

# PHYSICAL REVIEW B

## CONDENSED MATTER AND MATERIALS PHYSICS

THIRD SERIES, VOLUME 57, NUMBER 5

1 FEBRUARY 1998-I

### BRIEF REPORTS

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#### Hydrogen atoms in $\text{KH}_2\text{PO}_4$ crystals

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(Received 31 July 1997)

Hydrogen atoms have been produced at 77 K in single crystals of potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$  or KDP) using either 60-kV x rays or the fourth harmonic (266 nm) of a pulsed Nd:YAG (yttrium aluminum garnet) laser. The electron-paramagnetic-resonance spectrum from these hydrogen atoms exhibits a characteristic 500-G hyperfine splitting and is easily saturated with microwave power. These atoms occupy interstitial sites and are electron traps. The corresponding hole trap is the well-known  $(\text{HPO}_4)^-$  hole center identified by its 31-G phosphorus hyperfine splitting. Both the hydrogen atoms and the hole centers thermally decay in the temperature range between 80 and 200 K. The observed displacement of protons by 266-nm photons provides direct evidence in support of the proton-transport mechanism recently proposed by Davis, Hughes, and Lee [Chem. Phys. Lett. **207**, 540 (1993)] to explain laser-induced transient optical absorption at room temperature in KDP. [S0163-1829(98)03906-X]

Potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), better known as KDP, is an important nonlinear optical material with many applications in the ultraviolet. Among these are the generation of the third (355 nm) and fourth (266 nm) harmonics of pulsed Nd:YAG (yttrium aluminum garnet) lasers. Problems can arise, however, when unwanted defect-related optical-absorption bands are produced by pump lasers operating at high peak powers. Despite their importance, little is presently known about the optically active point defects in KDP, including possible defect formation mechanisms. Thus, fundamental studies are being undertaken to identify and characterize those defects that limit device performance. We anticipate that a better understanding of the point defects will lead to improvements in the power-handling capability of KDP crystals (i.e., minimization of optical damage) and will permit the growth of more uniform KDP crystals.

A recent paper by Davis, Hughes, and Lee<sup>1</sup> reported the formation of a broad transient optical-absorption band covering much of the visible and near-uv region when KDP crystals were exposed to an intense 266-nm laser beam

( $\text{GW}/\text{cm}^2$ ) at room temperature. The absorbing defect(s) decayed nonexponentially over periods approaching 20 s. Although their experimental techniques did not allow them to directly identify the defects involved, these investigators noted that the spectral dependence of the transient absorption matched that of a previously reported x-ray-induced spectrum<sup>2-4</sup> in KDP. The defect responsible for this absorption is the  $(\text{HPO}_4)^-$  center, which consists of a "proton vacancy" with a hole trapped on the nearest oxygen ion in the adjacent  $\text{PO}_4$  unit. These observations led Davis, Hughes, and Lee<sup>1</sup> to suggest that the transient optical absorption was initiated by a two-photon absorption event quickly followed by the transport of a proton or a hydrogen atom and the simultaneous formation of an  $(\text{HPO}_4)^-$  center. Marshall *et al.*<sup>5</sup> also studied the broad transient absorption induced in KDP by intense 266-nm laser beams. These latter investigators determined experimental values for the various parameters needed to characterize the phenomenon and then used their results to successfully model the effect of the transient absorption on the efficiency of fourth-harmonic conversion in KDP.

In the present paper, we provide direct spectroscopic evidence that protons in the regular KDP lattice can be displaced at 77 K using x rays or a 266-nm laser beam. These sources of ionizing radiation generate hydrogen atoms that are easily observed at low temperature with electron paramagnetic resonance (EPR). Also,  $(\text{HPO}_4)^-$  trapped hole centers are produced by the same irradiations and are monitored with EPR. Our results add to the general understanding of point defects in KDP and they strongly support the proton-transport mechanism proposed by Davis, Hughes, and Lee<sup>1</sup> to explain the laser-induced transient optical absorption at room temperature in KDP.

The KDP crystals used in the present investigation were grown at the Lawrence Livermore National Laboratory. Fast growth conditions were employed, as described elsewhere.<sup>6</sup> The EPR samples, with dimensions of approximately  $3 \times 2 \times 5 \text{ mm}^3$ , were cut from the pyramidal region of the boules. Two distinctly different sources of ionizing radiation were used to produce the paramagnetic defects at 77 K. One was an x-ray tube (Mo target) operating at 60 kV and 30 mA, resulting in a penetration depth in the crystals of approximately 2 mm. The other was the quadrupled output (266 nm) from a Nd:YAG laser (Continuum Powerlite 8000). The laser operated at a 10 Hz repetition rate, the pulse width was nominally 6 ns, and the energy per pulse in the quadrupled beam was 7 mJ. The fundamental (1064 nm) and the doubled (532 nm) output beams were not incident on the crystal during the 266-nm exposures. The samples were held in liquid nitrogen while being irradiated with the x rays or the 266-nm photons, and then were transferred without warming into the helium-gas flow system (Oxford Instruments Model ESR-900) extending through the microwave cavity. The EPR data were taken on a Bruker ESP 300 spectrometer operating at 9.450 GHz with 100-kHz modulation of the magnetic field. A Hewlett-Packard 5340A counter was used to measure the microwave frequency and a Varian E-500 digital gaussmeter was used to measure the magnetic field. A small MgO:Cr crystal was used to correct for the difference in magnetic field between the KDP sample and the gaussmeter probe (the isotropic  $g$  value for  $\text{Cr}^{3+}$  in MgO is 1.9800).

There were no observable EPR signals in our samples prior to their exposure to the x rays or the 266-nm laser beam. Paramagnetic point defects were, however, readily created by both types of radiation. Figure 1 shows the EPR spectrum of a KDP crystal after it was x-ray irradiated at 77 K for 1 h. These data were taken at 40 K with the magnetic field parallel to the  $c$  axis of the crystal. An identical spectrum was obtained, except for a reduction of approximately four in the size of the signals, after a crystal was subjected to the 266-nm laser beam for 72 min (a total of 43 200 shots) while the temperature was held at 77 K. A slow thermal anneal from 77 K to room temperature over a period of 15 min showed that the EPR spectra decayed between 80 and 200 K.

The outer pair of lines in Fig. 1, located at 3103.2 and 3605.6 G, is assigned to an interstitial hydrogen atom. These centers have a very long spin-lattice relaxation time at low temperatures and are easily saturated with microwave power. We found that they were best observed when only a few milliwatts of microwave power were incident on the cavity, which perhaps explains why earlier investigators did not re-

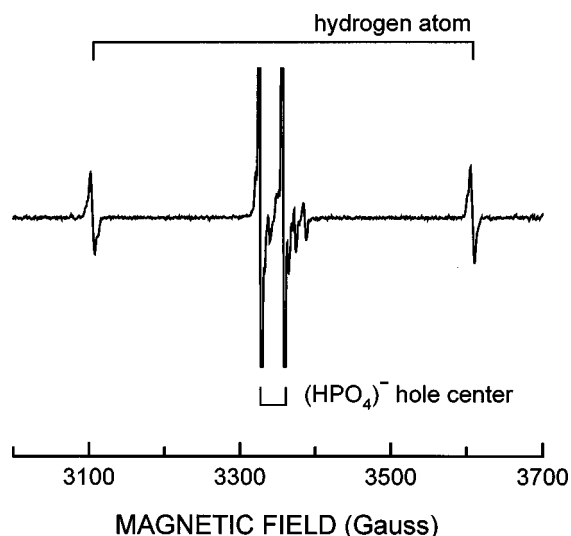


FIG. 1. EPR spectrum of a KDP crystal taken at 40 K with the magnetic field parallel to the  $c$  axis. The crystal has been x-ray irradiated at 77 K.

port their presence. This hydrogen atom spectrum exhibits no angular dependence, thus indicating both the  $g$  and the hyperfine matrices are isotropic. Using the two measured magnetic fields and the measured microwave frequency as input data, a fitting routine based on exact diagonalization of the spin-Hamiltonian

$$H = g\beta HS_z + AI_2S_z + A(I_-S_+ + I_+S_-)$$

gave  $g = 2.0017$  and  $A = 499.6 \text{ G}$ . For comparison, the hyperfine interaction for a hydrogen atom in free space is 506.8 G. We note that hydrogen atoms have been observed with EPR in a variety of other crystals including  $\text{CaF}_2$ , KCl, quartz, and  $\beta$ -alumina.<sup>7-10</sup>

There is a second pair of EPR lines, separated by approximately 31 G, present in the center of Fig. 1. This spectrum was first observed in the early 1960s and has been studied by numerous investigators.<sup>11-15</sup> They have assigned it to an  $(\text{HPO}_4)^-$  center, i.e., a hole trapped on a  $\text{PO}_4$  unit next to a "proton vacancy." The regular KDP lattice contains  $\text{K}^+$  ions and  $(\text{H}_2\text{PO}_4)^-$  units. Upon removal of a proton, an  $(\text{H}_2\text{PO}_4)^-$  unit becomes an  $(\text{HPO}_4)^{2-}$  unit, which then easily stabilizes a hole and forms a paramagnetic  $(\text{HPO}_4)^-$  center. The hole resides primarily on the oxygen ion next to the site of the missing proton and the 31-G splitting is due to a hyperfine interaction with the central phosphorus ion. This holelike spectrum exhibits  $g$ -matrix anisotropy. At low temperature and for an arbitrary direction of magnetic field, there are eight doublets. These reduce to a single doublet (as shown in Fig. 1) when the magnetic field is along the  $c$  axis of the crystal. Taking into account the different linewidths and different microwave power saturation behaviors, we determined that the concentrations of our hydrogen atoms and  $(\text{HPO}_4)^-$  hole centers are nearly equal following an exposure to x rays or the 266-nm laser beam. The absolute concentration of each center in Fig. 1 is approximately  $1 \times 10^{18} \text{ cm}^{-3}$ .

Figure 1 also shows several additional less intense EPR doublets in the region near the  $(\text{HPO}_4)^-$  signal. They are

holelike and exhibit splittings of approximately 31 G, presumably due to a hyperfine interaction with a phosphorus nucleus. Except for slightly different  $g$  values, these doublets strongly resemble the more intense  $(\text{HPO}_4)^-$  signal. Thus, we suggest that the responsible defects are variants of the  $(\text{HPO}_4)^-$  center, i.e., they are  $(\text{HPO}_4)^-$  centers with a slight perturbation such as an impurity on a neighboring potassium site, proton site, or phosphorus site.

Our data in Fig. 1 strongly suggest that point defects can be formed in a "perfect" KDP crystal during an exposure to ionizing radiation. Both the x rays and the 266-nm laser beam create free (i.e., uncorrelated) electrons and holes within the bulk of the crystal; this occurs directly in the case of the x rays but requires a two-photon event in the case of the 266-nm laser beam. Many of these electrons and holes will immediately recombine, radiatively or nonradiatively, to restore the perfect lattice. However, a portion of the electrons and holes will be trapped in the form of interstitial hydrogen atoms and  $(\text{HPO}_4)^-$  hole centers, respectively (see Fig. 1). These latter two defects, although reasonably stable at 77 K, decay rapidly at room temperature and are believed to be responsible for the transient optical absorption reported by Davis, Hughes, and Lee<sup>1</sup> and Marshall *et al.*<sup>5</sup>

The key event in the production of the hydrogen atom and the  $(\text{HPO}_4)^-$  hole center in the otherwise perfect crystal is the radiation-induced displacement of a proton from its normal lattice site. That this happens with relative ease in KDP is not surprising when one considers the hydrogen bonds that link the  $\text{PO}_4$  units to each other in the crystal.<sup>16</sup> These are weak bonds that result when a proton is positioned between two oxygen ions from adjacent  $\text{PO}_4$  units. A double potential well symmetrically located about the center of the bond allows the proton to be closer to one of the oxygen ions. The hopping of the proton between these two wells is temperature dependent; at temperatures well below the ferroelectric transition ( $T_c = 123$  K), the proton stays on one side of the bond, and at room temperature, the proton rapidly hops between the two wells. At any temperature, the free electrons created by the x rays or the 266-nm laser beam may be trapped by the bonding proton and form a hydrogen atom. This process of forming the hydrogen atom only involves the capture of a free electron in an existing "hydrogen bond" and does not require the recombination of an electron-hole pair at the proton site. Once formed, the neutral hydrogen atom easily moves away from the original site of the proton and slowly diffuses through the lattice from one interstitial site to another. The rate of diffusion, of course, depends on temperature. A second, and equivalent, way to envision this proton displacement process is to consider the  $\text{OH}^-$  mol-

ecule that exists in the perfect lattice when the proton occupies one side of the double-well potential. A free electron produced by the x rays or the 266-nm laser beam will be attracted to this  $\text{OH}^-$  molecule and thus form an  $\text{OH}^{2-}$  molecule. The resulting  $\text{OH}^{2-}$  molecule will be very unstable and will immediately dissociate into a hydrogen atom and an  $\text{O}^{2-}$  ion. After the hydrogen atom is produced, the final step in the defect creation process is to form an  $(\text{HPO}_4)^-$  center by trapping a free hole on the oxygen ion next to the newly formed proton vacancy.

It is important to note that a significant concentration of proton vacancies may exist in some KDP crystals prior to any irradiation. This might happen, for example, if there are a sufficient number of trivalent transition-metal impurity ions such as  $\text{Fe}^{3+}$  substituting for  $\text{K}^+$  ions in the crystal. The needed charge compensation would be provided by proton vacancies formed during growth. Then during an irradiation with x rays or 266-nm laser beams, the preexisting proton vacancies will trap the free holes being generated and form  $(\text{HPO}_4)^-$  centers while the trivalent transition-metal impurity ions will trap some of the free electrons being generated and convert to the divalent state. The transient optical absorption in a crystal containing impurities would have a similar spectral dependence as a crystal with no impurities since the same  $(\text{HPO}_4)^-$  centers would be primarily responsible for the absorption bands in each case. However, the lifetimes of the transient absorption may be different in the two cases because of possible differences in the thermal stability of the electron traps, i.e., the hydrogen atom versus the impurity ions. This possible dependence of lifetime on the presence of small concentrations of impurities may help to explain the variations in decay time reported by Marshall *et al.*<sup>5</sup> for a series of KDP samples.

In summary, we have used x rays and 266-nm photons to produce hydrogen atoms at 77 K in KDP crystals. The  $(\text{HPO}_4)^-$  hole center is created at the same time. These defects are stable at 77 K but decay rapidly at room temperature. Our results lend strong support to the suggestion by Davis, Hughes, and Lee<sup>1</sup> that proton transport is a major component of the mechanism responsible for transient optical absorption in KDP at room temperature. We conclude that impurities or other defects are not needed to serve as precursors to the defect formation, thus implying that transient optical absorption is an intrinsic phenomenon that occurs in "perfect" KDP crystals.

The authors wish to thank Gary Catella and Cleveland Crystals, Inc. for the loan of a KDP frequency-doubling element to provide 266-nm output from the laser.

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