad r \quad e^{-\alpha r^2/2}$$

where $\alpha = \frac{4\pi^2 \mu \nu}{h}$ and r is the displacement from equilibrium. The dipole moment can be written as a linear function of r

$$p = p_o + r \frac{dp}{dr}$$

In reality, there are always anharmonic terms but these are usually small, at least in the cases that we are concerned with here. A straight forward integration gives

$$p_{o,1} = \int_{-\infty}^{+\infty} \psi_o \left(p_o + r \frac{dp}{dr}\right) \psi_1 dr = \frac{1}{\sqrt{2\alpha}} \left(\frac{dp}{dr}\right)$$

Therefore

$$A = \frac{\pi N}{3\mu c} \left(\frac{dp}{dr}\right)^2$$

In c.g.s. units, A is in $cm^2 \ mole^{-1} \ sec^{-1}$.

In terms of wave numbers

$$\bar{A} = \frac{\pi N}{3\mu c^2} \left(\frac{dp}{dr}\right)^2$$

where the units are now cm $mole^{-1}$. The simplest model of a dipole consists of two fixed charges, $\pm \delta e$, whose equilibrium separation is called the bond length, r_o. Then $dp/dr = \delta e$ and

$$\bar{A} = \frac{\pi N}{3\mu c^2} (\delta e)^2 \qquad (10)$$

For OH, $\mu = 1.57 \times 10^{-24}$ gms. According to the tables compiled by Gribov (1964), the experimental values of $\bar{A}$ for the OH radical in 12 different organic compounds vary from 4 to 12×10^6 cm $mole^{-1}$. Substituting these values in eq. (10) gives $\delta e = 0.95 - 1.7 \times 10^{-10}$ e.s.u. Since the bond length in OH is about 1.0 A°, the value of the dipole moment $p_o = r_o \ \delta e$ = 0.95 to 1.7 D. The accepted value for the dipole moment of the free OH radical is 1.65 D. The agreement is quite good considering the crudity of the model. It should be emphasized that δe is not fixed but is itself a function of the bond length.

A useful quantity, called the oscillator strength, is defined by

$$f = \left(\frac{dp}{dr} / e\right)^2$$

where, $e = 4.80 \times 10^{-10}$ e.s.u.), is the electronic charge. From the above data for OH, $f = 0.04$ to 0.11.

C. Quantum Theory of Electrical Susceptibility

In classical mechanics the dipole moment of a system of charged particles, is defined by $\bar{p} = \Sigma\, e_i\, \bar{r}_i$. It can be shown (Van Vleck, 1932) that if H is the classical Hamiltonian of the system in an electric field the component of the dipole moment in the direction of the field E, is simply

$$p_1 = - \frac{\partial H}{\partial E}$$

It is assumed that this expression also holds in quantum mechanics in the form

$$p_1\ (njm) = - \frac{\partial W_{njm}}{\partial E}$$

where E is the electric field, W_{njm} the energy of an atom or molecule in the quantum state described by the quantum numbers njm, and $p_1(njm)$ is the component, in the direction $\bar{E}$, of the electrical dipole of the system in the given quantum state. In the case we are concerned with, diatomic molecules at room and low temperatures, it is sufficient to specify only two quantum numbers j and m since the other quantum numbers will almost invariably be zero.

If the molecule has a permanent dipole p_1 the Hamiltonian in an electric field is

$$H = H^\circ + EH'$$

where H° is the unperturbed Hamiltonian of a rigid rotator and

$$EH' = Ep \cos \theta$$

is the perturbing Hamiltonian. The energy of the molecule can be expanded in a power series in E

$$W_{jm} = W^\circ_{jm} + EW'_{jm} + E^2 W''_{jm}$$

where

$$W^\circ_j = j(j + 1) \hbar^2/2I$$

is the unperturbed energy level and

$$W'_{jm} = H'_{jm,jm} = p \int \psi^{\circ *}_{jm} \cos \theta \quad \psi^\circ_{jm} \sin \theta \, d \, \theta$$

$$W''_{jm} = - \sum_{j'm'} \frac{| H'(j'm', jm) |^2}{W^\circ_{j'} - W_j^\circ}$$

are the additional energies due to the first and second order perturbation.

The unperturbed wave function Ψ°_{jm} are

$$\psi^{\circ}_{jm} = \sqrt{\frac{(2j+1)(j-m)!}{4\pi\,(j+m)!}}\; p_j^{\,m}(\cos\theta)\; e^{im\phi}$$

where $p_j^{\,m}(\cos\theta)$ are the associated Legendre functions. It can be shown that

$$H'(j'm', jm) = 0$$

unless $m' = m$ and $j' = j \pm 1$. If $j' = j - 1$"

$$H'(j'm, jm) = p\sqrt{\frac{j^2 - m^2}{(2j+1)(2j-1)}}$$

and if $j' = j + 1$

$$H'(j'm, jm) = p\sqrt{\frac{(j+1)^2 - m^2}{(2j+3)(2j+1)}}$$

A straight forward calculation now gives

$$W'_{jm} = 0$$

$$W''_{jm} = \frac{I}{\hbar^2}\,p^2 \left| \frac{j(j+1) - 3m^2}{j(j+1)(2j-1)(2j+3)} \right| \qquad (j \neq 0)$$

$$W_{oo}'' = - \frac{I\, p^2}{3\hbar^2}$$

We now have, for the component of the permanent dipole, p, in the direction of the field

$$p_1 = - \frac{\partial W_{nm}}{\partial E} = - W'_{nm} - 2\, E W''_{nm}$$

$$p_1 = \frac{2\, I\, p^2}{3\hbar^2}\, E \qquad (j = 0)$$

$$p_1 = \frac{- 2\, I\, p^2}{\hbar^2} \left| \frac{j\,(j+1) - 3m^2}{j\,(j+1)(2\,j-1)(2\,j+1)} \right| E \qquad (j \neq 0)$$

The total polarization of a system on non-interacting dipolar diatomic molecules is

$$P = \frac{N \sum\limits_{j,m} p_1\,(jm)\; e^{-W_{jm}/kT}}{\sum\limits_{j,m} e^{-W_{jm}/kT}}$$

where N is the number of dipoles per unit volume. We make the expansion

$$e^{-W_{jm}/kT} = e^{-W_j^{\circ}/kT} \left(1 - \frac{EW'_{jm}}{kT} - \frac{2\, E^2 W''_{jm}}{k^2 T^2} + \cdots\cdots\right)$$

and keeping only terms linear in E, we obtain

$$p = \frac{-2N \sum_j \left[\sum_m W''_{jm}\right] e^{-W_j^\circ/kT} E}{\sum_j (2j+1)\, e^{-W_j^\circ/kT}}$$

The factor (2j + 1) appears in the denominator since the unperturbed energy states are (2j + 1) - fold degenerate. The electric susceptibility is

$$\chi = \frac{p}{E} = \frac{-2N \sum_j \left[\sum_m W''_{jm}\right] e^{-Wj^\circ/kT}}{\sum_j (2j+1)\, e^{-W_j^\circ/kT}}$$

If $j \neq 0$

$$\sum_m W''_{jm} = \frac{-2I}{\hbar^2}\, p^2 \sum_{m=-j}^{j} \frac{j(j+1) - 3m^2}{j(j+1)(2j-1)(2j+1)}$$

$$= \frac{-2Ip^2}{\hbar^2}\, \frac{j(j+1)(2j+1) - 3\sum_{-j}^{j} m^2}{j(j+1)(2j-1)(2j+1)} = 0$$

since

$$3 \sum_{-j}^{j} m^2 = (2j+1)\; j(j+1)$$

Therefore

$$\chi = \frac{2\,NIp^2}{3\hbar^2} \Big/ \sum_j (2j+1)\; e^{-j(j+1)\;\hbar^2/2\,IkT}$$

If kT is sufficiently large so that most of the molecules have large values of j, we can make the approximation

$$\sum_{j=o}^{\alpha} (2j + 1) \quad e^{-\frac{j(j + 1)\hbar^2}{2IkT}} = \int_0^{\alpha} 2j \; e^{-j^2\hbar^2/2IkT} dj = \frac{2IkT}{\hbar^2}$$

Finally we obtain

$$\chi = \frac{Np^2}{3kT}$$

which is exactly the classical Langevin-Debye formula for permanent dipoles. Van Vleck (1932) has shown that the Langevin-Debye formula holds true for any molecule with a permanent dipole moment provided that kT is much larger than adjacent energy levels. Since the zero field splitting for OH^- corresponds to about 0.3°K, the Langevin-Debye formula should hold down to 4.2°K, the lowest temperature at which dielectric measurement made in this work.

CHAPTER III

APPARATUS AND EXPERIMENTAL TECHNIQUES

A. Crystal Annealing

The removal of OH^- ions from alkali halide crystals can be achieved by annealing them in HCl gas. The method consists of heating the crystal in HCl at a temperature close to the melting point for several days and then cooling in vacuum. To induce HCl the same procedure is followed except that the crystal is cooled in the gas.

A schematic diagram for the apparatus used is shown in fig. 3. The sample was put in a small quartz boat (a). This boat was inserted inside a vycor glass tube (b) which was put inside a furnace. The tube had one open end with a ground flange. It was 40" long and 2 $\frac{1}{2}$ " in diameter.

The vycor tube was connected to a vacuum pump and to an HCl cylinder by means of a system of nickel tubes and monel valves. The nickel tube leading directly to the vycor cylinder was hard soldered into a nickel plated stainless steel flange, a flat rubber O-ring was placed between the glass and steel flange which were pressed gently together with the aid of C-clamps. Since the pressure in the cylinder was always kept below 14 lbs/in.^{2}, the flanges were firmly joined by the excess atmospheric pressure.

A 99% pure HCl gas obtained from Matheson Company was used in this experiment. The gas was passed through a trap cooled with dry ice to get rid of any water vapour which might

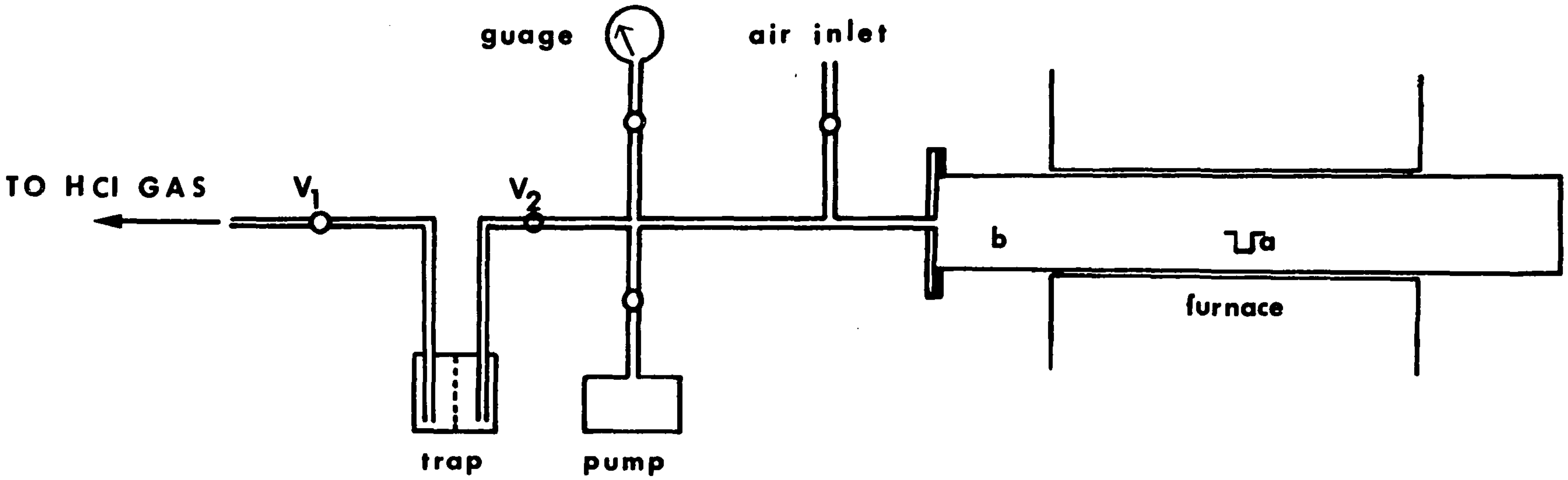

Fig. 3 Crystal annealing apparatus.

be present. The trap was made of a stainless steel cylinder 8" long and 2 $\frac{1}{4}$ " diameter. This cylinder was divided into two chambers by a stainless steel sheet with eight holes. Two tubes were inserted to the bottom of the two chambers, one of these tubes was connected, through valve (V_1), to the HCl gas cylinder, the other was connected to the crystal container through valve (V_2).

The pressure in the crystal container was measured by a monel pressure gauge Model # 63-5312 from Matheson Company. It was adjusted to read 14.2 lb/in^2 under normal atmospheric conditions and zero in vacuum.

The HCl gas was evacuated from the system by means of an Edwards pump Model # BS.2405 which was filled with an anti-corrosive oil # 8.

The following procedure was used in annealing the crystals.

After putting the sample in the vycor glass tube and connecting it to the nickel plated stainless steel cylinder, the whole system was evacuated. The temperature was then raised slowly to 740° C. After heating the crystal container for about 2 hours the dry HCl gas, after passing through the cold trap, was admitted into the container by opening valve (V_2) which was closed after the required pressure (usually 9 - 10 lb/in^2) had been obtained.

It took about one hour for the HCl gas to reach equilibrium after which the pressure in the container remained almost constant for the rest of the experiment. A small decrease in pressure over a period of one or two days possibly due to a reaction between the HCl gas and the nickel tubing was noted. When it was desired to cool the crystal in vacuum the gas was pumped out keeping the temperature at 740°C. The temperature was then decreased slowly at the rate of 50°C per hour approximately; below 200°C the rate of decrease in temperature was much less. Air was let in only after about 24 hours by which time the crystal had returned to room temperature.

B. Dielectric Constant Measurement

1) The Capacitance Bridge

The dielectric constant of the sodium chloride crystals was determined by measuring the capacitance of a parallel plate guard ring capacitor with the crystal as the dielectric. Details of the guard ring and the capacitor will be given in sec. (B-3) of this chapter.

A transformer ratio arms bridge was used to measure the capacitance. The accuracy of the bridge is determined by the accuracy of the transformer ratio which depends upon the magnitude of the ratios, the frequency and the load connected to the transformer, and by the accuracy of the standard capacitors (Cs) used. A simplified circuit diagram for the bridge is shown in fig. 4. Here V is the input voltage, Vs, Vx, are the voltages at the secondary under the actual load. Mps, Mpx, Msx, are the mutual inductances, Cs is the standard capacitor, Cx is the unknown, and D is the detector.

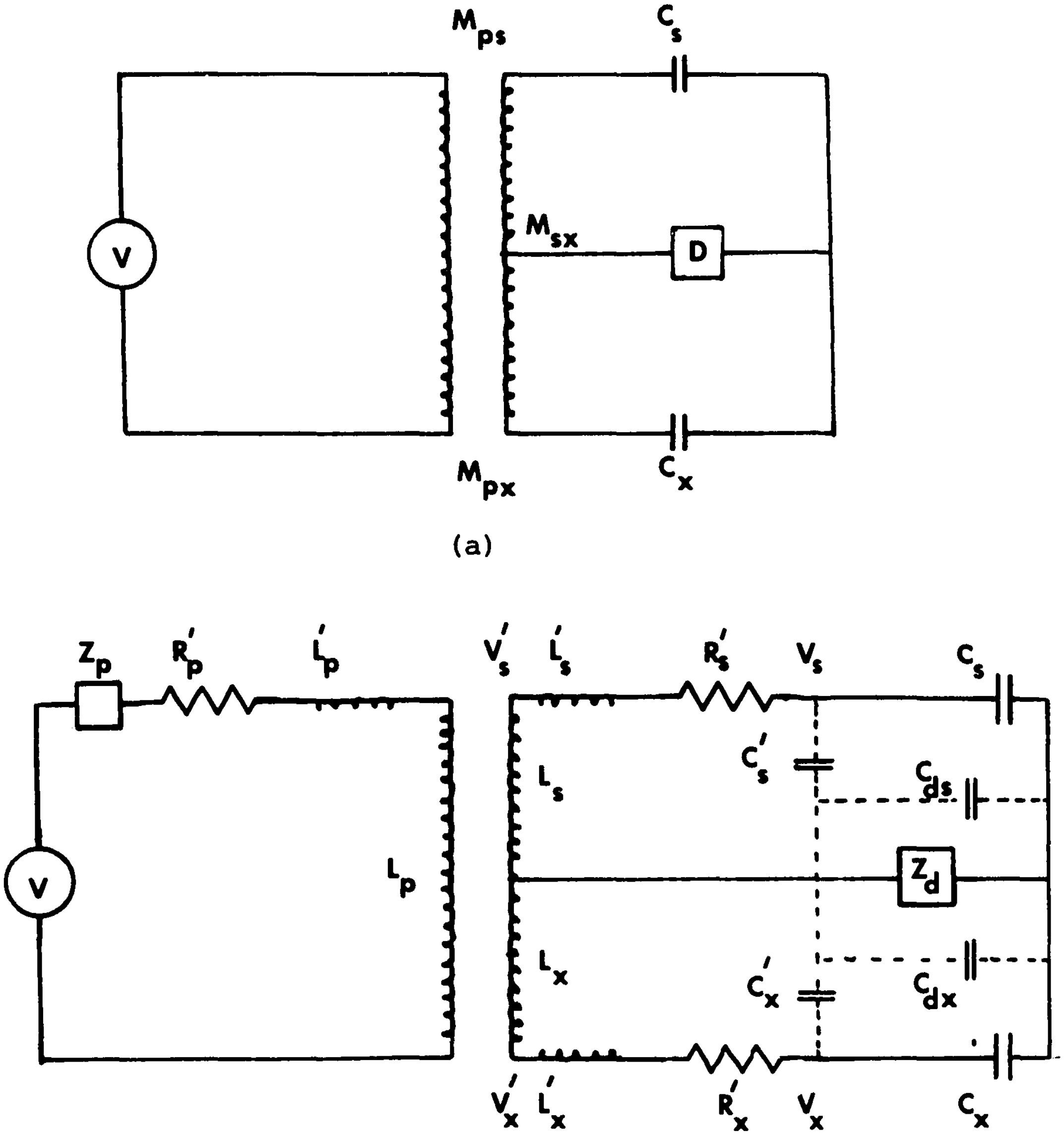

Fig. 4 The capacitance bridge.

An equivalent circuit is shown in fig. 4(b). Here, Z_p is the output impedance of the voltage generator, Rp', Rs', Rx', are the resistances of the winding, Lp, Ls, Lx, represent the inductances of the primary and the two arms of the secondary of an equivalent perfect transformer with Lp', Ls', Lx', representing the leakage inductances. Cs' and Cx' are the stray capacitances of the secondary, Z_d is the input impedance of the detector, and Cds, Cdx, are the stray capacitances of the detector. For a well constructed transformer the ratio of the open circuit voltages in the two arms of the secondary is equal, to within 1 p.p.m., to the ratio of the number of turns so that

$$\frac{Vs'}{Vx'} = \frac{Ns}{Nx} = \frac{Mps}{Mpx}$$

At the frequency used (1300 HZ) the output impedance Ls', Rs', Lx', Rx' amounted to about one ohm. On the other hand the load due to Cs, Cx, and the stray capacitances Cs', and Cx', was about 1 MΩ. Therefore, with negligible error the ratio of the actual secondary voltages

$$\frac{Vs}{Vx} = \frac{Vs'}{Vx'} = \frac{Ns}{Nx'}$$

The balance conditions are simply

$$\frac{Cx}{Cs} = \frac{Ns}{Nx}$$

A transformer ratio arm bridge type 1615-A from General Radio Company was used to measure the capacitance. It has a comparison accuracy of one part in 10^6, a 6-figure resolution for capacitance with a range from 10^{-5} pf to 11 μf, and a very low output impedance in the secondary winding. These conditions permit a very accurate three-terminal measurements.

2) The Detector

Because of the small value of the unknown capacitor Cx (about 1 - 10 pf) the output impedance of the bridge was very high (of the order of 10 - 100 MΩ). Long cables were used to connect the unknown capacitance to the bridge without appreciably effecting the balance. However, the additional stray capacitance Cs' and Cx' arising from the use of these cables would have reduced the sensitivity of the detector if a purely resistive input had been used. In order to tune out these capacitances a large inductor, about 8 henries, was connected between ground and gate of the input MOSFET transistor. Tuning was achieved either by varying the capacitance in parallel with the inductor or shifting the frequency of the generator. The input impedance was estimated to be 10 MΩ.

The diagram of the preamplifier is given in fig. 5. The output from the field effect transistor is R-C coupled to a low noise amplifier T_2, followed by an emitter follower T_3 to provide a low output impedance to the next stage, a General Radio type 1232-A tuned amplifier.

1mf = 10^{-6} farad

1pf = 10^{-12} farad

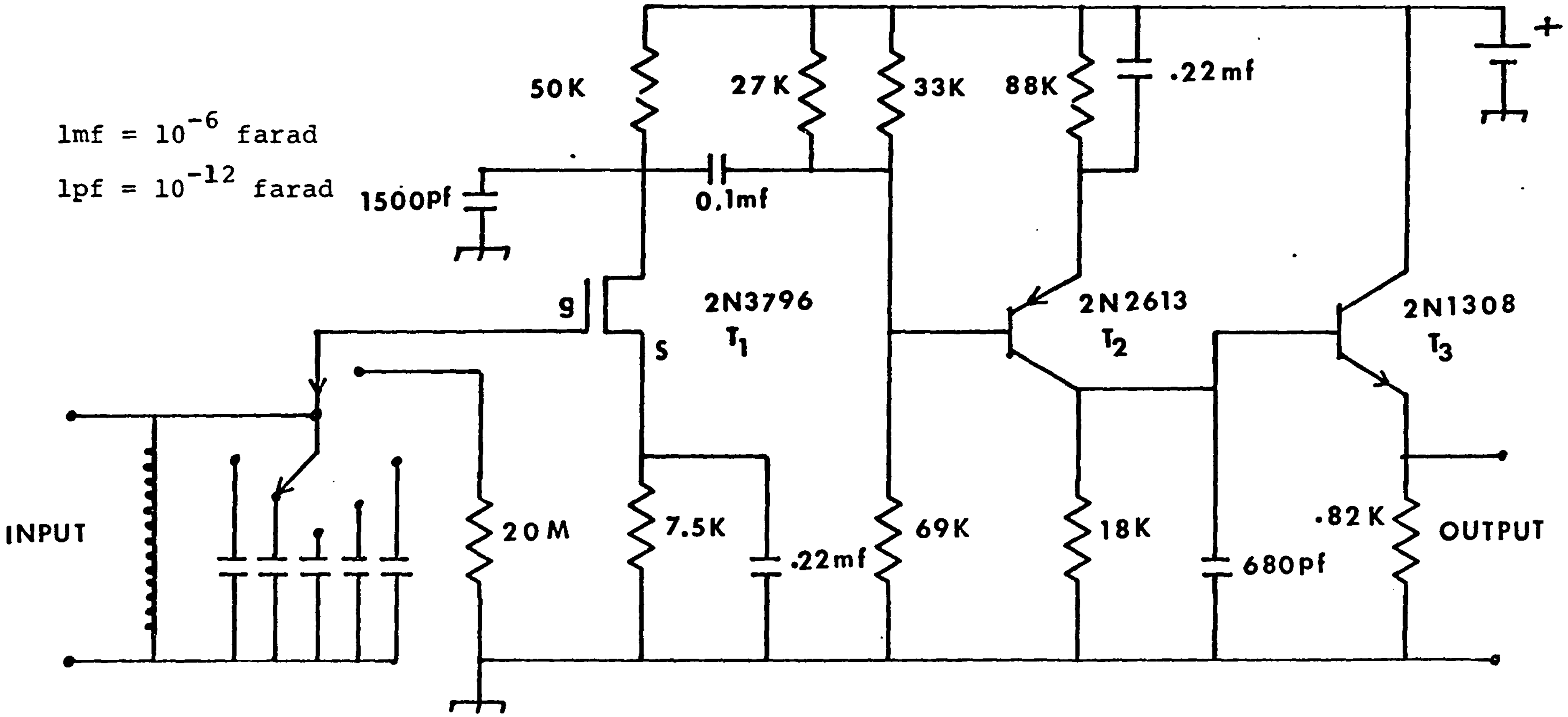

Fig. 5 The pre-amplifier.

The amplified output signal was detected by two phase-sensitive detectors connected in parallel. One of the detectors rectified the capacitive component of the input signal which was fed to one pen of a two pen recorder (the other pen was used to measure the temperature). The other rectifier, which was 90° out of phase with the first, detected the resistive component of the input signal which was read by a voltmeter.

3) The Sample Holder

The sample holder used in this experiment is shown in fig. 6 on the following page. Before placing the sample between the two electrodes (e_u, e_ℓ) it was first cleaned by gently rubbing over a damp cloth. After placing a thin masking ring on one side, both sides of the crystal were then gold plated thus producing a guard ring capacitor. The crystal was then placed between the gold plated copper discs. On the guard ring side the diameter of the inner disc was less than the diameter of the guarded electrode, and the inner diameter of the outer disc was greater than the inner diameter of the outer electrode. Therefore the electric dimensions of the capacitor were determined only by the gold plated electrodes. The inner electrode was pressed on to the crystal by three springs with a small piece of teflon placed under each spring to avoid electrical contacts between the inner electrode and the ground. To make a good thermal contact between the sample holder and the crystal while avoiding electrical contact a gold plated crystalline quartz disc was put under the lower electrode as shown in fig. 6.

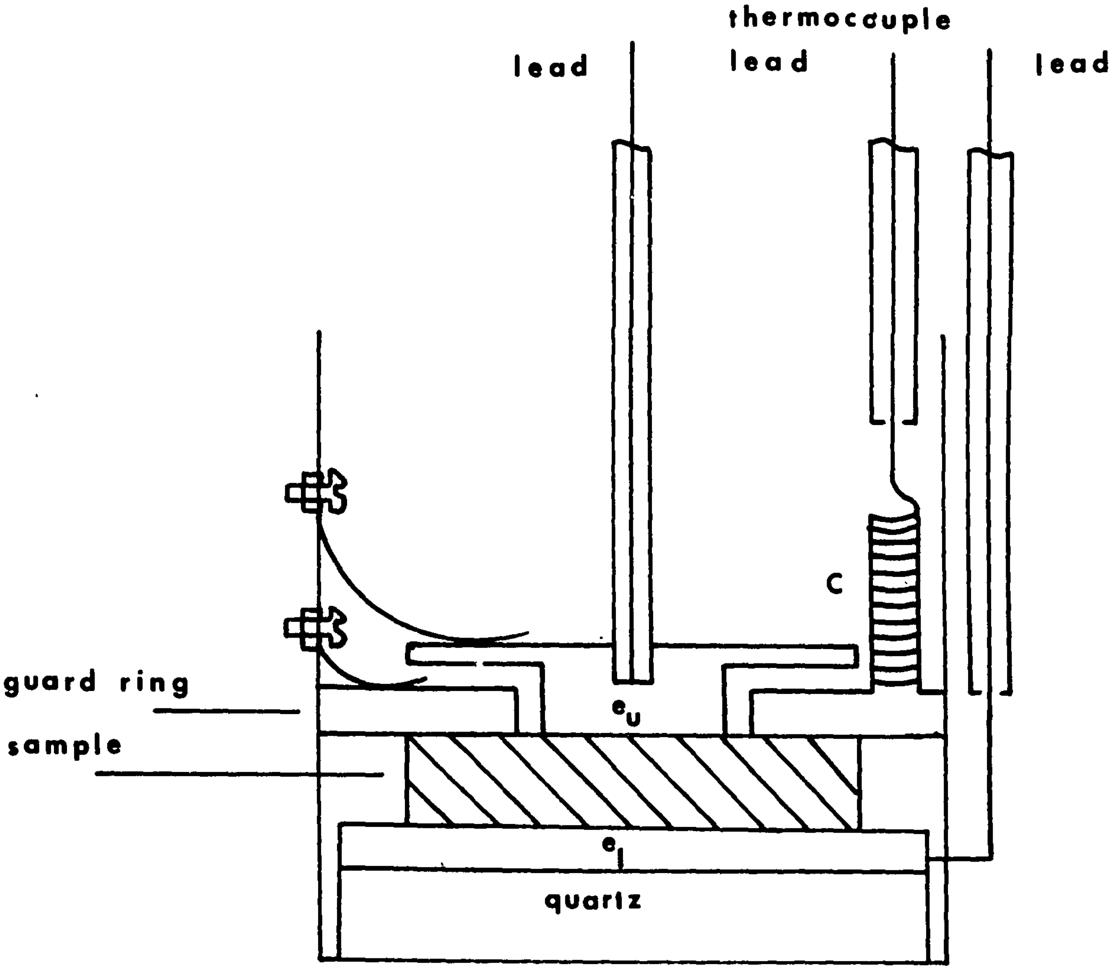

Fig. 6 The sample holder.

The temperature of the crystal was determined by using a gold-0.02% iron versus normal silver thermocouple for temperatures between 4.2°K and 14°K, and a gold-3% cobalt versus a normal silver thermocouple for temperatures above that. The thermocouples were joined to two copper wires in a water triple point cell.

It was not possible to connect the thermocouple to the crystal directly because of the possibility of destroying the symmetry of the electric field. To connect the thermocouple to the guard ring a small copper cylinder (C) was soldered on the guard ring and an insulated copper wire was wound on that cylinder, varnished and then baked for one day at 90°C. The thermocouple wire was then soldered to one end of the copper wire. The electromotive force of the thermocouple was measured by a Guildline potentiometer type 9180. The off-balance signal being amplified by a Guildline D.C. microvolt amplifier type # 9790. The amplified signal controlled the second pen of the recorder (the first pen of the recorder measured the capacitive component of the off-balance signal from the capacitance bridge).

The sample holder was housed inside a vacuum tight copper can situated about $\frac{1}{3}$ up from the bottom of a helium dewar. Leads were brought into the can through thin walled stainless steel tubing. All vacuum seals were made at room temperatures.

CHAPTER IV

EXPERIMENTAL RESULTS

In this chapter we shall discuss the effect of annealing in HCl gas on the infrared spectra and low temperature dielectric constant of NaCl crystals.

The crystals were given to us by Dr. J. Rolfe. Their origin were as follows: (1) Harshaw Company, (2) natural rock salt, and (3) NaCl doped with KO_2 grown at the National Research Council by Dr. Rolfe. The u.v. absorption measurements of the OH^- band for the three crystals were: (1) $\alpha \sim 10\ cm^{-1}$, (2) $\alpha \sim 0.1\ cm^{-1}$ and (3) $\alpha >> 50\ cm^{-1}$ respectively. Dr. Rolfe had interpreted (2) as indicating that OH^- was practically absent and (3) as indicating a high concentration of OH^-. Apparently the KO_2 acted to absorb water vapour from the atmosphere. The i.r. spectra were taken on a Perkin-Elmer # 521 double-beam spectrophotometer which was made available to us by the Chemistry Department of this University. All measurements were made at room temperature. Unless otherwise stated all spectra shown were taken with the spectrophotometer adjusted as follows

Slit program = 2 x 1000
Gain = 4.2
Attenuator = 5.5
Scan time = 16 cm^{-1}/min.
Vertical scale expansion = 10x

Fig. 7 shows the dielectric constant of Harshaw crystal (Sample # 1) as a function of temperature. It can be seen from this

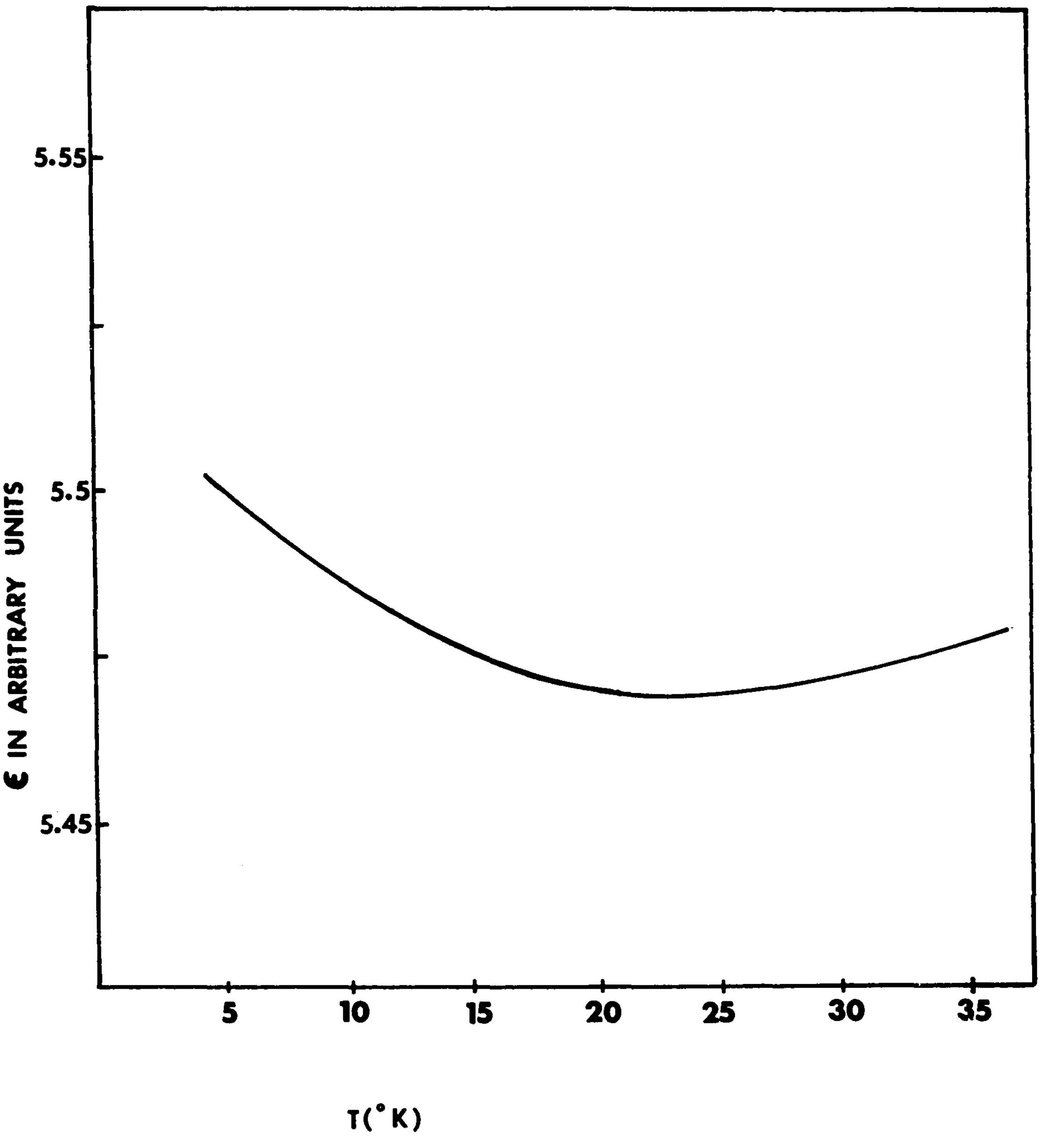

Fig. 7 The dielectric constant of NaCl Harshaw crystal before annealing in HCl gas.

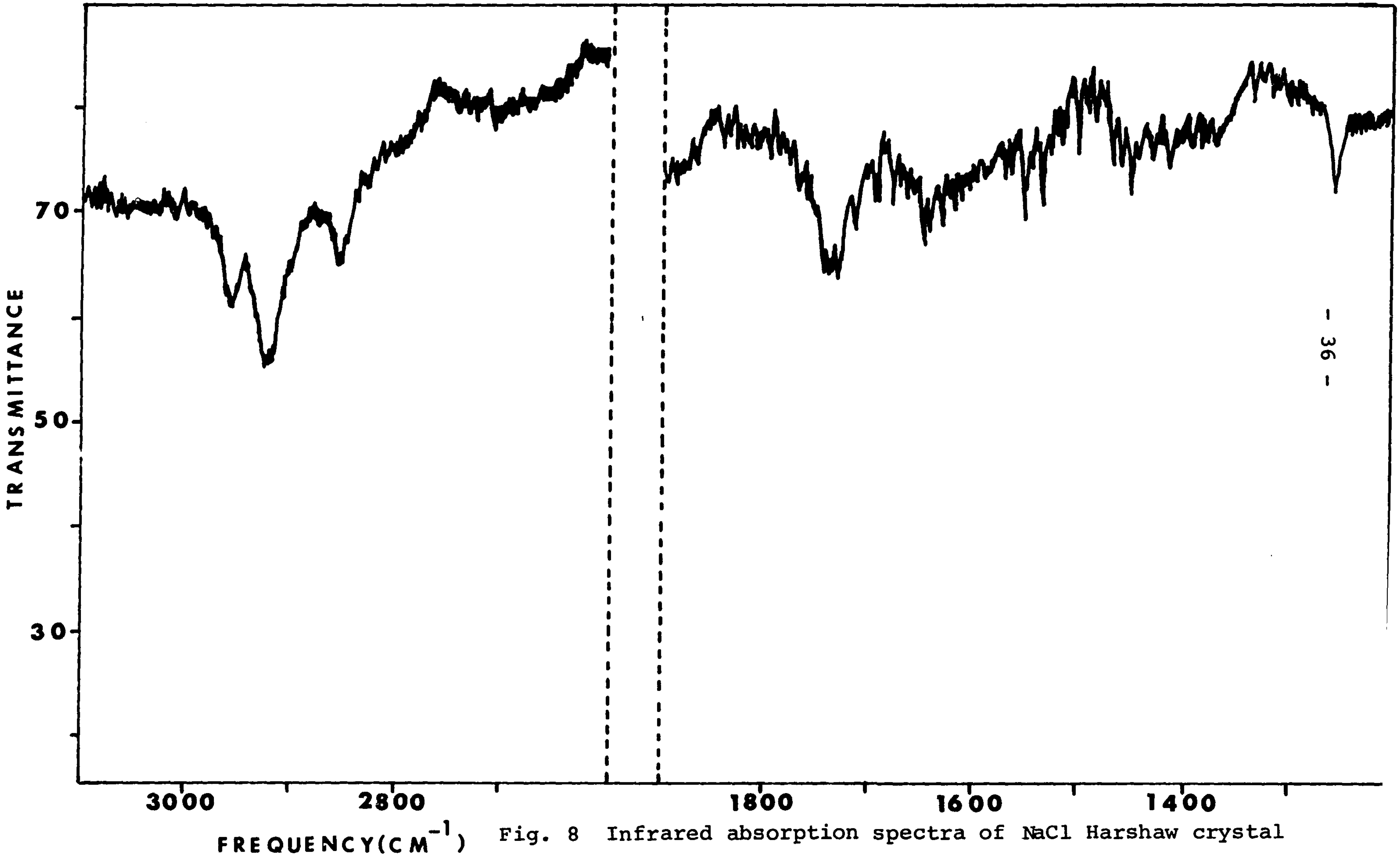

Fig. 8 Infrared absorption spectra of NaCl Harshaw crystal before annealing.

that ε has a minimum around 24.5°K after which ε increases as the temperature is decreased down to 4.2°K. The position of the minimum agrees with the one found by Robinson and Hollis Hallet (1966) for NaCl Harshaw crystals. The infrared spectrum for this sample is shown in fig. 8. Here two absorption bands centered around 2880 cm^{-1} and 1740 cm^{-1} are observed. The first band coincides almost exactly with that of free HCl (Herzberg, 1950), the second band may be due to H_2CO which has a peak at 1760 cm^{-1} (Gribov, 1964).

Fig. 9a shows ε as a function of T for the same sample after annealing in HCl gas at 740°C and 10 lb/in^2 for a period of four days and cooling in vacuum, (the time was so chosen because it was found that annealing a Harshaw crystal for one day and cooling in HCl did not affect the dielectric constant versus temperature graph or the i.r. bands). The minimum in the dielectric constant has disappeared. The i.r. spectrum is shown in fig. 10. The absorption bands at 2880 cm^{-1} and 1740 cm^{-1} have disappeared completely. The dielectric constant is increasing at 4.2°K. The dielectric constant versus temperature graph and the infrared spectrum of the same crystal, after further annealing for four days at 740°C and 10 lb/in^2 and cooling in the gas, are shown in figures 9b and 11 respectively. The derivative of ε with T at 4.2° is now almost zero, but appears to be slightly positive. At the same time the absorption band centered around 2880 cm^{-1} has reappeared. Figures 9c and 12 give the same graphs for the crystal after it had been left for an additional two days at 740°C and 12 lb/in^2

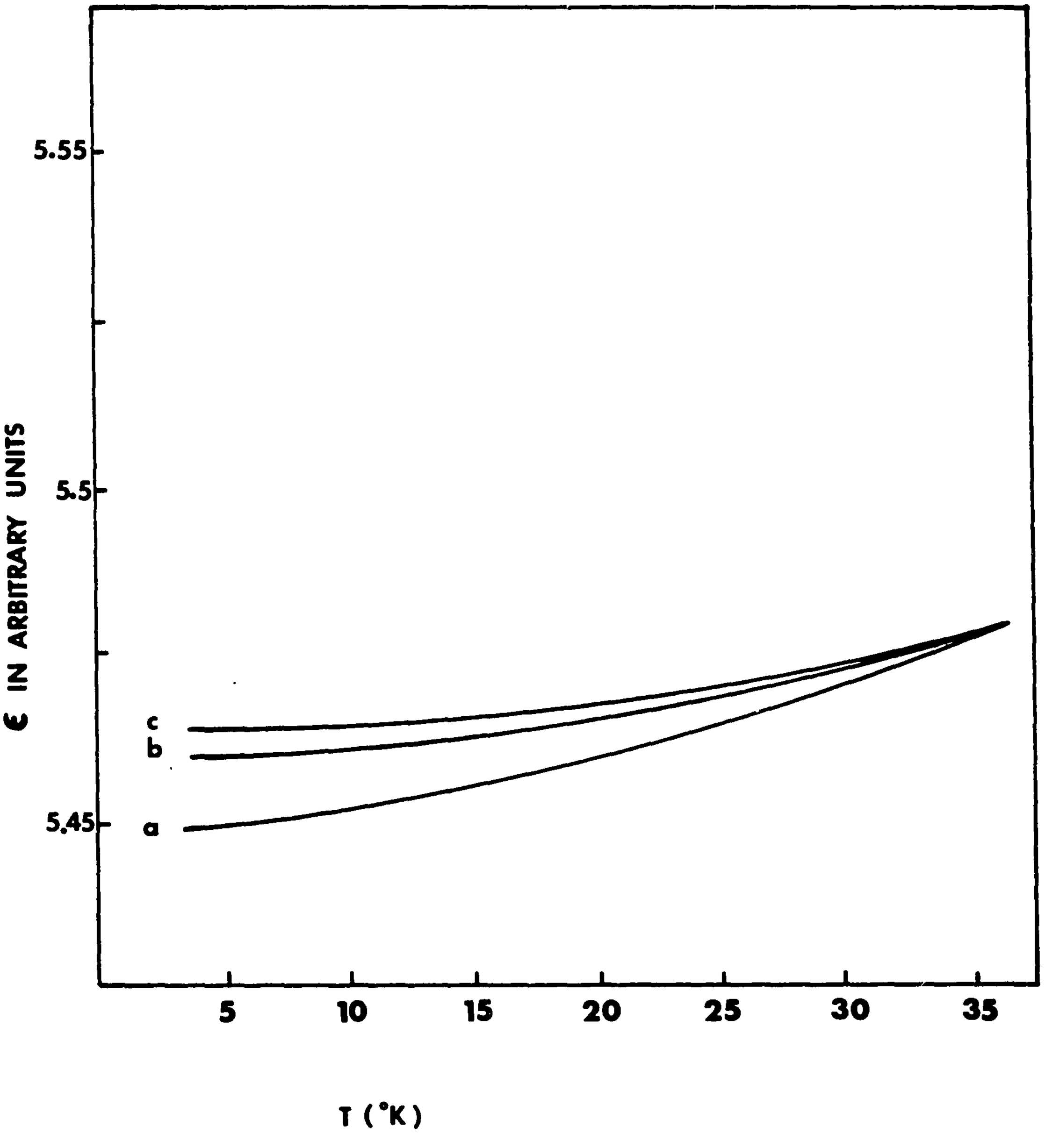

Fig. 9 The dielectric constant of NaCl Harshaw crystal after annealing in HCl gas. (a) cooled in vacuum, (b) and (c) cooled in HCl gas.

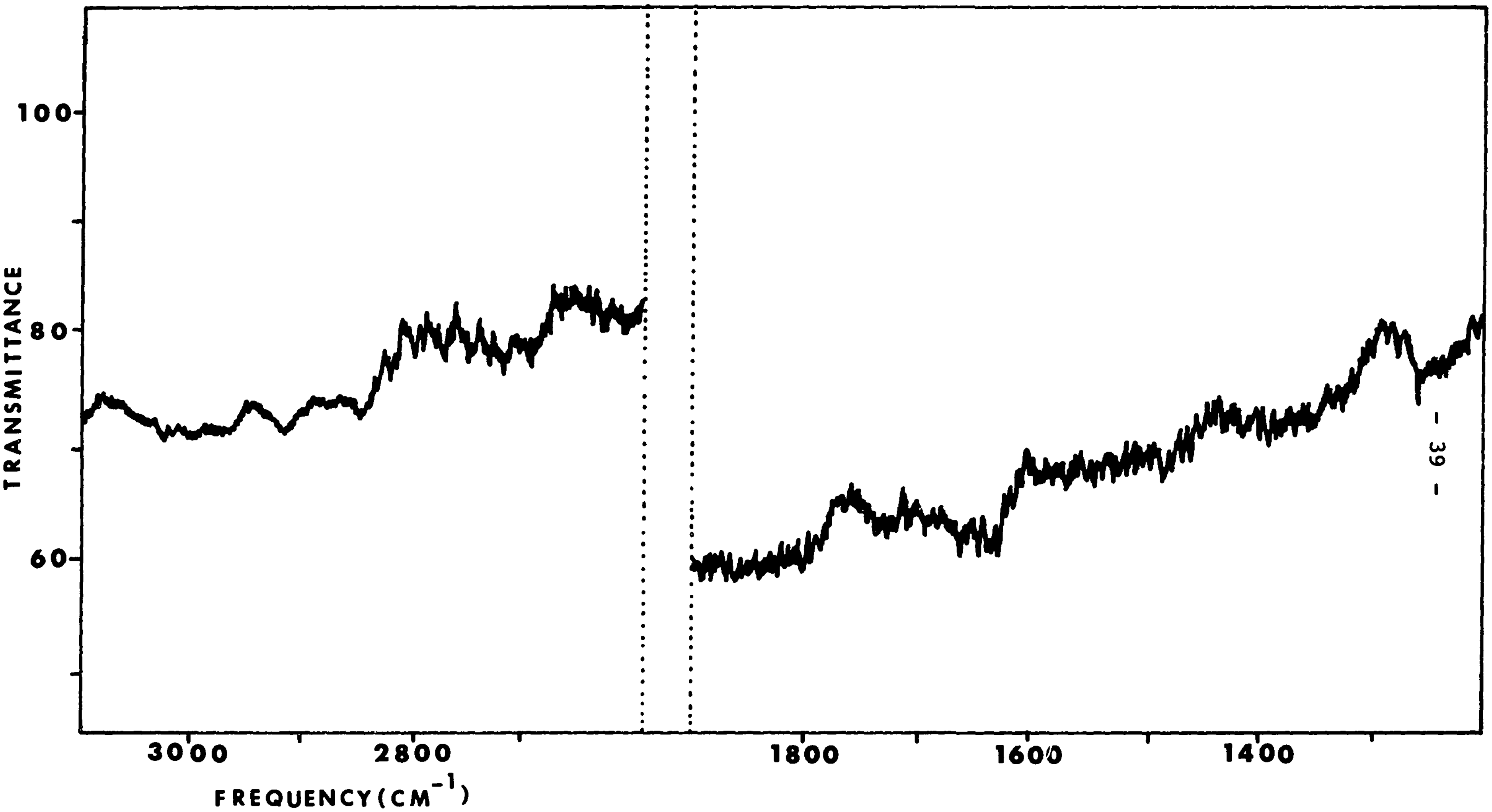

Fig. 10 Infrared absorption spectra of NaCl Harshaw crystal after annealing in HCl gas for four days and cooling in vacuum.

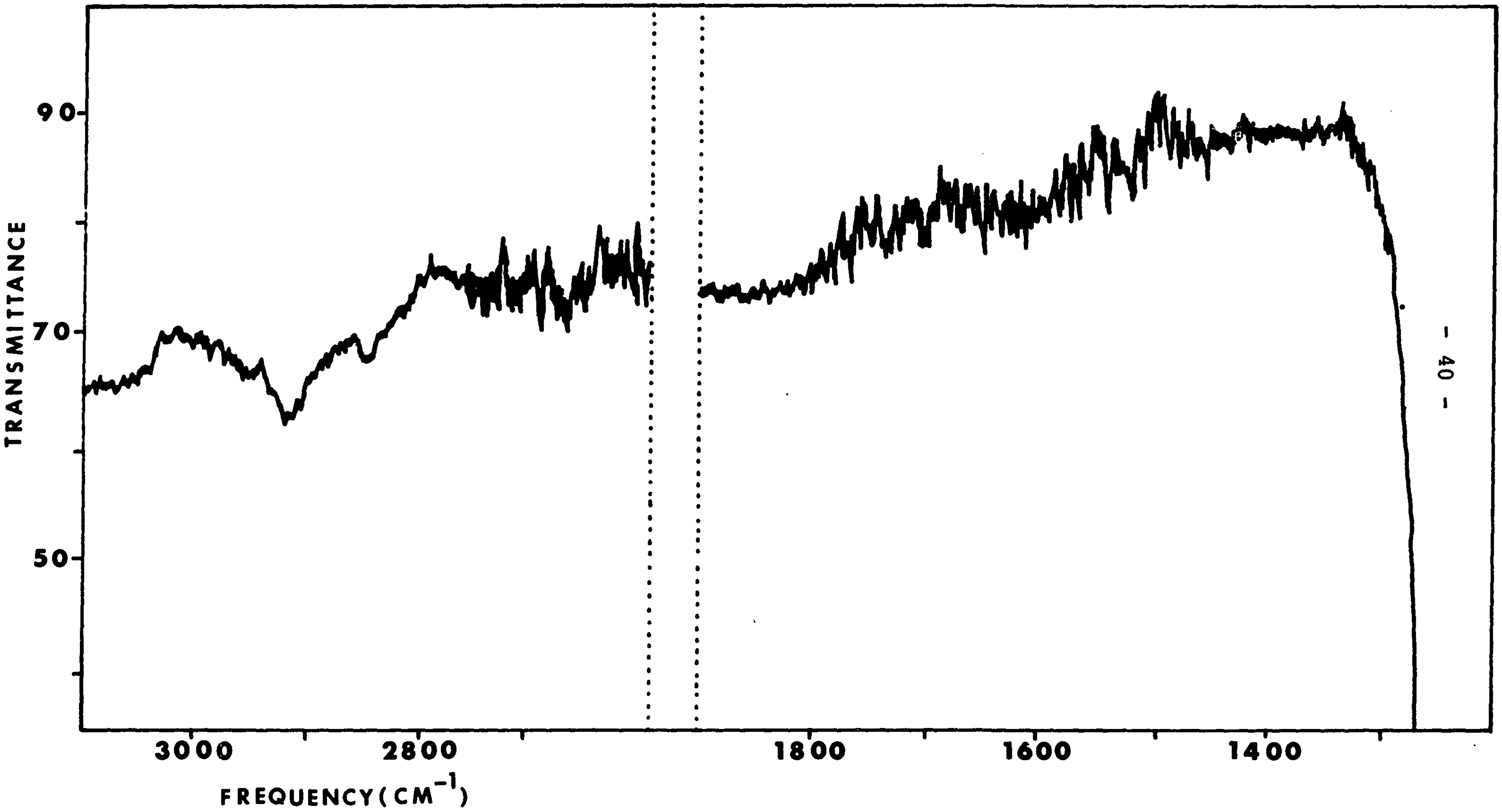

Fig. 11 Infrared absorption spectra of NaCl Harshaw crystal after annealing for 8 days and cooling in HCl gas.

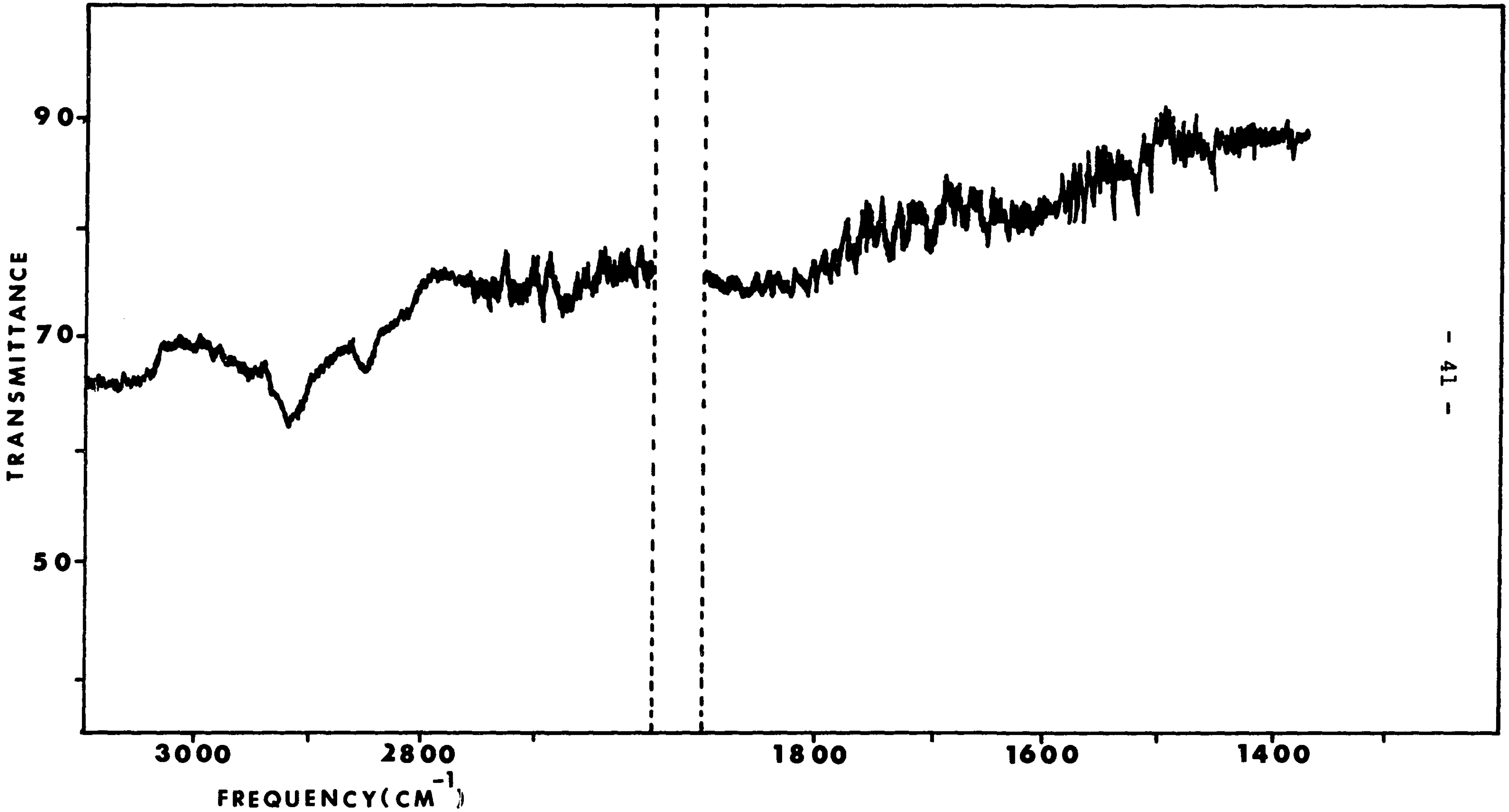

Fig. 12 Infrared absorption spectra of NaCl Harshaw crystal after annealing for 10 days and cooling in HCl gas.

in HCl. The absorption band around 2880 cm^{-1} has not changed noticably after this second doping with HCl. However, the derivative of the dielectric constant at 4.2°K is less than after the first doping.

Fig. 13 shows the dielectric constant as a function of temperature for the natural NaCl crystal (#2). The temperature derivative at 4.2°K is negative and the minimum occurs at 9°K.

A high resolution infrared spectrum of this sample, with the spectrophotometer adjusted as follows

Slit program = 2 x 700
Scan speed = 2 cm^{-1}/min.
Vertical scale expansion = 10 x

is shown in fig. 14. The HCl band is again present and much stronger than for any of the other NaCl crystals. Fig. 15 shows the i.r. spectra of the same crystal after it had been annealed in HCl at 740°C and 9 lb/in^2 for four days and cooled in vacuum. The absorption band have disappeared. The dielectric constant was not measured after annealing.

The infrared spectrum for NaCl crystal doped with KO_2 is shown in fig. 16. Here too we have the two absorption bands around 2880 cm^{-1} and 1740 cm^{-1}. The dielectric constant was not measured for this crystal.

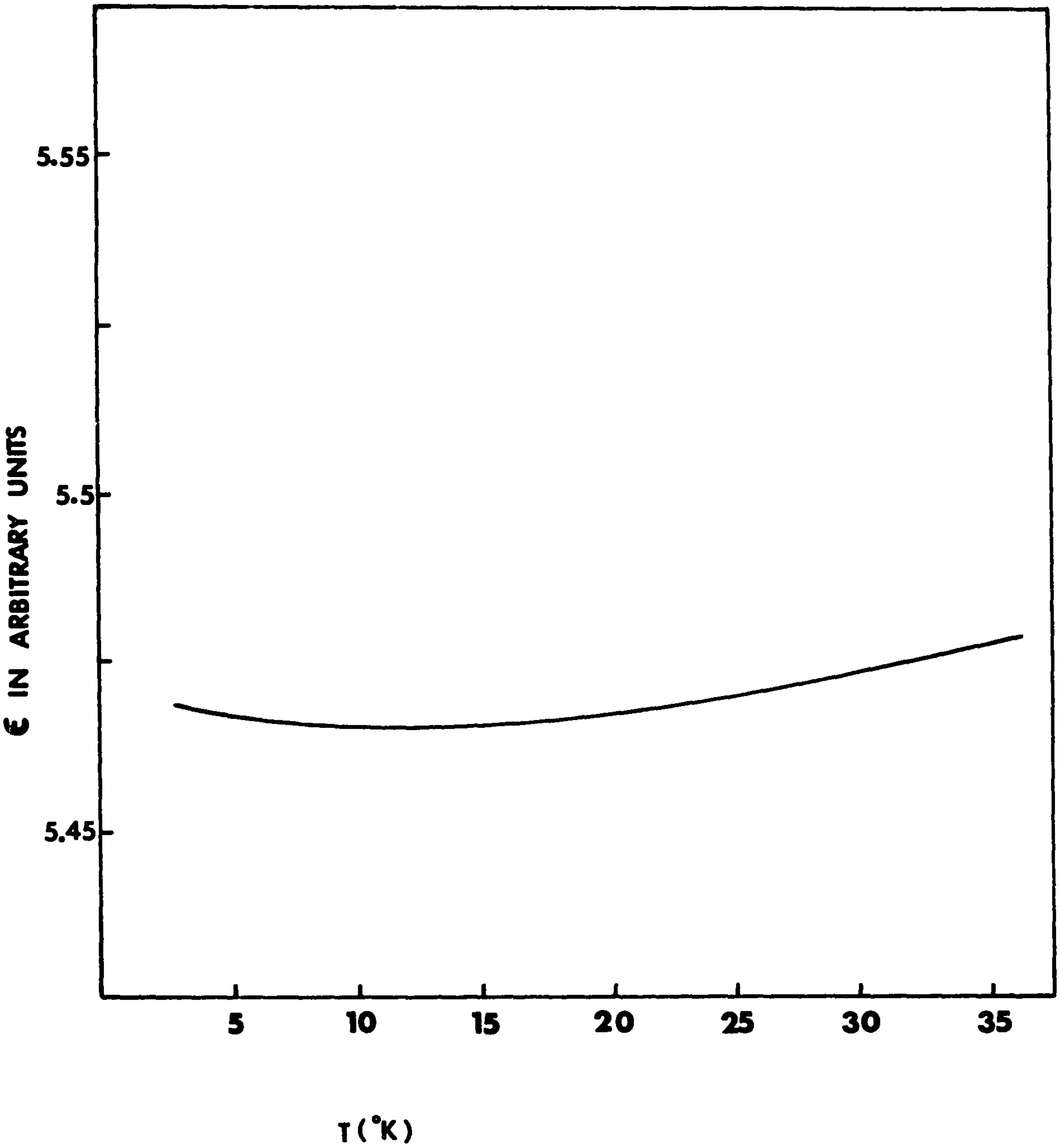

Fig. 13 The dielectric constant of a natural NaCl crystal with $\alpha_{OH} \sim 0.1$ cm^{-1}.

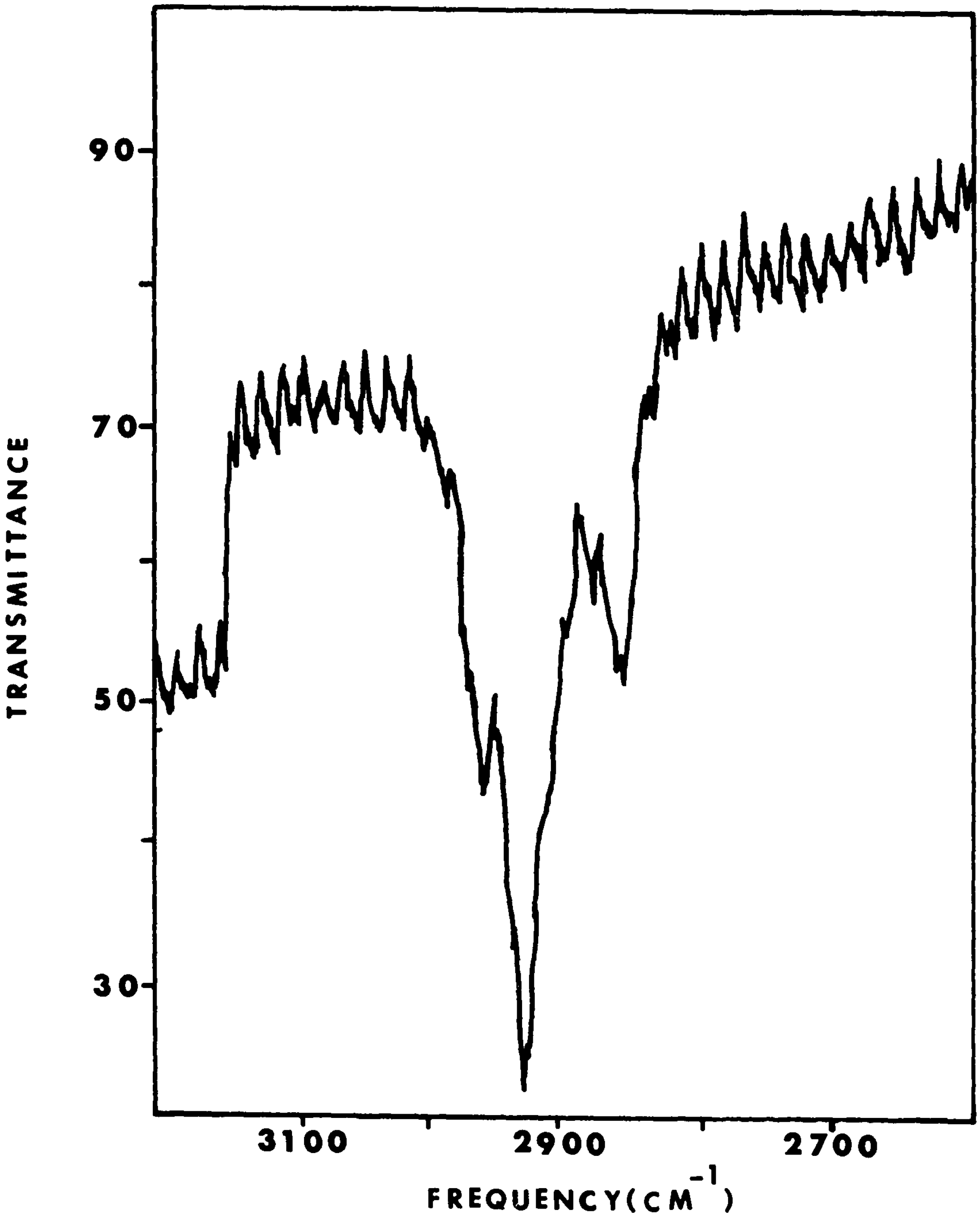

Fig. 14 High resolution infrared absorption spectra of the natural NaCl crystal before annealing.

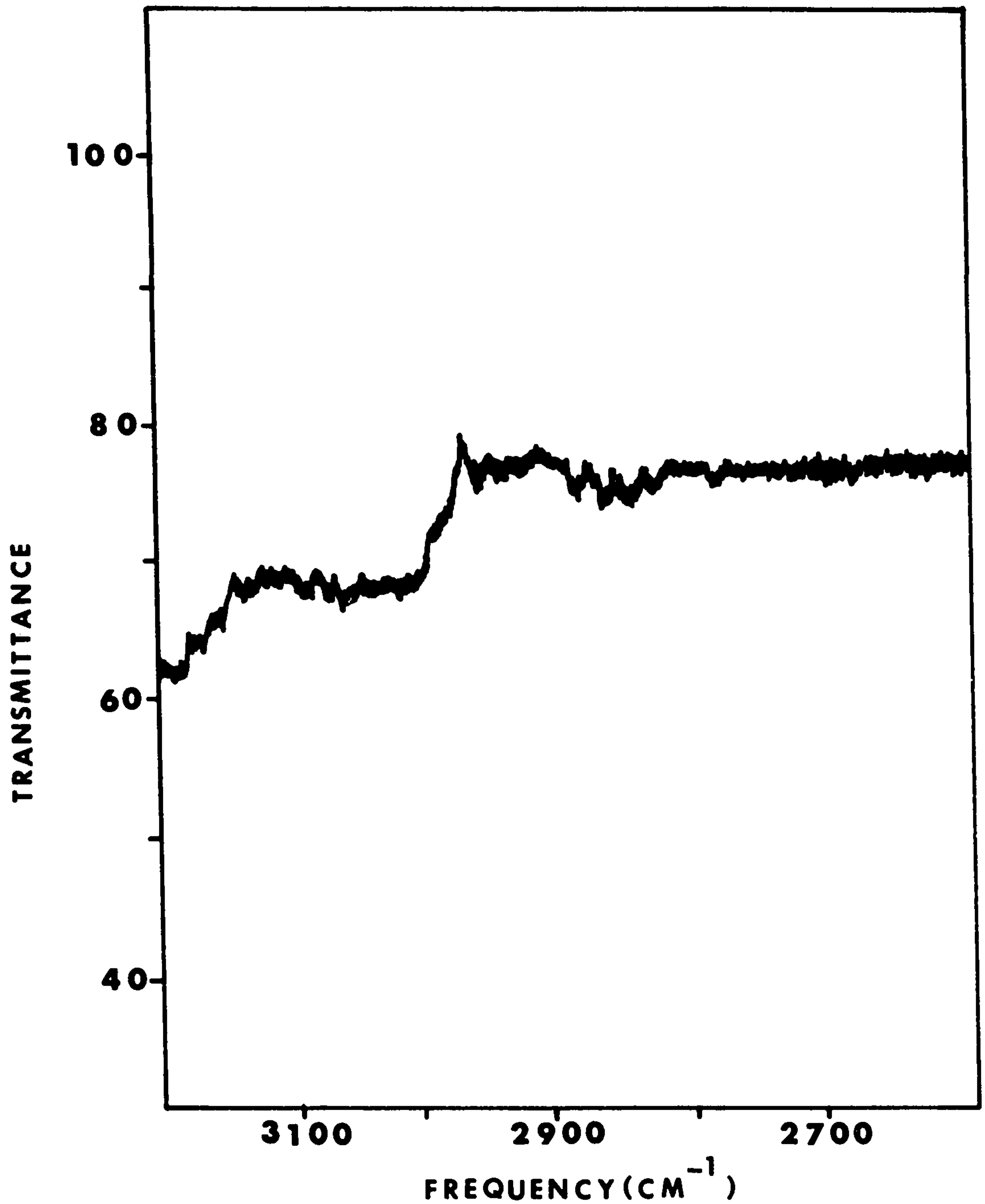

Fig. 15 High resolution infrared absorption spectra of the natural NaCl crystal after annealing in HCl for four days and cooling in vacuum.

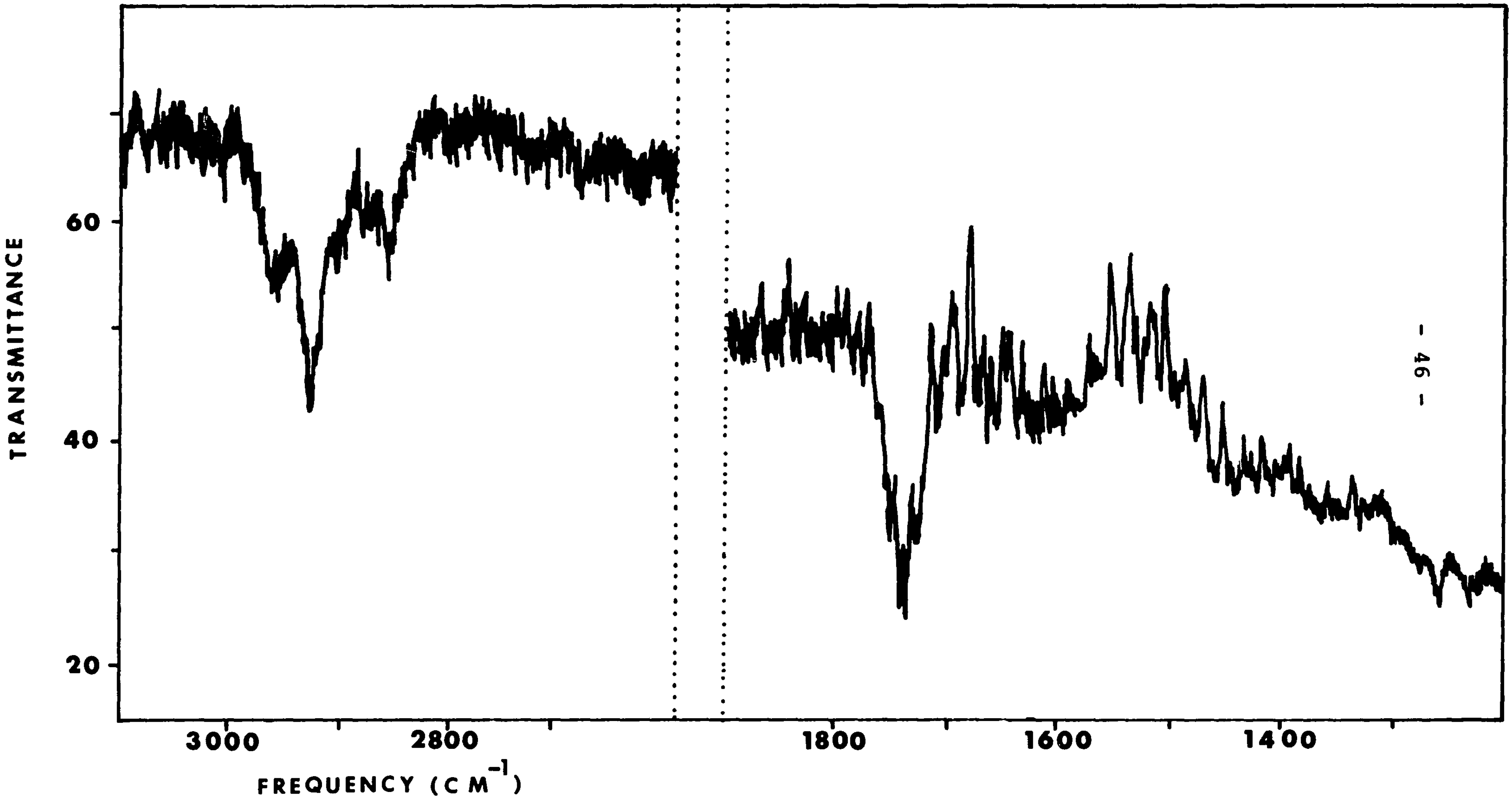

Fig. 16 Infrared absorption spectra of NaCl crystal doped with KO_2.

CHAPTER V

DISCUSSION

It is our contention that the results of our experiment support the hypothesis that there is some dissociation of OH^- or H_2O in NaCl to give HCl. We shall also try to show that this hypothesis enables one to understand the apparent contradictions, noted in the introduction, concerning the behaviour of OH^- in the alkali halides.

All untreated NaCl crystals examined showed an absorption band centered at 2880 cm^{-1}. This band is similar to the HCl band observed for the free gas (Herzberg, 1950) and for HCl in argon (Bowers and Flygare, 1966), and an absorption band around 1740 cm^{-1} which might be due to H_2CO (Gribov, 1964).

As noted in the last chapter these bands disappeared from all samples annealed in HCl gas and then cooled in vacuum. Presumably this is due to a reaction between the impurities, which are mobile near the melting point, and HCl. The main chemical reaction is assumed to be

$$NaOH + HCl \rightarrow NaCl + H_2O$$

with H_2O escaping to the atmosphere. Any HCl absorbed will also escape while the crystal is cooling in vacuum. Only the absorption band centered around 2880 cm^{-1} reappeared after further annealing and cooling in HCl gas (figs. 11 and 12). We feel that this is a strong indication that the 2880 cm^{-1} band is due to HCl molecules in NaCl crystals. However, the fitting of the curve poses some difficulties when compared with the theory of the rotation-vibration spectrum of a free HCl molecule. If we assume that the peak at 2926 is due to an R(2) transition ($j = 2 \rightarrow j = 3$) and the peak at 2853 is due to a p(1) transition ($j = 1 \rightarrow j = 0$) then we obtain a value for $\bar{B}$ of 9.1 cm^{-1}. This compares with $\bar{B} = 10.4$ for free HCl (Herzberg, 1950) and $\bar{B} = 8.5$ for HCl in argon (Bowers and Flygare, 1966). If we now proceed to determine the probability distribution of rotational states at room temperature according to the Boltzman formula

$$N_j = N_o(2j + 1) \quad e^{- j(j + 1) \quad B/kT}$$

where $B = hc \bar{B}$, we obtain a maximum at $j = 3$ (fig. 17). We would therefore expect absorption maxima corresponding to the R(3) and p(3) transitions.

One possible explanation of this discrepancy is that we are now dealing with a hindered rotator. The resonance at 2853 cm^{-1} and at 2926 cm^{-1} may be due to the rotational transitions $3T_{1u} \rightarrow 2T_{2g}$ and $3T_{2u} \rightarrow 4T_{1g}$. This assumption would account at least quantitatively for the shift towards higher frequency for p(3) and towards lower frequency for R(3). The fact that different HCl molecules may be in different environments, (e.g. some may be next to vacancies), may also contribute to the differences in the spectra of HCl in NaCl and of free HCl.

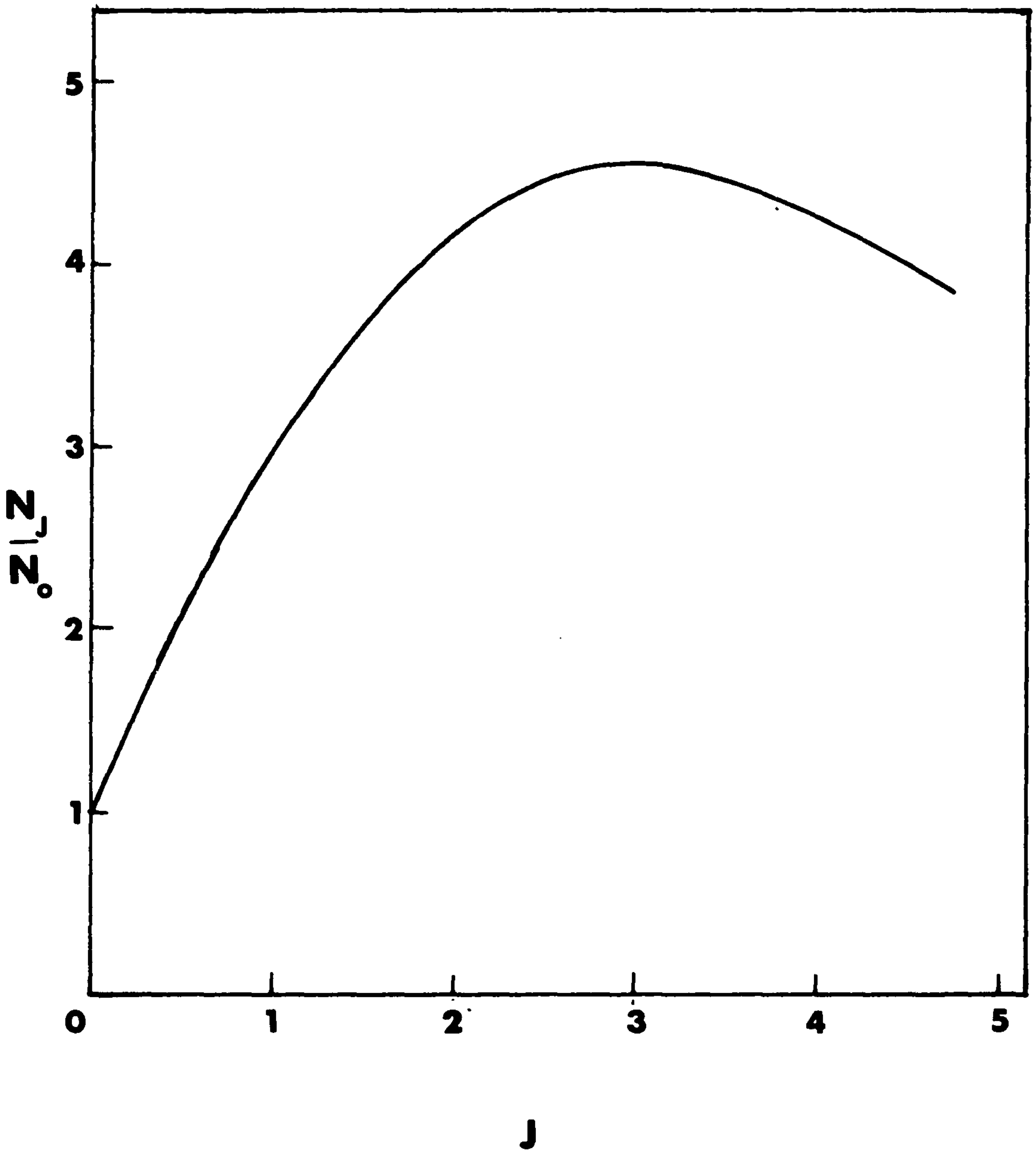

Fig. 17 Population of the various rotational energy levels at room temperature for HCl molecules with $\bar{B} = 9\ cm^{-1}$.

The only source for HCl in the untreated crystals would be the dissociation of H_2O or OH^- ions which enter the crystal during the growing process. We suggest the reaction

$$Cl^- + OH^- \rightleftarrows O^{--} + HCl$$

The dielectric constant measurements indicate that most of the hydrogen ions are closely bound to the chlorine ions to form neutral HCl molecules occupying Cl^- sites in the NaCl crystal. In the crystals that were annealed in HCl gas a small fraction of the H^+ ions would be associated with a vacancy left by Na^+ ions. These ions could tunnel from one Cl^- ion to another around the vacancy site, thus constituting an effective dipole. We have here a case analogous to Li^+ in KCl. This hypothesis would explain the increase in the dielectric constant after the crystal had been cooled in HCl gas.

We shall now attempt to show that the assumption of OH^- dissociation contributes to an explanation of some of the difficulties noted in the introduction.

First of all, we note that our results for $NaCl:OH^-$ and $NaCl:H^+$ are in agreement with those of Hocherl et. al. (1967) on $KCl:OH^-$ and $KCl:H^+$. Both this work and their paraelectric resonance measurements indicate dissociation of OH^- in the alkali halides.

The supposition of OH^- dissociation also accounts for the weakness of the OH^- absorption band at 3650 cm^{-1} when this ion is present in alkali halides. As noted in Chapter II, the oscillator strength of the vibrational transition of OH in different organic compounds varies from 0.04 to 0.11. Wedding, however, finds that, for OH^- in KCl at room temperature, $f = 5.1 \times 10^{-3}$, while for OH^- in NaCl at room temperature $f = 0.35 \times 10^{-3}$. That is f appears to be from one to two orders of magnitude less for OH^- in alkali halides, than for OH in other compounds.

This decrease in f would be equivalent to a decrease in $(dp/dr)^2$. If, however, there was such a large change in dp/dr, one would expect a considerable rearrangement of the electronic configuration accompanied by a large change in the force constant and in the vibrational frequency. One finds, however, that the vibrational frequency for OH in methanol is 3644 cm^{-1}, while for OH^- in KCl and NaCl $\nu = 3643\ cm^{-1}$ and 3654 cm^{-1} respectively. Thus the resonance frequency remains unchanged, while f apparently decreases by two orders of magnitude.

It seems to us that the supposition of partial dissociation of OH^- in the alkali halides is a more plausible explanation. If we assume that the OH oscillator strength remains more or less constant then we are lead to the conclusion that 90% of OH^- in KCl and 99% of OH^- in NaCl dissociates.

The assumption of OH^- dissociation also is in agreement with the surprisingly large dipole moment, p, that must be ascribed to OH^- in the alkali halides. If one uses the Onsager formula for the effective electric field

$$E_{eff} = \frac{3\varepsilon}{2\varepsilon + 1} E$$

then one obtains values of p varying from around 3 to 4 D. (Chandra and Agrawal, 1967, and Shepherd, 1966). This value is from 50% to 100% higher than the accepted value of p_{OH}. Some authors (Kuhn and Luty 1964, Kanzig et. al. 1964) actually use the Lorentz expression for the effective field

$$E_{eff} = \frac{2\varepsilon + 1}{3} E$$

to obtain p = 2 D as was originally expected. However there is no doubt that one should use the Onsager and not the Lorentz field (Frolich, 1958, and Von Hippel, 1954).

Actually the high value of p is the one to be expected if one assumes that OH^- sits off-center by 0.3 A° (Bron and Dreyfus, 1967) or alternatively O^{--} sits off-center by about the same amount. In the case of OH^- we obtain an additional dipole moment of 0.3e = 1.4 D which when added to an intrinsic dipole moment p_{OH^-} = 2.2 D, gives a total effective dipole moment of 3.6 D. In the case of O^{--}, the dipole moment is simply p = 0.3 x 2 e = 2.9 D. Due to the uncertainty in the experimental determination of p and the off-center displacement, either of the two above calculations of p are acceptable.

The results of Kuhn and Luty (1964) on the lining up of OH^- dipoles by an electric field can be reinterpreted in terms of an off-centered dipole. We suggest that the electric field forced the OH^- dipole considered as a single ion (or the O^{--}) into one of the six < 100 > directions. As noted in the introduction, one would expect OH^- to be lined up in the < 110 >

direction. We believe, therefore, that our hypothesis is more plausible.

It should be noted that the dissociation of OH^- was actually to be expected on the basis of energy consideration. Herzberg (1950) gives the dissociation energy of OH to be 4.35 while that of HCl is slightly higher, 4.43. In view of the fact that only a very small fraction of the Cl are replaced by O^{--} one would assume both from the point of view of minimum energy and probability that the H^+ would be associated with Cl^- rather than O^{--}.

The main objection to our conclusion is that outside of Robinson and Hollis Hallet (1966), and ourselves nobody else has reported observing the band at 2880 cm^{-1}. Thus in the infrared spectrum shown by Fritz, Luty, and Anger (1963) of KCl doped with KOH and K_2CO_3 there is no sign of the above mentioned band. We are unable to understand this. On the other hand in one of Wedding's spectra (1967) of KCl and KBr doped with OD and OH, there is an absorption band at 2902 and 2905 cm^{-1}. Wedding does not discuss these bands. Also the apparent oscillator strength of OH^- in NaCl is 12 times less than in KCl, which we consider to be due to a greater degree of dissociation in NaCl. It may be that our rough estimates of 90% and 99% dissociation in KCl and NaCl are too high, especially in the case of KCl.

CHAPTER VI

CONCLUSION

It has been shown that the OH^- ion can be removed from NaCl crystals by annealing them in HCl gas at temperatures near the melting point and cooling in vacuum. The HCl molecules can be introduced into the pure crystals by annealing and cooling in the gas. It has also been shown from i.r. measurements on untreated and treated samples that there is some dissociation of the OH^- ions into hydrogen and oxygen ions. The dielectric constant measurements indicate that H^+ ions occupy off-center positions and thus show a paraelectric effect. This work was semi quantitative in that no calculation was carried out to obtain the oscillator strength of the HCl band or to calculate the number of HCl molecules in the crystals.

It has been shown that our results can be used to explain the apparently excessively large value of the dipole moment of OH^- in the alkali halides and the surprisingly small value of the oscillator strength.

Further investigations of the $NaCl:H^+$ system should include

1. Paraelectric resonance measurements.
2. The determination of the position and direction of minimum energy configuration.

3. Measurements of ε at lower temperatures and with higher concentrations.
4. Infrared measurements at low temperatures.
5. Calculation of the i.r. oscillator strength.
6. Calculation of the spacing between the various energy levels at low temperatures.

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