proximation

$$\frac{\Delta E}{\Delta T_\lambda}=\frac{\rho[S(T_\lambda)-S(T_\lambda-\Delta T_\lambda)]}{E[\epsilon(T_\lambda)-\epsilon(T_\lambda-\Delta T_\lambda)]}.$$

This estimate gives $\Delta T_\lambda = 0.5$ mdeg for $E = 1.2$ MV/cm, which is three times smaller than the measured $\Delta T_\lambda = 1.5$ mdeg. This interpretation is suggested as an alternative to the previous explanations of the electric field effects on T_λ given in Atkins[5] which depend on the negative slope of the λ curve.[6]

Since we now have a measured value of the suppression of the λ point of liquid helium in an electric field, we can estimate the effect of van der Waals forces on the λ point of thin films and extremely fine pores.[7] For typical forces,[5] the λ point 50 Å from a wall should be suppressed by 3 mdeg. Consequently, the role of electric field effects on extremely small pores and thin films needs careful examination.

We have observed electric field effects on superfluid flow and have successfully suppressed T_λ in liquid helium with an electric field. Further investigations are in progress to determine electric field and pore size effects on superfluid flow with possible application to Josephson junctions for liquid helium.

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[3] C. Boghosian et al., Phys. Rev. 146, 110 (1966).

[4] This analysis is in direct analogy with the case of a superconductor in which a first-order phase transition occurs only in the presence of a magnetic field. Hence, the analysis assumes a latent heat and a discontinuous dielectric change for the helium transition in an electric field. At present there is no experimental proof for or against such a first-order transition in liquid helium; so it remains an interesting open question.

[5] K. R. Atkins, Liquid Helium (Cambridge University Press, New York, 1950), p. 225.

[6] Since the electric fields in this geometry are confined to the immediate vicinity of the porous mica and not to the baths in general, any flow effects due to the modification of the chemical potential by the fringing fields should be irrelevant to the steady-state effects observed.

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DOMAIN SWITCHING IN IRRADIATED FERROELECTRIC KH_2PO_4 OBSERVED BY ELECTRON SPIN RESONANCE*

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The first direct observation of domain switching in radiation damaged ferroelectric KH_2PO_4 using electron spin resonance is reported. This switching is demonstrated by the observation of a reversal in orientation for the $\cdot OPO_3H^-$ free-radical ions during polarization of the damaged crystal by an electric field. The reversal is accomplished by an intramolecular charge transfer which permits reversal of the damage sites on the microscopic level.

While potassium dihydrogen orthophosphate KH_2PO_4 (KDP) is a well-known ferroelectric material, very little work has ever been published concerning the effects of radiation on it. In this paper we report results of some radiation damage studies in which ESR is used as a probe to study the microscopic radiation-damage sites and to observe the influence of an applied electric field on these sites. It is found that the switching of the ferroelectric domains can be observed directly on the microscopic level and that the observed damage sites are themselves microscopically reversible.

At room temperature, KDP forms tetragonal crystals (space group $I\bar{4}2d$) in which each tetrahedral orthophosphate (PO_4^-) group is hydrogen-bonded to its four neighboring PO_4^- groups.[1] The time-averaged position of each hydrogen atom is located symmetrically between an upper oxygen of one orthophosphate tetrahedron and a lower oxygen of a neighboring tetrahedron. Thus each hydrogen is shared equally between two PO_4^- tetrahedra. In the ferroelectric phase (below 123°K) the time-averaged position of each hydrogen atom is no longer symmetrically located along a hydrogen bond. Each hydrogen becomes closely associated with either an upper or a lower oxygen, and is no longer shared equally between two PO_4^- tetrahedra. The structure then can more properly be thought of as consisting of distinct $H_2PO_4^-$ ions. Within a single ferroelectric domain both hydrogens in each ion are associated with the two upper oxygens, while in a domain of the opposite polarization both hydrogens are associated with lower oxygens. In an unpolarized crystal domains of both polarities are equally present.

Radiation-damaged KDP exhibits strong ESR signals when irradiated and studied at 77°K, although the signals disappear irreversibly on warming to temperatures much above the Curie temperature.[2] The paramagnetic species has been identified as the $\cdot OPO_3H^-$ radical which results from the loss of a hydrogen atom from a $H_2PO_4^-$ ion. Measurements of the highly anisotropic g factor indicate that the unpaired-electron spin density is predominantly localized on a single oxygen atom while the observed isotropic ^{31}P hyperfine splitting indicates a residual spin density of approximately 1% in the phosphorus 3s orbital. For arbitrary orientations of the crystals the observed spectrum consists of 16 equal-intensity lines which arise from the eight magnetically inequivalent oxygen sites (four each on the two inequivalent PO_4^- tetrahedra) together with the 32-G isotropic splitting associated with the ^{31}P hyperfine coupling.[2] When the magnetic field is perpendicular to the ferroelectric c axis there are still two inequivalent PO_4^- tetrahedra per unit cell. However, the two upper oxygen sites on a single PO_4^- tetrahedron become magnetically equivalent to each other. Also, the two lower oxygen sites become equivalent although remaining distinguishable from the upper oxygen sites. The spectrum thus degenerates to four doublets, two doublets from each of the two possible domains.

Figure 1(a) shows a typical ESR spectrum of x-irradiated KDP at 77°K.[3] The magnetic field is perpendicular to the c axis making an angle of approximately 35° with respect to the a or b axis. The four doublets are clearly visible. Crystallographic data[1] and knowledge of the g tensor[2] enable one to separate the four doublets into two doublets which arise from domains of one polarity (lines designated by A) and two doublets arising from domains of the other polarity (lines designated by B). It is not possible to distinguish which of the two domains corresponds to lines designated A or B, but it is known that all lines designated by A correspond to the same domain. Since in the unpolarized crystal both domains are equally prevalent, the lines from A and B sites are of equal intensity. After this spectrum was taken and while still in the ferroelectric phase an electric field of 9 kV/cm was applied to the crystal parallel to the ferroelectric c axis. The electric field was then removed and a second spectrum, shown in Fig. 1(b), was observed. As can be seen, the intensity of the two doublets designated by the letters A has decreased markedly, while the intensity of the other pair has increased. It is evident that the application of the electric field has depleted domains of one polarity in favor of the other. The weak doublets would be expected to disappear under complete polarization; however, since our data are obtained in the absence of an applied field, and because we may not have attained the coercive field, we observe a smaller remanent polarization in which some domains are polarized opposite to the dominant direction.

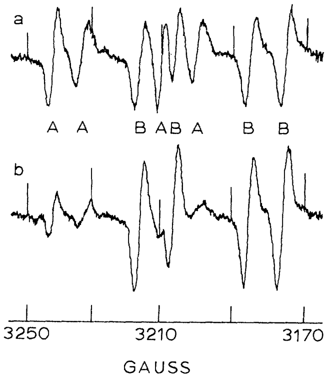

FIG. 1. (a) The ESR spectrum of x-irradiated KH_2PO_4 at 77°K, with the external magnetic field perpendicular to the ferroelectric c axis and at an angle of approximately 35° with respect to the a or b axis. The letters A and B differentiate the eight equal-intensity lines arising from paramagnetic sites in domains of different polarity. (b) The spectrum at the same orientation but after applying a 9-kV/cm polarizing electric field to the radiation-damaged crystal. Note that those lines which have decreased in intensity are from sites in domains of one polarity while the lines that have increased are from sites in domains of the other polarity.

What is more important is that the polarization mechanism is able to transfer the unpaired-electron spin density from an upper oxygen site to a lower oxygen site or vice versa. Presumably, each unpaired electron is associated with one of the two oxygen atoms on adjacent molecules connected by a hydrogen bond prior to the irradiation. The damage, consisting of removal of the hydrogen atom from this bond, leaves the unpaired electron on one of these oxygens. Figure 2(a) shows a domain in which the unpaired electron is on an upper oxygen. During the domain switching, the unpaired-electron spin density is transferred to the lower oxygen on the adjacent molecule, as shown in Fig. 2(b). This transfer is believed to result from an intramolecular charge rearrangement accompanied by the formation of an additional covalent O-H bond within the original radical. As shown in Fig. 2, a damaged $\cdot OPO_3H^-$ group, which has an unpaired electron on an upper oxygen, will after switching of the hydrogens have its normal complement of two O-H bonds, while one of its neighboring groups which had two O-H bonds before switching is now lacking a hydrogen on one of its lower oxygens. This results in an unpaired electron disappearing from an upper oxygen site and reappearing on the adjacent lower oxygen across the broken hydrogen bond.

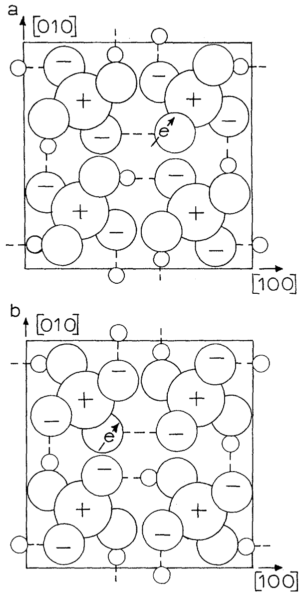

FIG. 2. (a) A c-axis projection of the unit cell. The upper oxygens are shown as full circles while the lower oxygens are shown partially eclipsed by the phosphorus (+) atom. The small circles indicate hydrogen atoms. The four PO_4^- groups reside in a domain where the hydrogen atoms have localized on upper oxygens. The unpaired electron appears on the oxygen atom near which a hydrogen atom had been localized prior to radiation damage. The formal charge distribution is also indicated. (b) The same four groups after the polarizing electric field has switched the hydrogen atoms from upper oxygens to lower oxygens. The unpaired electron now appears on that lower oxygen of the neighboring group with which the missing hydrogen atom would be associated.

The results presented here are very different from the results of similar experiments on KH_2AsO_4.[4,5] In that compound the radical produced by radiation damage is the AsO_4^{-4} ion which is stable at room temperature. Here the unpaired electron resides predominantly on the central arsenic atom.[4] Blinc, Cevc, and Schara analyzed the proton hyperfine splitting in the AsO_4^{-4} radical for which equal coupling to four protons is observed at room temperature.[5] Their measurements show that the proton switching frequency decreases as the temperature is lowered. No change in the ESR spectrum at the Curie temperature (97°K) is observed since the unpaired electron even in the paraelectric phase below ~225°K is already under the influence of the hyperfine field due to only the two ordered protons. These authors also report that the application of a polarizing electric field has no effect on the ESR spectrum. This result in no way conflicts with our observations since their spectra were taken with the magnetic field parallel to the ferroelectric c axis where, due to crystal symmetry, all sites and all protons are magnetically equivalent. Thus different domains are indistinguishable in their experiment. More recently Blinc and Šentjurc have performed ESR experiments on Cu^{+2}-doped Rochelle salt under the influence of a polarizing electric field.[6] These experiments show a Stark-effect splitting in the ESR hyperfine components of the Cu^{+2} ions, which differs for different sites in the ferroelectric region. Their effect in distinction to ours is a dynamic effect which is observable due to the presence of the applied field.

The effect of radiation on ferroelectric materials frequently destroys or at least inhibits polarization reversal.[7] Boutin, Frazer, and Jona have classified the effects of radiation on ferroelectrics into two categories according to the type of damage produced.[8] The first type consists of stable local damage centers distributed throughout the sample while the second type consists of mobile damage centers which congregate along existing imperfections. The first type can be either microscopically reversible or irreversible. As there is no evidence from our measurements that the damage in KDP extends beyond the unit-cell level it is classified as microscopically reversible local damage. This type is not expected to have as great a tendency to clamp existing domain structure into a crystal during irradiation. This is consistent with our ability to reverse the polarization. In addition there would be no tendency for the damage to internally bias the crystal. Of course, nonparamagnetic damage centers cannot be detected in our experiment and if these exist they may have an additional influence on the ferroelectric properties of the irradiated crystal.

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†Who is expected to present a dissertation containing this work to the faculty and graduate school of Clark University in partial fulfillment of the requirements for a Ph.D. in Physics.

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MEASUREMENT OF PHOTOABSORPTION OF THE LITHIUM HALIDES NEAR THE LITHIUM K EDGE

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Most of the work on optical absorption of alkali halides has been performed in the fundamental absorption region and gives information about transitions from p-like valence-band states to s- and d-like conduction-band states.[1] The investigation of transitions from s-symmetry core states (e.g., K shells) to p-like conduction-band states should give additional information. We have measured fine structure of photoabsorption in LiF, LiCl, LiBr, and LiI near the Li K edge (photon energy ~60 eV). Such measurements have been reported only for LiF by Lukirskii *et al.*[2] For all Li halides some of the most prominent structure has been measured in electron energy-loss experiments by Creuzburg.[3]

We used the continuous spectrum of synchrotron radiation at the 6-GeV Deutsches Elektronen-Synchrotron as a light source.[4] The samples were mounted between the synchrotron and a grazing-incidence, scanning-type spectrometer with a resolution of 0.1 eV at 60-eV photon energy. The samples were evaporated *in situ* from molybdenum boats onto Al films of 1000 to 2000 Å thickness. For measurements at energies below the Al $L_{2,3}$ edge (73 eV), these Al films serve not only as substrates but also as filters to reduce the influence of higher order reflections of the grating.

Figure 1 shows the spectral dependence of the absorption coefficient of the lithium halides. As film thickness was not determined, no absolute values are given. The peaks are labeled with capital letters beginning at the onset of absorption. The positions of the maxima are given in Table I. The values are compared with the optical measurements in LiF by Lukirskii *et al.*[2] The agreement is excellent for the most prominent peak (B), but less ideal for the others. The peaks found in electron