behavior of the $F_{2u}$ ($\Gamma_{25}$) mode as a function of temperature. We believe that the predicted phonon behavior will be more readily observed by studying phonons at the $R$ point, rather than the $\Gamma$ point. [Note added in proof.—Neutron scattering in the vicinity of the $R$ point is currently being studied by G. Shirane and Y. Yamada. Their preliminary results confirm the predictions of our model. We are grateful to these authors for communicating their results prior to publication.] Third, the effects of phonons on the semiconducting and superconducting[15] properties of doped $SrTiO_3$ should be re-examined, especially in view of the presence of additional soft-phonon modes in the tetragonal phase. Finally any crystal properties associated with band structure, such as optical absorption in the uv, should be affected by the halving of the Brillouin zone at 110°K. For example, we expect that the indirect band gap, as calculated by Kahn and Leyendecker[16] in the cubic phase, should become direct below 110°K.

We are grateful to D. C. O'Shea for freely discussing his work on $SrTiO_3$, for providing us with a copy of his thesis, and in particular, for pointing out the temperature dependence of modes $A$ and $D$. We also thank L. E. Cheesman for technical assistance, W. Pleibel for crystal polishing, and T. W. Armstrong, Jr., for electrode evaporation.

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# EPR OF ATOMS AND RADICALS IN RADIATION-DAMAGED SOLID $H_2$ AND HD*

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Paramagnetic resonance of electronic states of atoms and radicals trapped in solid $H_2$ and HD at 4.2°K after $4\times10^6$ R of radiation damage have been investigated at 24 GHz. The apparent spin-lattice relaxation time of resonances of H atoms is damaged solid HD formed from gas containing $3\times10^{-4}$ $O_2$ was found to be 0.14 msec at 4.2°K and approximately 0.27 msec at 1.2°K. Furthermore, these H atoms in solid HD remained stably trapped at 4.2°K for periods in excess of two months.

Paramagnetic resonance of electronic states of atoms and radicals trapped in solid $H_2$, HD, and $D_2$ at liquid-helium temperatures has particular interest because dynamically oriented nuclei in HD and $D_2$ would constitute polarized targets useful for the study of elementary particles. In previous experiments[1,2] with trapped atoms produced by radiation damage of these solids, relaxation times for the paramagnetic transitions were too long to permit effective dynamic orientation. We have investigated the spectrum for EPR at 24 GHz of radiation-damaged solid $H_2$ and HD prepared both from relatively pure gases and from gases containing several parts in $10^4$ impurity of $O_2$, and have observed substantial reduction of the apparent spin-lattice relaxation time of resonances of H atoms trapped in solid HD with an $O_2$ impurity. We have also detected a paramagnetic radical formed by the damage when an $O_2$ impurity was present, which has been tentatively identified as $\dot{O}_2H$ or $\dot{O}_2D$. Formation of other paramagnetic radicals related to other impurities has been briefly explored.

Gaseous samples were prepared from $H_2$ gas with less than $5\times10^{-6}$ impurities, $O_2$ gas with less than $5\times10^{-4}$ impurities, and HD gas which was chemically purified by a liquid-nitrogen trap containing a Linde 13X molecular sieve. The resulting HD gas, though chemically pure, contained 3.5% $H_2$ and 16.5% $D_2$ impurities. Solid $H_2$ and HD were formed by flowing the gaseous material into a microwave cavity which was maintained at 4.2°K by a surrounding bath of liquid helium and which contained 5 Torr of helium gas. The solids resulting were thought to have condensed directly from the gaseous phase without intermediate liquefaction, so that molecules of impurities, such as $O_2$, could be readily trapped in the lattice. These samples were subjected to approximately $7\times10^5$ R/hr radiation for 5-7 h in a thick-target bremsstrahlung beam having a maximum energy of 60 MeV. Helium gas in the cavity was required during irradiation to aid transfer of heat delivered by the beam between the solid $H_2$ or HD and the copper walls of the cavity.

Examples of spectra for EPR at 24 GHz and 4.2°K of the atoms and radicals induced by radiation damage in samples of various constitution are presented in Fig. 1(a)-1(e). Spectrum (a), which was observed for damaged solid $H_2$ and ascribed to trapped hydrogen atoms, consisted of two groups of partially resolved sharp resonances with each group near the field for a resonance of free hydrogen atoms. The individual resonances were sharp because the paramagnetic H atoms converted neighboring $H_2$ molecules to their nonmagnetic para states and thus eliminated broadening from electron-nucleus dipole-dipole interaction. The structure within each group has not been explained and may not be fully reproducible from sample to sample. Moreover, trapping of the H atoms in solid $H_2$ was not stable over extended times, in agreement with the results of Wall, Brown, and Florin,[3] since the amplitude of the spectrum decreased, though not exponentially, to half its initial magnitude in 18 h. Spectrum (b) was observed in damaged solid HD and ascribed to trapped hydrogen and deuterium atoms. It consisted of two resonances near the fields for resonances of free hydrogen atoms with an 11-G full width at half-maximum and of three resonances of similar width near the fields for resonances of free deuterium atoms. While trapping of the H atoms in solid HD at 4.2°K was stable and the amplitudes of their resonances did not significantly decrease over several days, trapping of the D atoms was not and the amplitudes of their resonances decreased to half the initial magnitude in 3 h. Dissimilar stability in trapping D and H atoms during irradiation when the temperature of the solid was slightly elevated could explain the initial ratio of $\frac{1}{10}$ for the amplitudes of their resonances, D to H, rather than the ratio of $\frac{2}{3}$ expected statistically.

When $2\times10^{-4}$ impurity of $O_2$ by volume was added to the $H_2$ gas, and $3\times10^{-4}$ to the HD gas, from

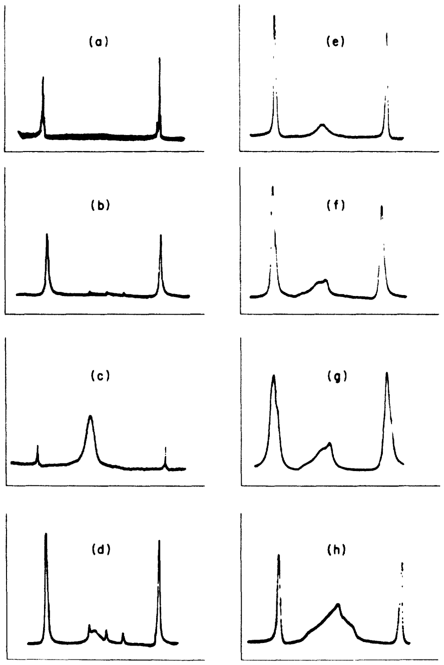

FIG. 1. Spectra for EPR of radiation-damaged solid $H_2$ and HD observed with a reflection spectrometer having crystal video detection. Spectrum (a) was observed for $H_2$ at 4.2°K; (b), HD at 4.2°K; (c), $H_2$ with $2\times10^{-4}$ impurity of $O_2$ at 4.2°K; (d), HD with $3\times10^{-4}$ impurity of $O_2$ at 4.2°K; (e), HD with $3\times10^{-4}$ impurity of $O_2$ at 4.2°K after 12 h storage; (f), HD with $3\times10^{-4}$ impurity of $O_2$ at 1.2°K after storage; (g), large sample of HD with $3\times10^{-4}$ impurity of $O_2$ at 1.2°K after storage; (h), HD without purification at 4.2°K after storage. The duration of the sweep of the magnet was approximately 10 sec, and the extent of the sweep may be judged by the 504-G separation of the clearly visible resonances of H atoms trapped in the solid. The direction of increasing field is from left to right, and the vertical scale is arbitrary.

which the solids were formed, spectra (c) for $H_2$ and (d) for HD were observed after irradiation. In addition to the resonances observed previously, these spectra each display a resonance with a 55-G full width at half-height whose center corresponds to a $g$ factor given by

$$g = 2.0154 \pm 0.0004,$$

which was determined by comparison with the resonances of the trapped H and D atoms and the measurements of Jen et al.[4] This measurement agrees with the $g$ factor for the weighted mean of the broad, structured resonance attributed to $\dot{O}_2H$ radicals trapped in other hosts.[5,6] We therefore attribute the broad resonance for solid $H_2$ with $O_2$ impurity to $\dot{O}_2H$ radicals formed when the unstably trapped H atoms reacted with $O_2$ molecules, and the broad resonance for solid HD with $O_2$ impurity to $\dot{O}_2D$ radicals formed when unstably trapped D atoms reacted with $O_2$ molecules. The $\dot{O}_2H$ and $\dot{O}_2D$ radicals appear to be stably trapped, as are the H atoms in solid HD with $O_2$ impurity. Spectrum (e) was observed for the same sample of damaged HD with $O_2$ impurity 12 h after irradiation had been completed and displayed resonances of the H atoms and $\dot{O}_2D$ radicals undiminished in amplitude, but no trace of the resonances of the D atoms.

Figures 1(f) and 1(g) show spectra for damaged solid HD with $3\times10^{-4}$ impurity of $O_2$ after the temperature had been reduced to 1.2°K. Both samples had been stored long enough at 4.2°K for the resonances of the D atoms to disappear. Spectrum (f) indicated that the resonances of the H atoms had broadened to 20-G full width at half-height and suggested that the broad resonance of the $\dot{O}_2D$ radicals had developed structure. Spectrum (g) was observed with an excessive amount of sample which distorted the resonances of the H atoms, but which clearly displayed structure of the resonance of the $\dot{O}_2D$ radicals. Both the increase in width of the resonances of the H atoms and the appearance of structure in the broad resonance of the $\dot{O}_2D$ radicals developed continuously as the temperature was reduced from 4.2 to 1.2°K, and neither effect has been satisfactorily explained.

The apparent spin-lattice relaxation times $T_1$ for the EPR of H atoms in damaged solid HD at 4.2°K have been measured by saturating a resonance and observing its recovery at a reduced power, and are reported in Table I. These measurements have an absolute accuracy of ±20%; however, the difference between relaxations of the high-field and low-field resonances of H atoms in solid HD with $3\times10^{-4}$ impurity of $O_2$ at 1.2°K is significant. The 95-msec relaxation time at 4.2°K found when no impurity was purposely mixed with the HD gas from which the solid was formed was thought to be established by residual chemical impurities. Investigators using samples of higher purity have found somewhat longer times.[2] When $3\times10^{-4}$ impurity of $O_2$ was mixed with the HD gas, the relaxation time at 4.2°K decreased to 0.14 msec. Samples having this relaxation time independently of the amount of radiation damage could be reproduced consistently if the pressure of the helium gas in the cavity when the sample was formed and the design of the cavity itself were not varied. Any alteration which substantially reduced the efficiency in transfer of heat resulted in a solid with a longer relaxation time and smaller relative amplitude of the $\dot{O}_2D$ resonance. These variations might be explained by less rapid formation of the solid from gaseous HD and concomitantly less efficient capture of the $O_2$ impurity in the resulting solid, because of slower transfer of heat to the liquid helium. Upon reducing the temperature of damaged HD containing $O_2$ impurity from 4.2 to 1.2°K the relaxation time approximately doubled and a difference developed between the times for the high-field and low-field resonances. The relaxation time of the resonance of the $\dot{O}_2D$ radicals could not be measured, since it could not be saturated with the 0.3-G rms microwave field

Table I. Apparent $T_1$ for resonances of H atoms in solid HD.

| Material | $T_1$ at 4.2°K (msec) Low-field resonance | $T_1$ at 4.2°K (msec) High-field resonance | $T_1$ at 1.2°K (msec) Low-field resonance | $T_1$ at 1.2°K (msec) High-field resonance |
|---|---|---|---|---|
| HD | 95 | 95 | ... | ... |
| HD and $3\times10^{-4}$ $O_2$ | 0.14 | 0.14 | 0.25 | 0.29 |

available.

The apparent spin-lattice relaxation time for the EPR of H atoms in damaged HD at 1.2°K and 24 GHz which have been achieved with an added impurity of $O_2$ are sufficiently short to permit substantial dynamic polarization of the nuclei, both protons and deuterons, if the relaxation times of the NMR are as long as several hundred seconds. Relaxation times for the magnetic resonance of protons of 8000 sec at 1.2°K have been found by Hardy and Gaines[7] in extremely pure HD, and preliminary evidence[8] indicates that relaxation times for magnetic resonance of protons and deuterons at 1.2°K and 8.6 kG up to 300 sec are possible in HD with added impurities. If such times persist in HD with $O_2$ impurity, the dynamic polarization induced into protons and deuterons will be limited by the fractional width of the EPR which might be reduced at higher fields.

Production of trapped radicals other than $O_2D$ from impurities other than $O_2$ by reaction with unstably trapped D atoms in damaged solid HD at 4.2°K was demonstrated by spectrum (h). Spectrum (h) was observed at 4.2°K for radiation-damaged solid HD prepared from a commercial gas without chemical purification which was known to contain substantial amounts of $O_2$, $N_2$, $CO_2$, Ar, diethyl ether, and unidentified organic compounds. It displayed resonances of trapped H atoms and a broad, complex distribution of resonances attributed to trapped radicals. Resonances of the unstable D atoms had disappeared before this spectrum was recorded; however, amplitudes of the resonances of H atoms and radicals did not decrease significantly after storage for two months at 4.2°K. Although the radicals present in this spectrum have not been specifically identified, substantial production of several species which were stably trapped in an environment suitable for observing their EPR was distinctly indicated.

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# BAND STRUCTURE AND ULTRAVIOLET OPTICAL PROPERTIES OF SODIUM CHLORIDE*

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The empirical pseudopotential method is used to calculate the electronic band structure and the frequency-dependent dielectric function, $\epsilon_2(\omega)$, of NaCl. The results allow an identification of the interband transitions responsible for the prominent structure in the measured optical spectrum.

In this Letter, we report the first application of the empirical pseudopotential method[1] (EPM) to an alkali-halide crystal. This calculation allows an analysis of the measured optical spectrum[2] of NaCl and an identification of the interband transitions responsible for the prominent optical structure. The analysis of the optical data is made by comparing the calculated and measured frequency-dependent dielectric function, $\epsilon_2(\omega)$, and this comparison shows good agreement between experiment and theory for both the location in energy and the shape of the promi-