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E.E. Haller

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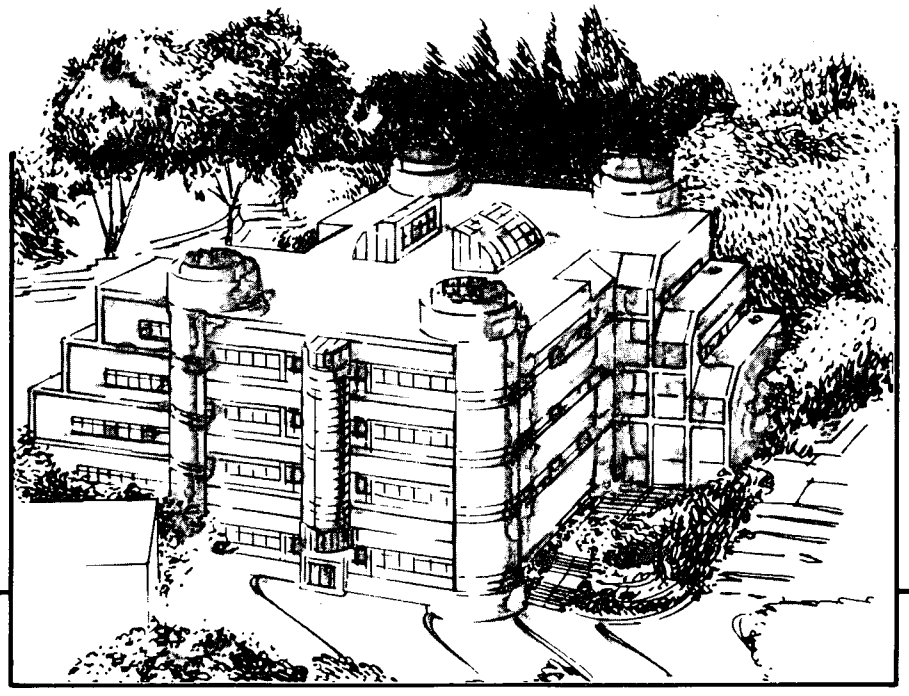

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

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HYDROGEN IN COMPOUND SEMICONDUCTORS

E.E. HALLER

Department of Materials Science and Mineral Engineering
University of California

and

Center for Advanced Materials, MATERIALS SCIENCES DIVISION
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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HYDROGEN IN COMPOUND SEMICONDUCTORS

Eugene E. HALLER

Lawrence Berkeley Laboratory and University of California at Berkeley, Berkeley, CA 94720 USA

Abstract

Progress in the understanding of hydrogen and its interactions in III/V and II/VI compound semiconductors is reviewed. Donor, acceptor and deep level passivation is well established in III/V compounds based on electrical measurements and on spectroscopic studies. The hydrogen donor levels in GaAs and GaP are estimated to lie near E_V+0.5 eV and E_V+0.3 eV, respectively. Arsenic acceptors have been passivated by hydrogen in CdTe and the very first nitrogen-hydrogen local vibrational mode spectra in ZnSe have been reported. This long awaited result may lead to an explanation for the poor activation of nitrogen acceptors in ZnSe grown by techniques which involve high concentrations of hydrogen.

I. Introduction

The rich variety of effects caused by hydrogen in semiconductors was first recognized in ultra-pure germanium during the development of this material for large volume gamma ray and particle detector diodes.[1] In the early 1980s, after the discovery of effective acceptor passivation in silicon by hydrogen,[2] the topic of hydrogen in semiconductors became a major solid state research activity. A large body of experimental findings and theoretical results have accumulated and have produced a rather complete picture of the role of hydrogen in silicon and to a lesser degree in germanium. These findings have been reviewed in detail.[3]

This brief review focuses on the state of the understanding of the complex nature of hydrogen in compound semiconductors. As may be expected, hydrogen is understood best in the most highly developed compound semiconductor GaAs. The compounds GaP and InP have also been investigated in regard to properties of hydrogen and related effects. Only a small number of studies on group II/VI compound semiconductors have been reported in the literature despite the fact that these semiconductors have recently attracted much interest because of their promise for the fabrication of blue light emitting diodes and lasers.

For this review I have chosen recent results which appear unambiguous. This will naturally lead to a preference for articles reporting spectroscopic studies. This preference is perhaps further enhanced by the author's personal experience and interest. Very little will be said about the various techniques used to introduce hydrogen into semiconductors, about hydrogen on surfaces, about high energy proton implantation with the resulting radiation damage, or about theory. These are topics which would each require their own, dedicated review.

The discussion of hydrogen in a semiconductor can be subdivided into three sections: **isolated hydrogen** with its location and charge states; **motion of hydrogen** dominated by diffusion or electric field drift; and interaction of hydrogen with impurities and defects leading to **formation of complexes and dopant passivation.** I will attempt to address these three points in the following sections for III/V and II/VI semiconductors. Work predating ~1990 has already been reviewed[3,4] and I will focus on more recent contributions. I will refer to earlier contributions only where necessary for a general understanding.

II. Hydrogen in Group III/V Compound and Alloy Semiconductors

In close analogy to silicon one finds a large number of acceptor-hydrogen and donor-hydrogen complexes in group III/V semiconductors. Infrared spectroscopy has been the major tool for establishing the structure and the composition of such complexes. Substitution of hydrogen with deuterium leads to a reduction of hydrogen stretch vibrational mode frequencies by a factor close to but a little smaller than $\sqrt{2}$. Early studies of hydrogen passivation concentrated on n-type GaAs. Direct binding of hydrogen to the donor was established through local vibrational mode spectroscopy[3] (Fig. 1a).

Carbon-hydrogen in GaAs is by now perhaps the most thoroughly studied acceptor-hydrogen complex. Carbon acceptor doping has become very attractive because of the low diffusivity of carbon and because of the very high acceptor concentrations which can be achieved during epitaxial growth. Carbon doping by implantation does not lead to the same high acceptor concentrations but carefully controlled co-implantation with Ga leads to excellent carbon activation.[5] A carbon atom occupies an arsenic site and binds a hydrogen oriented along a [111] bonding direction (Fig. 1c). This complex was first identified by Clerjaud et al.[6] and it presents a very rich spectrum of infrared absorption lines. The high frequency stretching mode of H-^{12}C is located at 2635.15 cm^{-1} while that of D-^{12}C is found at 1968.55 cm^{-1}. The ratio of the two frequencies is 1.3386, quite a bit smaller than $\sqrt{2}$. This deviation is one of the experimental findings supporting the structural model of hydrogen bound directly to carbon. In a very recent paper B.R. Davidson et al.[7] have

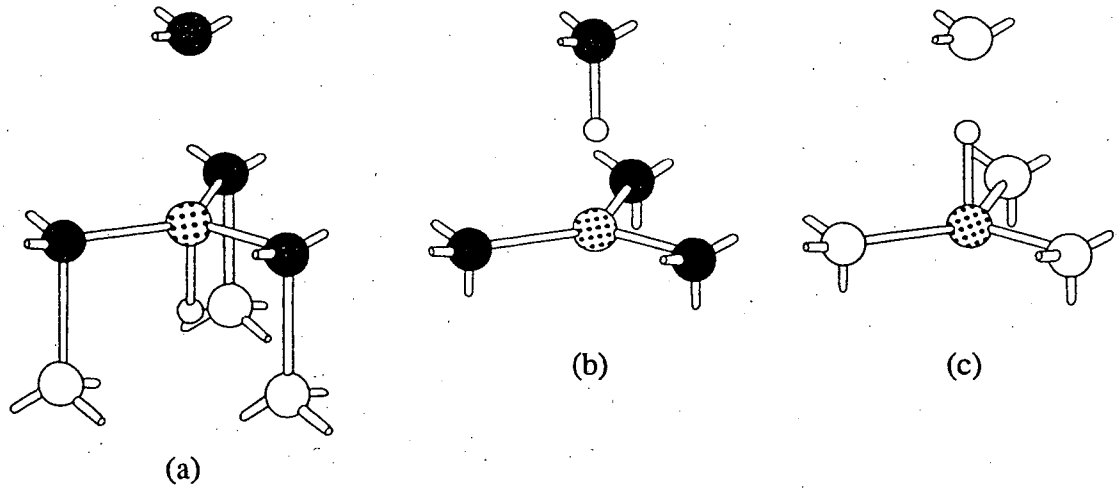

Fig. 1. Schematic representations of dopant-hydrogen complexes in III/V semiconductors; filled spheres: group V host atoms, empty spheres: group III host atoms, dotted sphere: impurity atom; a) group IV donor-hydrogen complex (e.g. GaAs:$Si_{Ga}H$), b) group II acceptor-hydrogen complex (e.g. GaAs:$Be_{Ga}H$), c) group IV acceptor-hydrogen (e.g. GaAs:$C_{As}H$). (from Ref. 3 and 13)

investigated practically all the possible local vibrational modes which exist for all the combinations of hydrogen or deuterium bound to ^{12}C and ^{13}C. With the exception of the H-^{12}C and H-^{13}C wag modes, all other sixteen modes are now experimentally established and rather well supported by the calculations of Jones and Öberg.[8)]

Kozuch et al.[9)] have studied carbon acceptor passivation in heavily doped metal organic molecular beam epitaxy (MOMBE) and metal organic vapor phase epitaxy (MOVPE) grown layers. One of the major questions concerns the source of the hydrogen which passivates the carbon acceptors. Is it the hydrogen from the metal organic compounds or from the carrier gas? In epilayers grown by the MOMBE technique only 3-12% of the carbon acceptors were passivated when He carrier gas and a trimethylgallium source were used. For H_2 carrier gas the fraction of passivated C rose to 25%. In samples cooled in AsH_3 down to 450°C and then in H_2 down to 100°C the passivated carbon acceptor fraction rose to 60%. For the technologist it is important to know that a brief annealing cycle to ~500°C in the absence of hydrogen reactivates all the carbon acceptors. The surprising aspect of these findings is the effective hydrogenation by H_2 gas. The dissociation temperature of H_2 at GaAs surfaces has to be lower or comparable to the temperature at which C-H complexes decay!

Hydrogen passivation of group II acceptors has been studied by a number of investigators. Johnson et al.[10)] and Pajot et al.[11)] have studied Zn acceptor passivation. The spectroscopic data clearly showed that hydrogen is bound directly to one arsenic

neighbor of the group II impurity (Fig. 1b). The Zn acceptor forms bonds with three neighbors and moves away from the T_d site towards a planar structure. The other group II acceptors Cd and Be interact with hydrogen in a very similar way. An interesting exception is Mg which does not seem to form Mg-H complexes. It is not understood why Mg does not become hydrogen passivated but arguments invoking low electronegativity have been forwarded.[12] In a recent paper, Rahbi et al.[13] have combined studies of hydrogen diffusion and acceptor passivation of all the known acceptors in p-type GaAs. They find full consistency with the earlier studies and reconfirm that the structure of group II acceptor-hydrogen complexes is the one presented in Fig. 1b, while all the group IV acceptors (C, Ge, Si) form complexes as shown in Fig. 1c.

Reports on interaction of hydrogen with deep level impurities and defects are numerous for Si and Ge.[3] In GaAs Hofmann et al.[14] have demonstrated passivation of both acceptor levels of the double acceptor Cu. Frova and Capizzi[15] have summarized some deep level passivation by hydrogen in GaAs epilayers.

Formation of acceptor-hydrogen and donor-hydrogen complexes has been studied in III-V semiconductors other than GaAs. Results of experiments with GaP and InP have been reported by various groups. Clerjaud et al.[16] demonstrated convincingly that C-H and N-H formation in GaP only occurs if the Fermi level lies in a specific energy range in the band gap. Neutral hydrogen is responsible for the formation of N-H complexes in n-type crystals while C-H complexes form in p-type crystals. This makes the co-existence of the two types of complexes improbable and resolves the apparent contradiction between the reports by Singh and Weber[17] and Mizuta et al.[18]

A number of hydrogen related, sharp infrared absorption lines have been found in as-grown GaP crystals. Dischler et al.[19] tentatively assigned the lines between 2050 and 2250 cm^{-1} to a multi-hydrogen (4H) center with between one and four H atoms bound to phosphorus. The strongest line in this series located at 2204.3 cm^{-1} has been interpreted by Clerjaud et al.[20] with a single hydrogen model.

The affinity of H for P is especially evident in InP. A number of hydrogen passivated acceptors including Be, Zn and Cd show single H stretch vibration lines with similar frequencies near 2300 cm^{-1}, all close to the frequency observed in PH_3 molecules.[21] Substitution of H with D leads to the expected frequency reduction by roughly $\sqrt{2}$. The very weak dependence of these H stretch frequencies on the acceptor species strongly indicates that H is bound to a P atom neighboring the acceptor. It is most interesting that first overtones of some of these vibrations have now been observed with intensities of ~0.5% of the main lines. The quantitative study of overtone spectra allows the

determination of the anharmonicity parameters of such vibrations.[22] A large number of P-H vibration related lines have been observed in semi-insulating InP:Fe. Most of these lines are rather weak and have been associated with unintentional impurity contaminations. The line at 2202 cm^{-1} has been assigned to the native In vacancy defect with one hydrogen $V_{In}(PH)$,[20] while the strong line at 2316 cm^{-1} has been convincingly associated with the In vacancy decorated with four hydrogen atoms, $V_{In}(PH)_4$. Uniaxial stress studies favor these assignments.[21]

A very brief account on acceptor and partial donor passivation in GaSb has been reported by Polyakov et al.[23] The general behavior is very similar to the better studied III/V semiconductors. The position of the donor level H^+/H^0 is estimated to lie near E_v+0.1 eV, which would explain the efficient acceptor passivation and the relatively weak donor passivation.

Passivation of acceptors and donors by hydrogen may have important consequences for a number of device properties. The major question in this regard concerns the stability of the electrically neutral complexes. Early studies addressing the stability missed a crucial process: retrapping of hydrogen after complex dissociation. This effect leads to apparent stabilities which are too large. The development of a technique for the study of hydrogen drift motion in electric fields has led to much improved complex stability studies. The dissociating complexes are located within the depletion zone of a reverse biased diode in which charged hydrogen species quickly move away from the acceptors. Pearton et al.[24] have studied the stability of a number of acceptor- and donor-complexes in GaAs. They find very similar dissociation energies ranging from 1.2 eV to 1.5 eV and attempt frequencies between 10^{13} and 10^{14} s^{-1}. In contrast, Roos et al.[25] found for Si_{Ga} donor-hydrogen complexes an attempt frequency which was close to six orders of magnitude smaller. In p-type InP where H is bound to P next to an acceptor, Pearton et al.[26] again found energies between 1.2 and 1.4 eV and a prefactor near 10^{13} s^{-1}.

For practical purposes it is important to realize that elimination of hydrogen passivation depends on a number of factors including: complex dissociation, hydrogen charge state, local electric field, Fermi level position, ambient gas and geometric dimensions. No simple way exists to predict accurately the maximum temperature at which passivation occurs. Experiments should be performed for the particular set of conditions. Nevertheless one can state that passivation effects may persist up to 400 or 500°C for typical circumstances.

Despite the importance of the hydrogen donor and acceptor energy levels and hydrogen mobilities, very few experiments have been attempted to determine these

properties. Clerjaud et al.[6] studied the formation of various dopant-hydrogen complexes as a function of the Fermi level position in GaAs. He found the donor level H^+/H^0 near E_V+0.5 eV. Similar studies in GaP by the same group[16] lead to a donor level at approximately E_V+0.3 eV.

Chevallier et al.[28] used n-type $Ga_{x-1}Al_xAs$ alloys to determine the position of the acceptor level H^-/H^0 in GaAs. It appears that the level is just resonant with the bottom of the conduction band minimum at the center of the Brioullin zone. Hydrogen in its negative charge state is not expected to move far distances, presumably because of H_2 formation. This is one of the reasons why donor passivation by negatively charged H is typically more difficult to achieve than acceptor passivation by positively charged protons.

In closing this section on impurity-hydrogen complexes and dopant passivation in III/V compounds, I would like to draw attention to a very unusual finding by Theys et al.[27] After hydrogenation of InAs layers on GaAs substrates they measured an increase in the free carrier concentration by one order of magnitude. This "inverse" effect is attributed to the passivation of structural defects at the interface which compensate a major fraction of the dopants. For progress in the theoretical treatment of hydrogen in GaAs the reader is referred to the work by Pavesi and Gianozzi.[29]

III. Hydrogen in II/VI Semiconductors

As early as 1954 Mollwo[30] studied the effects of exposure of ZnO to high pressure H_2 gas at elevated temperatures on electrical conductivity and luminescence. The green luminescence was reversibly quenched in crystals exposed to 20 atm H_2 at 500°C. A pronounced increase in electrical conductivity was observed under similar hydrogen treatment. Mollwo correctly interpreted his results as in- and out-diffusion of hydrogen. What he called a "reaction" leading to an electron concentration increase may simply have been a passivation of acceptor defects in his materials. Despite this very early interest in the effects of hydrogen, very little work has been reported on modern, higher quality II/VI semiconductor bulk crystals and thin films. Hydrogen-acceptor pairing has been demonstrated in epitaxial CdTe layers which were grown by MOVPE on GaAs substrates.[31] The CdTe layers were doped with As_{Te} acceptors and passivation was unintentionally caused by the H_2 carrier gas during MOVPE. One sharp line at 2022 cm^{-1} is the signature of the As-H stretch mode. Secondary Ion Mass Spectroscopy (SIMS) was used to quantitatively determine the large hydrogen concentrations in the CdTe films. Despite the broad interest in various Zn compounds which are being most intensively studied in the context of blue light emitting and laser fabrication, very little work has been reported on effects caused by hydrogen. The difficulties encountered with deliberate

hydrogenation of II/VI semiconductors have recently been overcome by an encapsulation technique reported by Pong et al.[32] These authors successfully hydrogenated ZnSe capped by SiO_2. The deuterium distribution was measured by SIMS and the presence of D changed the photoluminescence spectrum.

The severe problems encountered in acceptor doping of ZnS and ZnSe layers have drawn special attention to possible detrimental effects of hydrogen which may be unintentionally introduced during epi-growth or processing. The highest free hole concentrations in ZnSe, close to 10^{18} cm^{-3}, have been achieved in MBE grown, N doped layers. MOVPE growth on the other hand leads to significantly lower free hole concentrations despite the fact that SIMS clearly shows similarly high N concentrations in the MOVPE films as in those found in MBE layers. H passivation of the N acceptors is the most obvious conjecture for the difference between such epilayers. Many groups have searched for a clear signature of N-H complexes. We are very pleased to report that two vibrational modes which can clearly be attributed to N-H have been observed with IR transmission and Raman spectroscopy in ZnSe:N layers which were grown on GaAs substrates at 350°C under intense illumination.[33] IR absorption spectroscopy was performed at 9K with a Fourier transform spectrometer operated at resolution of 0.5 cm^{-1}. Fig. 2 shows the local vibrational mode peaks at 3194 cm^{-1} and 783 cm^{-1}. The high frequency peak is assigned to a N-H stretch vibration while the low frequency mode may be due to a wag mode of N-H. We propose one of the structures shown in Fig. 2 for the N-H complex. It would be helpful to obtain samples with D substituting H and ^{15}N substituting ^{14}N. Spectroscopy with such samples, using uniaxial stress, would clarify the detailed structure of the complex. Raman spectroscopy results with the typical polarization geometries are fully consistent with the models proposed in Fig. 2. From our early findings we cannot determine what fraction of the N acceptors is indeed H passivated. Quantitative experiments are required for this purpose.

IV. Summary and Conclusions

In this brief review I have tried to bring together recent results on hydrogen in compound semiconductors. Much effort was required to quantitatively determine effects including acceptor- and donor-hydrogen complex formation, complex stability, isolated hydrogen energy levels and charge states, etc. In general, hydrogen interacts in compound semiconductors in similar ways as in silicon. Hydrogen is an amphoteric deep level impurity which easily binds to shallow and deep level impurities and defects, rendering these neutral. Hydrogen "pushes" energy levels out of the forbidden gap making the crystal more "perfect". Relatively little is known about hydrogen in II/VI compound semiconductors and their alloys. The first local vibrational modes of the N-H complex have

been observed in ZnSe. This may be the first indication that the much reduced acceptor activity in epilayers grown in the presence of hydrogen is indeed due to hydrogen passivation.

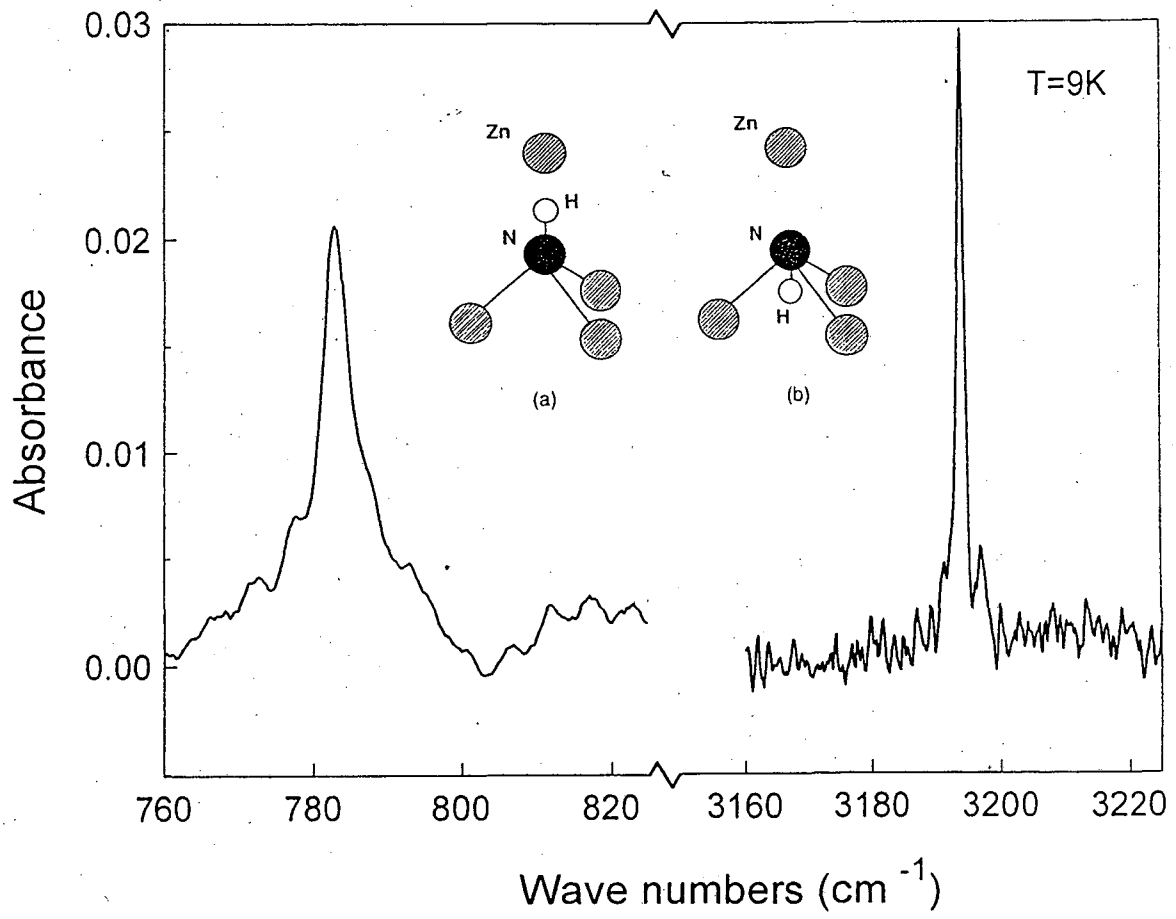

Fig. 2. Infrared absorption lines in N doped ZnSe containing H. The H stretch vibration mode (3194 cm^{-1}) and the H wag mode (783 cm^{-1}) are shown. Two configurations shown as inserts in a) and b) are fully compatible with the IR and Raman spectroscopy data. (from Ref. 33)

With the omnipresence of hydrogen in most semiconductor processing steps starting with crystal growth, it appears prudent to study the properties of this impurity most carefully under a wide variety of circumstances. The low stability of many hydrogen-impurity complexes cannot be taken as a guarantee that all hydrogen related effects are irrelevant to semiconductor technology. Such an assumption is both unwise and potentially dangerous.

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LAWRENCE BERKELEY LABORATORY
CENTER FOR ADVANCED MATERIALS
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720