## Anomalous Isotope Dependence of Tunnel Splitting of OH<sup>-</sup> and OD<sup>-</sup> Defects in KCl and NaCl Crystals

S. Ludwig, A. Brederek, and C. Enss

Kirchhoff Institut für Physik, Universität Heidelberg, Albert-Ueberle-Strasse 3-5, 69120 Heidelberg, Germany

C.P. An and F. Luty

Department of Physics, University of Utah, Salt Lake City, Utah 84112

(Received 11 August 2000)

We report low temperature high resolution Fourier-transform infrared stretching mode absorption and dielectric susceptibility measurements of  $OH^-$  and  $OD^-$  defects in potassium chloride and sodium chloride crystals. Although very low concentrated samples have been used in this investigation, we find in all cases significant deviations from the behavior expected for isolated tunneling defects. The most interesting result is the observation that the tunneling of hydroxide and deuteroxide defects in both host crystals exhibits a rather unusual isotope dependence, since the level splitting associated with the tunneling motion of the heavier defect ion  $OD^-$  is larger than that due to  $OH^-$  defects.

PACS numbers: 61.72.Ji, 77.22.Gm, 78.30.Ly

Among the three important paraelectric-paraelastic defect systems—substitutional Li<sup>+</sup>, CN<sup>-</sup>, and OH<sup>-</sup> ions in alkali halides—the first two are the simplest and best understood [1]. In contrast, the behavior of substitutional OH<sup>-</sup> ions is far more complicated, because they carry electric and elastic dipole moments with comparable strength for defect-lattice and defect-defect interaction. Moreover, the misfit in size and the highly asymmetric (pear-type) shape of an OH<sup>-</sup> molecule compared to the occupied spherical anion vacancy can lead to sizable off-center shifts along its axis. Therefore, their reorientation can involve independent or coupled rotational and translational motions of the molecule.

For seven host crystals with (100) oriented OH<sup>-</sup> dipoles, the observed linear temperature dependence of the reorientational relaxation rate  $\tau^{-1}$  at low temperatures indicates at least indirectly the existence of tunneling [2]. The observed strong decrease of the rate  $\tau^{-1}$  with rising host lattice constant (NaCl  $\rightarrow$  RbBr) shows, however, that the increasing lattice distortions do hinder the reorientational motion of the  $OH^-$  molecule. This leads to renormalization of the "bare" tunnel splitting  $\Delta_b$  to a new effective value  $\Delta_0$ , which decreases exponentially with the strength of the so-called dressing effect [2-4]. For 90° tunneling the bare tunnel splitting can be estimated by  $\Delta_b \propto (V/2I)^{1/2} \exp[-(2IV/\hbar^2)^{1/2}]$  using the WKB method. Here V denotes the barrier height and I the moment of inertia. The dressed or renormalized tunnel splitting can be expressed by  $\Delta_0^2 = \Delta_b^2 \exp(-D_0)$ , where  $exp(-D_0)$  is a type of Debye-Waller factor that depends on the interaction between the defect and the lattice [3].

Only for the two hosts NaCl and KCl with highest OH<sup>-</sup> relaxation rate  $\tau^{-1}$  and smallest dressing, a sizable effective  $\Delta_0$  is expected and has been attempted to be measured with various techniques; with rather large uncertainties,  $\Delta_0/k_B$  values in the range of 1.5 K and 0.3 K have been

reported for NaCl [1] and KCl [2], respectively, based on a  $\langle 100 \rangle$  model with only 90° tunneling [5].

One important advantage of OH<sup>-</sup> has hardly been exploited so far in experiments investigating its tunnel splitting. Isotope variation  $OH^- \rightarrow OD^-$  will change strongly the moment of inertia for molecular rotation around the center of mass (c.m.), but affects very little  $(17 \rightarrow 18)$  the total mass for translational motion. Nothing is known so far about the isotope influence on the important dressing effect. In spite of the complicated nature of the rotationaltranslational tunneling motion, it has always been assumed, but never experimentally tested, that the effective  $\Delta_0$  value should decrease under  $H \rightarrow D$  isotope variation. In this work we have investigated this problem for the two host crystals KCl and NaCl with two different and complementary techniques: high resolution Fourier-transform infrared (FTIR) absorption measurements of the OH<sup>-</sup> and OD<sup>-</sup> stretching mode and dielectric susceptibility measurements. The very surprising result is that the lighter ion (OH<sup>-</sup>) shows the smaller tunnel splitting in both host crystals.

The dielectric susceptibility has been measured at frequencies of a few kHz, 150 and 850 MHz, in the temperature range between 10 mK and 30 K. The experiments have been performed on NaCl and KCl crystals containing dilute amounts of hydroxide or deuteroxide ions in order to avoid any influence of interaction between the defects. Note that the dielectric susceptibility at high concentrations has been investigated previously [6–10]. All crystals were grown with different dopings in the melt by the Czochralski technique at the Utah Crystal Growth Laboratory. The actual defect concentrations in the crystals were determined by their integrated  $OH^-$  and  $OD^-$  stretching mode absorption calibrated with *p*H titration techniques.

The susceptibility data at low frequencies have been taken using a noncommercial bridge. Details of the experimental setup have been described in previous publications [11,12]. To carry out the experiments at high frequencies, the samples were placed in the uniform electric field region of a reentrant microwave cavity with a helical center conductor. The dielectric susceptibility taking into account corrections for the local field is obtained from the measured values of the dielectric constant via the well-known Clausius-Mossotti equation.

For defects with potential minima along the  $\langle 100 \rangle$  crystal direction, like isolated OH<sup>-</sup> and OD<sup>-</sup> ions in KCl and NaCl, the static dielectric susceptibility should be given by [5]

$$\chi_{\rm isol} = \frac{np^2}{3\epsilon_0 \Delta_0} \frac{1 + 3e^{-2\Delta_0/k_B T} - 4e^{-3\Delta_0/k_B T}}{1 + 3e^{-2\Delta_0/k_B T} + 2e^{-3\Delta_0/k_B T}}.$$
 (1)

This expression has been derived under the assumption that the transition matrix element for 90° orientational tunneling is by far larger than the corresponding matrix element for 180° tunneling. Although this might seem a plausible assumption, several experiments on NaCl crystals containing OH<sup>-</sup> indicate that the tunneling motion is far more complicated in this system [13–19]. In particular, the detailed analysis of millimeter wave absorption experiments [19] leads to the conclusion that the matrix element for 180° tunneling is  $\Delta_r/k_B = -0.6$  K, while that for 90° tunneling is  $\Delta_0/k_B = 1.6$  K. These values are consistent with the other spectroscopy data cited above. In addition, the experiments by Suto et al. [19] indicate that the c.m. of the OH<sup>-</sup> ion in NaCl exhibits a quite large off-center shift of about 0.8 Å. Therefore the tunneling motion of OH<sup>-</sup> in NaCl involves not only reorientation but also a translational motion. In the case of OH<sup>-</sup> in KCl, nuclear magnetic resonance studies [20] suggest that the c.m. of the hydroxide ion is displaced by 0.4 Å from the center of the anion vacancy site. A similar conclusion can be drawn from the large value of the electrical dipole moment of OH<sup>-</sup> defects in KCl [21].

In Fig. 1 the dielectric susceptibility of a NaCl crystal containing 16 ppm OH<sup>-</sup> is shown as a function of temperature for several frequencies. The observed temperature dependence of  $\chi_{OH^-}$  is for this system qualitatively similar to the predicted curve (solid line) calculated with Eq. (1), which should be a good approximation at frequencies  $\omega \ll \Delta_0/\hbar$ . However, the observed frequency dependence reveals the presence of relaxation processes. Since isolated and fully symmetric defects are not expected to contribute to relaxational processes we conclude that the OH<sup>-</sup> ions reorient in potentials which do not have perfect cubic symmetry. Such an asymmetry may well arise from the elastic coupling of the defects to random internal strains in the host crystal, and can result in a distribution of the energy splittings of the tunneling states. A comparison between the data and a fit calculated with Eq. (1) (solid line in Fig. 1) displays characteristic differences which, indeed, indicate a distribution of energies of the tunneling states. The fact that the data at the highest two frequencies overlap perfectly leads to the conclusion that no sig-



FIG. 1. Dielectric susceptibility of a NaCl crystal doped with 16 ppm OH<sup>-</sup> at several frequencies as a function of temperature. The dashed line indicates the classical 1/T behavior. The solid line represents the temperature dependence of  $\chi_{OH}$  according to Eq. (1).

nificant contribution of relaxation processes occurs in this frequency domain.

From the data in the classical 1/T regime ( $k_BT \gg \Delta_0$ ) we can deduce the dipole moment of the OH<sup>-</sup> ions in NaCl and find the rather large value of 0.95e Å. Comparison with the dipole moment of a free OH<sup>-</sup> ion indicates that the c.m. is shifted off center by approximately 0.8 Å in very good agreement with the findings of Suto *et al.* [19].

Dielectric susceptibility measurements on NaCl and KCl crystals containing  $OH^-$  or  $OD^-$  showed qualitatively very similar results. The off-center shift of the hydroxide ions in KCl is about 0.32 Å and thus is less than half as large as in NaCl. In addition, the distribution of the energy splittings of the tunneling states in KCl seems to be systematically broader than in NaCl.

The most surprising result of this investigation, however, is the fact that the tunnel splitting of the OH<sup>-</sup> system is smaller than that of OD<sup>-</sup> in both KCl and NaCl. This unexpected isotope effect can best be demonstrated by comparing the high frequency susceptibility data, because in this way the influence of relaxational contributions can be avoided. A convincing plot of the high frequency data can be made by normalizing them with respect to the dielectric susceptibility at the lowest temperatures, providing an additional test of the isotope dependence of the tunneling matrix element. In this case, the temperature where the dropoff of  $\chi$ —the transition to the classical regime occurs is determined by the tunnel splitting  $\Delta_0$ . Figure 2 shows that the data of both host crystals containing OD<sup>-</sup> dropoff at a higher temperature, which again reflects the fact that the tunnel splitting of the heavier isotope is larger in these systems. Moreover, although the tunnel splitting associated with the reorientation of hydroxide ions in the



FIG. 2. Normalized dielectric susceptibility  $\chi/\chi(T \rightarrow 0)$  of KCl and NaCl crystals doped with OD<sup>-</sup> or OH<sup>-</sup> at 150 MHz as a function of temperature. The data have been normalized with respect to the low temperature values of  $\chi$ . The solid lines are guides for the eyes.

two host crystals is different by about a factor of 8, the relative isotope shift appears to be very similar in both cases. This indicates that the observed isotope dependence does not result from just some peculiarity of one particular host crystal, but has a more general origin.

Let us now turn to the results of high resolution FTIR absorption measurements of the OH<sup>-</sup> and OD<sup>-</sup> stretching mode (SM). For low concentrations of interaction-free ions, tunneling in their six-well orientational potential with  $\langle 100 \rangle$  minima will split the SM ground state (v = 0) and excited state (v = 1) into multiplets of states of gerade (g) and ungerade (u) symmetry. As the electric dipole transition  $0 \rightarrow 1$  is allowed only between g and u states, this splitting appears at low temperatures as a spectral fine structure of the sixfold degenerate classical SM transitions. Figure 3 shows the SM absorption for 24 ppm OH<sup>-</sup> (a) and 33 ppm OD<sup>-</sup> (b) in KCl measured at 4 K. These somewhat higher concentrations are necessary to obtain reasonable absorption strength above the noise level even for the used thick ( $\approx 2$  cm) samples. Both spectra are plotted on the same frequency scale but with appropriate reduced mass shift to make the OH<sup>-</sup> and OD<sup>-</sup> central SM maxima coincide. The triple absorption spectrum observed for both OH<sup>-</sup> and OD<sup>-</sup> can be decomposed into three components (dotted lines): a rather sharp Gaussiantype central line, accompanied by Stokes and anti-Stokes shifted sidebands of Lorentzian shape. The central line represents the inhomogeneously broadened classical SM of the molecules under sizable stress of field effects from interaction.

More important are the Lorentzian sidebands, which we assign to  $g \leftrightarrow u$  transitions between the tunneling mul-



FIG. 3. Low temperature stretching mode absorption spectra of  $OH^-$  (a) and  $OD^-$  (b) defects in KCl. Points indicate the best possible FTIR resolution.

tiplets of the v = 0 and v = 1 SM states. Their spectral separation yields the sum  $(\Delta_0 + \Delta_1)$  of the tunneling splittings of the ground  $(\Delta_0)$  and the excited state  $(\Delta_1)$  of the SM. Without going into details comparing the absorption curves, Figs. 3(a) and 3(b) show clearly that the optically resolvable tunnel splitting  $(\Delta_0 + \Delta_1)$  for OD<sup>-</sup> is a factor of 1.6 larger than the value for OH<sup>-</sup>, which agrees well with the ratio observed in the dielectric susceptibility measurements shown above. Though with similar high resolution FTIR the even larger SM splitting of OH<sup>-</sup> in NaCl can be detected very well, comparison to the OD<sup>-</sup> case is made impossible by the extremely small SM oscillator strength of OD<sup>-</sup> in NaCl.

The tunnel splitting of  $OH^-$  defects in NaCl has also been studied in phonon spectroscopy experiments, in which a minimum in the phonon transmission rate is observed due to the resonant absorption of phonons by the tunneling systems [17]. A comparison of these former results with preliminary data on NaCl containing  $OD^$ obtained with the same technique shows also an inverse isotope dependence in full quantitative agreement with the dielectric experiments presented here [22,23]. This is an important additional piece of information since the transitions within the tunneling multiplet contributing in acoustic experiments are different because of the selection rules.

Let us now discuss the cause of the unexpected isotope dependence. Since the hydroxide and deuteroxide ions occupy off-center positions in both host crystals, their tunneling motion is a combined rotation and translation. If the tunnel splitting were mainly determined by the translational motion, one would expect only a very small "ordinary" isotope effect since the mass for translational motion is similar for OH<sup>-</sup> and OD<sup>-</sup>. Therefore, other isotope dependent phenomena may become visible in this system which influence the tunnel splitting. Two such phenomena might be the zero point energy and the dressing effect. The influence of the zero point energy is expected to be small and, more important, should generally lead to a higher tunnel probability for the lighter isotope, in contrast to our findings. Therefore, at this point it seems most likely that the strong dressing effect is responsible for the inverse isotope dependence of the tunnel splitting. If the elastic dipole moment of the two isotopes were different in a way such that OH<sup>-</sup> couples more strongly to the lattice, a larger renormalization of the tunnel splitting of OH<sup>-</sup> would be conceivable. In fact, very recent studies of the elastic properties of OH<sup>-</sup> and OD<sup>-</sup> in NaCl indicate that the deformation potential of OH<sup>-</sup> is about 3 times as large as for OD<sup>-</sup> in NaCl [24]. Moreover, these vibrating reed measurements show once again the inverse isotope effect of the tunnel splitting for this system.

In summary, we have investigated the dielectric susceptibility and the SM absorption of  $OH^-$  and  $OD^-$  defects in KCl and NaCl crystals at low defect concentrations. We find that the properties of these samples differ considerably from the expected behavior of isolated defects. The most surprising result is that the tunnel splitting shows an inverse isotope effect in both host crystals. This could be explained by a different renormalization of the tunnel splitting, due to different deformation potentials of the two isotopes.

The authors gratefully acknowledge many stimulating discussions with S. Hunklinger, R. Weis, and G. Weiss. This work has been supported by the Deutsche Forschungsgemeinschaft (Contract No. En299/1) and the National Science Foundation (Contract No. DMR96-32959). One of us (F.L.) acknowledges support by the Alexander von Humboldt Foundation.

- [1] For an early review, see F. Bridges, Crit. Rev. Solid State Mater. Sci. 5, 1 (1975).
- [2] S. Kapphan, J. Phys. Chem. Solids 35, 621 (1974).
- [3] L. M. Sander and H. B. Shore, Phys. Rev. B 3, 1472 (1971);
  H. B. Shore and L. M. Sander, Phys. Rev. B 12, 1546 (1975).
- [4] R. Pirc and P. Gosar, Phys. Kondens. Mater. 9, 377 (1969).
- [5] H.B. Shore, Phys. Rev. 151, 570 (1966).
- [6] W. Känzig, H. R. Hart, and S. Roberts, Phys. Rev. Lett. 13, 543 (1964).
- [7] A. T. Fiory, Phys. Rev. B 4, 614 (1971).
- [8] D. Moy, R.C. Potter, and A.C. Anderson, J. Low Temp. Phys. 52, 115 (1983).
- [9] R.C. Potter and A.C. Anderson, Phys. Rev. B 24, 677 (1981).
- [10] C. Enss, S. Ludwig, M. Kreft, C. P. An, and F. Luty, Physica (Amsterdam) 263–264B, 129 (1999).
- [11] J. Classen, C. Enss, C. Bechinger, G. Weiss, and S. Hunklinger, Ann. Phys. 3, 315 (1994).
- [12] C. Enss, M. Gaukler, S. Hunklinger, M. Tornow, R. Weis, and A. Würger, Phys. Rev. B 53, 12094 (1996).
- [13] G. Feher, I. W. Shepherd, and H. B. Shore, Phys. Rev. Lett. 16, 500 (1966).
- [14] L. Rosenbaum, C. Chau, and M. V. Klein, Phys. Rev. 186, 852 (1969).
- [15] R. D. Kirby, A. E. Hughes, and A. J. Sievers, Phys. Rev. B 2, 481 (1970).
- [16] J.G. Peascoe and M.V. Klein, J. Chem. Phys. 59, 2394 (1973).
- [17] R. Windheim and H. Kinder, Phys. Lett. 51A, 475 (1975).
- [18] T. Nanba, K. Hirota, S. Suto, and M. Ikezawa, J. Phys. Soc. Jpn. 53, 449 (1984).
- [19] S. Suto and M. Ikezawa, J. Phys. Soc. Jpn. 53, 438 (1984).
- [20] D.L. Hagrman and W.D. Ohlsen, Phys. Rev. B 3, 1918 (1971).
- [21] S. Kapphan and F. Luty, J. Phys. Chem. Solids 34, 969 (1973).
- [22] S. Ludwig, Ph.D. thesis, Universität Heidelberg, 2000.
- [23] S. Ludwig, F. Zeller, C. Enss, and K. Lassmann (to be published).
- [24] M. Burst, Diploma thesis, Universitt Karlsruhe, 1999 (unpublished); M. Burst and G. Weiss (to be published).