

## Oxidation of GaAs(110) with NO<sub>2</sub>: Infrared spectroscopy

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(Received 29 March 1990)

The oxidation of the GaAs(110) surface with NO<sub>2</sub> has been studied by Fourier-transform infrared spectroscopy, molecular-beam techniques, and transport measurements. We find that ambient NO<sub>2</sub> dissociatively adsorbs with an average low-coverage probability of 0.03 at room temperature and 0.14 at liquid-nitrogen temperature. In contrast, the molecular-sticking probability is greater than 0.5. We have identified the vibrational modes related to oxygen atoms, nitrogen atoms, NO, N<sub>2</sub>O, and dimerized NO<sub>2</sub> adsorbed on the (110) surface. We find significantly different vibrational frequency distributions for oxygen atoms directly deposited on the surface compared to those derived from NO<sub>2</sub> dissociative adsorption. Based on a variety of measurements we argue that NO<sub>2</sub> dissociation requires steps or defects. Both vibrational spectra and transport properties indicate that a small fraction of the adsorbed oxygen atoms migrates into the bulk of the GaAs crystal, creating an electronic level in the band gap.

### I. INTRODUCTION

We have studied the oxidation of the GaAs(110) surface with NO<sub>2</sub> using Fourier-transform-infrared-reflection-absorption spectroscopy (FTIR-RAS) and molecular-beam techniques. In addition, we have followed the surface oxidation by monitoring the bulk resistance of defect-compensated, high-resistivity GaAs and by measuring the minority-carrier lifetime during exposures with NO<sub>2</sub>. We report these results in this and a subsequent paper<sup>1</sup> (herein referred to as II). A preliminary report of the highlights of this work has been recently submitted for publication.<sup>2</sup> In this paper we concentrate on the spectroscopic aspects of the work. In II we focus on the results of the molecular-beam experiments and transport measurements.

An example of the basic observation which has motivated this study is given in Fig. 1. We show the simultaneous evolution of the specularly reflected He-beam intensity and the sample conductance during and after exposure of the sample to 2.3 L of NO<sub>2</sub> at room temperature [1 langmuir (L)  $\equiv 10^{-6}$  Torr sec]. As discussed in more detail in II, the attenuation of the specular He intensity has been shown to be an extremely sensitive monitor of low surface coverages, capable of high accuracy. In Fig. 1 the decrease in He reflectivity during exposure and the lack of recovery after cessation of the exposure reveal that the surface has undergone an irreversible change. Auger spectra show the presence of an oxygen peak at  $\sim 500$  eV after exposure to NO<sub>2</sub>, which corresponds to  $\sim 9\%$  oxygen coverage.<sup>3</sup> The constant He intensity following exposure indicates that neither the population nor the configuration of oxygen adsorbed on the surface changes significantly. The very slight decrease in He intensity (0.75%) in the first 5 min after cessation of the exposure observed in Fig. 1 would correspond to only a 0.15% increase of the oxygen coverage. As can be inferred from Fig. 1, the conductance also

proves to be a comparably sensitive monitor of the oxidation process, changing by as much as 50% for the adsorption of  $\sim 9\%$  oxygen. However, the conductance response is related to the oxidation process in a more complex manner. Whereas the He attenuation progresses nearly linearly with time, as does the oxygen-atom population, the conductance does not. More significantly, the conductance continues to change substantially after cessation of the NO<sub>2</sub> exposure, and in the opposite direction.

Based on a variety of spectroscopic results described below and molecular-beam and transport measurements described in paper II, we are able to deduce the elementary chemical steps to which these measured changes can be ascribed. We conclude that NO<sub>2</sub> adsorbs molecularly

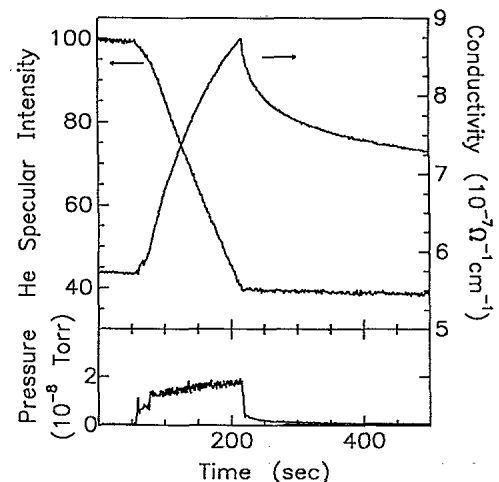


FIG. 1. Evolution of the specular He intensity and the bulk-averaged sample conductance during and after exposure of the GaAs(110) surface to 2.3 L of NO<sub>2</sub> at 300 K.

on the GaAs(110) surface with a high probability. A small fraction of the adsorbed NO<sub>2</sub> subsequently dissociates. This fraction is determined by the number of available defects and the competition between desorption and diffusion.<sup>4</sup> At room temperature both the undissociated NO<sub>2</sub> and the dissociation product NO desorb, leaving behind an oxidized surface. Most of the deposited oxygen atoms remain on the surface, while a fraction penetrates into the bulk of the semiconductor. The introduction of oxygen into the bulk gives rise to a deep electronic level,  $\sim 0.4$  eV below the conduction band. This newly created level acts as a donor, in addition to the existing dominant carrier trap (EL2),<sup>5</sup> and causes the observed relaxation of the conductance as well as a change in carrier lifetime (paper II), which have occurred after cessation of the NO<sub>2</sub> exposure.

This work is part of an ongoing experimental program aimed at the understanding of the electronic response of solids due to chemical processes at their surfaces.<sup>6,7</sup> For practical reasons semiconductors have proven to be the materials of choice in these studies. In particular, with respect to the kind of measurements we report in this study, the number of free carriers in the material can be decreased considerably below the number of surface sites. As a consequence, adsorption or desorption of an electro-positive or electronegative chemical specie can give rise to a profound effect on the bulk-averaged conductance of the semiconducting material.<sup>8</sup> This effect has been known for several decades and has been interpreted in terms of "band bending."<sup>9-11</sup> The motivation of the work described here is in part to understand the detailed mechanisms which cause the conductance of a semi-insulating material to respond to a chemical process at its surface, and in part to calibrate and exploit this response in order to provide a sensitive and unique low-coverage monitor of the surface chemical processes. Part of the calibration is accomplished by identification of the relevant species using infrared spectroscopy, which is the principal topic of this paper.

The oxidation of GaAs has been the subject of numerous studies in recent years. To some extent the extremely inefficient oxidation rate using O<sub>2</sub> ( $10^{-5}$ – $10^{-9}$  dissociation probability<sup>12,13</sup>) has deferred elucidation of the elementary steps which occur during oxidation. Part of the interest is the very limited success in obtaining a passivating surface layer for GaAs, with advantageous properties comparable to oxidized silicon. Much work has been devoted to the understanding of the initial oxidation, the chemisorption sites of oxygen, and the composition of the surface oxide layer.<sup>14-17</sup> Recent research focusing on oxygen impurities in the bulk has been stimulated by the observation that oxygen defects might compensate GaAs, and that its effects are easily confused with the EL2 As-antisite defect.<sup>18-20</sup>

## II. EXPERIMENT

In Fig. 2 we show a schematic of the experimental spectroscopy setup. The ir experiments were conducted in a turbopumped stainless-steel chamber with a base pressure typically  $2 \times 10^{-10}$  Torr. The chamber was

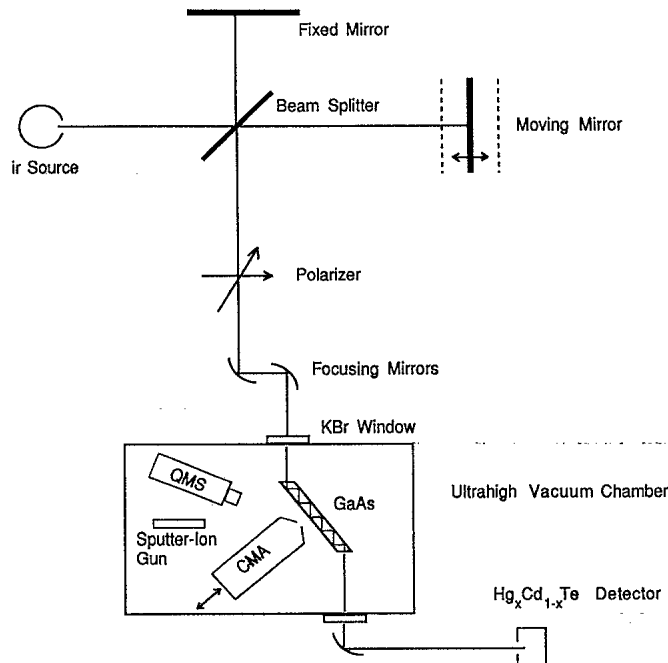


FIG. 2. Schematic sketch of the FTIR-RAS apparatus.

equipped with a cylindrical mirror analyzer (CMA) for Auger-electron spectroscopy (AES), a sputter-ion gun, and a quadrupole mass spectrometer (QMS). The chamber was attached to a Nicolet infrared interferometer. The radiation from the ir interferometer passed through a polarizer and was focused on the sample, entering the chamber through a differentially pumped KBr window. The beam traversed the sample in a multiple internal reflection geometry<sup>21</sup> and exited the chamber through a second KBr window. The beam was re-focused onto a liquid-N<sub>2</sub>-cooled Hg<sub>x</sub>Cd<sub>1-x</sub>Te detector. Hg<sub>x</sub>Cd<sub>1-x</sub>Te detectors of varying compositions (i.e., with varying spectral response and detectivity) were used for different wave-number regions to optimize the signal-to-noise ratio.

Several samples of compensated GaAs(110) [and GaAs(100) for reference to bulk properties] with resistivities exceeding  $10^6$   $\Omega$  cm, were supplied by Nimic Corp., Japan, and Wacker Chemitronic, West Germany. The compensation of GaAs is obtained by growing in an excess of As, which yields a midgap (EL2) donor state which controls the resistivity characteristic.

The samples were polished by grinding under a flow of trimethylbromine until  $\sim 100$   $\mu$ m had been removed from both sides. The final thickness of the 38 mm  $\times$  15 mm samples was  $\sim 0.4$  mm. The ends were beveled at 45°, which allowed ir radiation normally incident onto the entrance bevel to enter the sample and to undergo about 100 internal reflections on the front and back surfaces of the crystal before exiting at the opposite bevel. The samples were cleaned with methanol and mounted onto a sample holder capable of being cooled to  $T_s = 90$  K and heated to  $T_s \geq 900$  K using radiation from a nearby filament which supplemented passing current through the

sample. A freshly mounted crystal was  $\text{Ar}^+$  sputtered (at 1 keV) only once. Subsequently, it was only annealed to 850 K for 20 min prior to each exposure. This procedure resulted in a clean and ordered surface.<sup>22</sup> The surface composition was checked with AES before and after each exposure. Auger sensitivities were calibrated by means of an oxygen-atom source<sup>23</sup> and used to estimate the dissociative sticking probability of  $\text{NO}_2$ .

After cleaning, the sample was cooled to a stable operating temperature ( $T_s = 100$  K for most runs) within  $\sim 20$  min and background spectra recorded. The temperature variation during a 12-min run was less than 0.05 K/min.

Gases used for exposure were 99.996% purity  $\text{O}_2$ , 99.0% purity  $\text{NO}$ , 99.5% purity  $\text{NO}_2$ , 97.0% purity  $^{18}\text{O}_2$ , 99.0% purity  $^{15}\text{NO}$ , 99.0% purity  $^{15}\text{NO}_2$ , and a 47%:50% mixture of  $\text{N}^{18}\text{O}_2$ : $\text{N}^{16}\text{O}_2$  ( $\sim 3\%$  impurities). Exposures were measured using a Bayard-Alpert gauge, which was also used to dissociate oxygen molecules.<sup>24</sup> Exposures were carried out by dosing through a leak valve while continuing to pump the chamber. Both mass spectrometry and surface infrared spectroscopy indicated that some  $\text{NO}_2$  reacted at the walls to produce  $\text{NO}$  and  $\text{H}_2\text{O}$ .

An infrared absorption spectrum was typically acquired by collecting  $4 \times 10^3$  interferograms which required 12 min. After Fourier transformation, signal averaging of successively taken spectra was carried out in cases where the signal-to-noise ratio required improvement. Spectra were taken after each exposure and then ratioed to a background spectrum. The nominal resolution of the spectrometer was  $2 \text{ cm}^{-1}$ .

In this paper we do not focus on the (generally weak)

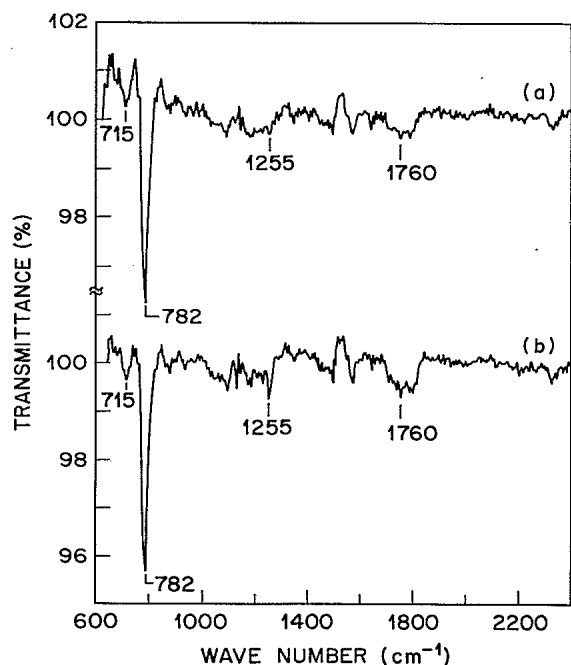


FIG. 3. ir spectra of GaAs(110) exposed to  $\text{NO}_2$  at 100 K. The exposures are (a) 2.4 L and (b) 4.64 L. The vertical axis gives the ratio of the sample transmittance before and after exposure.

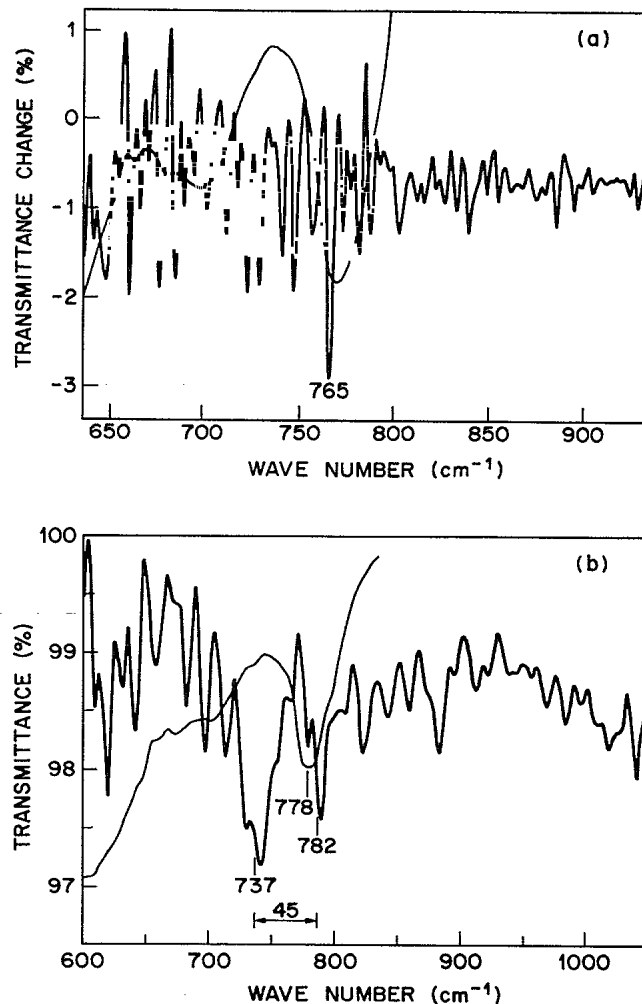


FIG. 4. (a) ir spectrum of GaAs(110) exposed to 2.4 L  $\text{NO}_2$  at 300 K (thick line) corrected for the phonon contribution (see text). The phonon contribution has been eliminated by plotting the difference of two ratioed ir spectra taken with and without exposure with the same temperature drift during the experiment. The thin line shows the uncorrected transmittance of the clean sample at 300 K (arbitrary units). (b) ir spectrum showing the relative transmittance change in the low-wave-number region caused by exposure to 2.4 L of an approximately 1:1 mixture of  $\text{N}^{16}\text{O}_2$  and  $\text{N}^{18}\text{O}_2$  (solid line at 100 K). The thin line shows the uncorrected transmittance of the clean sample (arbitrary units at 100 K).

polarization dependencies we observed. All spectra were taken with  $p$  polarization, except Figs. 3(a), 3(b), and 4(a) [ $s$  polarization with the electric field vector parallel to the troughs of the (110) surface].

### III. RESULTS

#### A. $\text{NO}_2$ exposure (low coverage)

In Fig. 3 we show the change in sample transmittance due to exposure to (a) 2.4 L and (b) 4.6 L  $\text{NO}_2$  at a sample temperature  $T_s = 100$  K. Both spectra were taken using a detector with a high sensitivity for wave numbers

600–1000 cm<sup>-1</sup>. As shown in Fig. 3(a), a sharp absorption appears at 782 cm<sup>-1</sup> after exposure to NO<sub>2</sub> at  $T_s = 100$  K. The same exposure was carried out at 300 K and yielded an absorption shifted to 765 cm<sup>-1</sup> [Fig. 4(a)]. The data at 300 K are much more noisy than at 100 K due to the substantially lower transmittance of GaAs in this wave-number region at higher temperatures. Frequency shifts as a function of temperature, typically 5–10 cm<sup>-1</sup> between 100 and 300 K, have been observed for vibrational modes associated with atoms or molecules on semiconductor surfaces<sup>25</sup> and on metal surfaces.<sup>26</sup> They have been attributed to anharmonic coupling of the observed vibrational modes to lower modes such as the bending modes of the adsorbate itself or phonon modes of the substrate. Most interestingly, the mode at 782 cm<sup>-1</sup>, which we observe to shift by 17 cm<sup>-1</sup> between 100 and 300 K, almost coincides with the third harmonic of the transverse-optical bulk phonon of GaAs (see below).

We used an approximately equal mixture of N<sup>16</sup>O<sub>2</sub> and N<sup>18</sup>O<sub>2</sub> in order to help assign the oxygen-related modes. A resulting spectrum is shown as a thick solid line in Fig. 4(b), where a second mode may be observed at 737 cm<sup>-1</sup>. This frequency shift of 45 cm<sup>-1</sup> is in accord with the association of this mode with adsorbed atomic oxygen. On the basis of the isotope experiment alone, we cannot exclude the presence of OH groups on the GaAs surface as a result of NO<sub>2</sub> reacting on the chamber surfaces. However, this mode does not appear when leaking water into the chamber, which results in a broad absorption below 900 cm<sup>-1</sup>. The apparent difference in intensity between the 737- and 782-cm<sup>-1</sup> modes is explained below. The high level of noise in the spectrum is due to the use of a thin sample in this experiment with a small throughput of ir radiation.

Based on the vibrational frequency of the diatomic molecule GaO (768 cm<sup>-1</sup>),<sup>27</sup> we assign this mode to O atoms bonded to Ga atoms on the (110) terraces.<sup>28</sup> Although we have strong evidence that NO<sub>2</sub> dissociates at steps or defects whereupon O is deposited,<sup>4</sup> the intensity of the mode and the O-coverage levels reached, which are far in excess of defect densities, require that oxygen diffuses back onto terraces under these conditions. The occurrence of atomic oxygen modes indicates that NO<sub>2</sub> has dissociated on GaAs(110) at temperatures as low as 100 K.

We occasionally observe a mode at 990 cm<sup>-1</sup>, which is considerably weaker than that at 782 cm<sup>-1</sup>. We believe this mode corresponds to an As-O stretch.<sup>27</sup> We are not able to correlate the appearance of this mode with any systematic aspect of our experimental procedure. However, we note that both Ga and As form stable oxides, and that extensive oxidation of GaAs produces a mixture of both.<sup>29</sup>

The vibrational frequency of the adsorbed oxygen atom overlaps the frequency range expected for the third harmonic of the transverse-optical phonon in the bulk of GaAs.<sup>30</sup> We could easily see this phonon absorption as a dip at 778 cm<sup>-1</sup> in the unratiod ir transmission spectrum [thin solid line in Fig. 4(b)] at 100 K. This phonon absorption shifted to 769 cm<sup>-1</sup> upon heating to 300 K [thin solid line in Fig. 4(a)]. We observed this same pho-

non absorption with GaAs(100), corroborating our interpretation of a bulk phonon feature. This absorption is not completely absent in the ratioed transmittance spectra due to inevitable small temperature drifts between the time of recording background spectra and of data taking after exposure. In some instances we were able to remove the phonon contribution by subtracting from the data a ratioed ir spectrum (without exposure) taken with the same temperature drift as in the experiment with exposure. This has been done in the case of Fig. 4(a). We note that a decrease in temperature during this period reduces the phonon absorption and gives rise to a maximum in the ratioed transmittance spectra. Thus the measurement of GaO vibrational mode is degraded due to the overlap of the bulk phonon feature. In particular, the apparent difference in width of the oxygen peaks at 737 and 782 cm<sup>-1</sup> in Fig. 4(b) is consistent with the convolution of the phonon spectrum after the slightly descending temperature we recorded during the measurement. After an estimated correction has been made,<sup>31</sup> we estimate the full width at half maxima (FWHM) of both modes to be ~25 cm<sup>-1</sup>. The FWHM of the corresponding mode at 300 K (765 cm<sup>-1</sup>) we are not able to estimate due to the high noise level in this temperature range.

We note that in Fig. 3 the mode at 715 cm<sup>-1</sup> is the reported value for the vibrational frequency of oxygen atoms occupying As vacancies in the GaAs bulk.<sup>32</sup> The occurrence of this mode upon dissociative adsorption of NO<sub>2</sub>, coupled with the observation described below of a new bulk electronic level at ~0.4 eV below the conduction band, indicates that a small fraction of the oxygen atoms has penetrated into the bulk. This diffusion process is what is responsible for the conductance change shown in Fig. 1 after cessation of NO<sub>2</sub> exposure. We were unable to observe the temporal evolution of this 715-cm<sup>-1</sup> feature in the infrared apparatus, to compare with the conductance data, due to the signal-averaging time required to obtain a spectrum.

In Fig. 5 we plot the dissociative sticking probability of

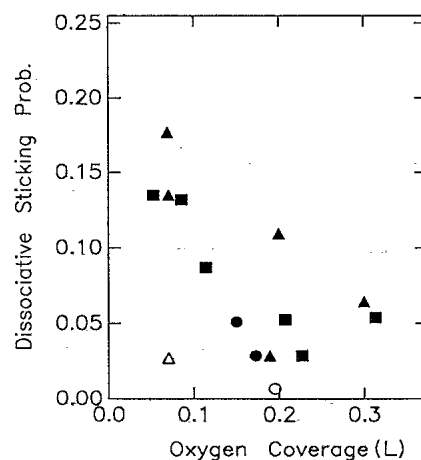


FIG. 5. Plot of the dissociative sticking probability for oxygen vs oxygen coverage for three different samples (O, □, and △) and two different temperatures of the GaAs(110) surface (open symbols, 300 K; solid symbols, 100 K).

$\text{NO}_2$  for several samples. Although we found substantial scatter in the values, typically the average  $\text{NO}_2$  dissociative sticking probability is 0.03 at  $T_s = 300$  K and 0.14 at  $T_s = 100$  K for oxygen coverages up to  $\sim 8\%$ . We also observed a scatter in the apparent saturation oxygen coverage after  $\text{NO}_2$  exposure, ranging from 0.2 to 0.4 monolayers for different samples which correlated with the  $\text{NO}_2$  dissociative adsorption probability. As we discuss below, we think this correlated scatter is a manifestation of the role of defects in the  $\text{NO}_2$  dissociative adsorption. In a subsequent paper we present strong evidence for the role of defects in the dissociative adsorption of  $\text{NO}_2$  on GaAs(110).<sup>4</sup>

### B. $\text{NO}_2$ exposure (higher coverage), NO exposure

The mode at  $782\text{ cm}^{-1}$  [Figs. 3(a) and 3(b)] is nearly saturated at about 4% absorption after exposure to 2.4 L of  $\text{NO}_2$  at  $T_s = 100$  K. In addition, the isotope experiment consistently yielded a value of  $\sim 2\%$  absorption for each mode of the  $737\text{--}782\text{ cm}^{-1}$  doublet (after correcting for the phonon contribution). In contrast, the increased exposure of 4.6 L of  $\text{NO}_2$  at 100 K caused new absorption features to grow at  $1255\text{ cm}^{-1}$  and near  $1760\text{ cm}^{-1}$ , which we relate to physisorbed  $\text{NO}_2$ , as will be discussed below (Fig. 6).

In order to investigate the vibrational modes at  $1255\text{ cm}^{-1}$  and in the range of about  $1760\text{ cm}^{-1}$ , we carried out isotopic experiments using a detector with increased sensitivity in this wave-number region. In Fig. 6 we show

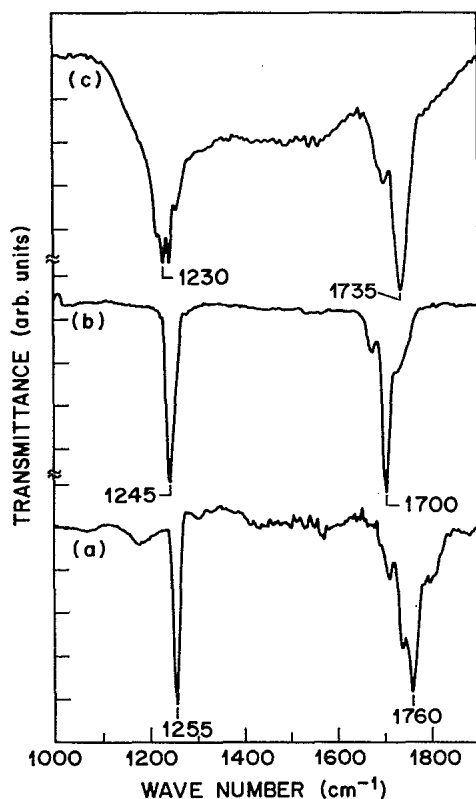


FIG. 6. ir spectra of GaAs(110) exposed to (a) 2.2 L  $\text{NO}_2$ , (b) 1.2 L  $^{15}\text{NO}_2$ , and (c) 1.5 L of  $\text{N}^{16,18}\text{O}_2$  at 100 K.

the spectra obtained upon exposing to various isotopes of  $\text{NO}_2$ . The absorption at  $1760\text{ cm}^{-1}$  showed a fine structure varying gradually with exposure, which rendered it difficult to accurately determine isotopic shifts. However, the general observation is that both absorption bands exhibit approximately appropriate isotopic shifts upon substituting either  $^{15}\text{N}$  or  $^{18}\text{O}$ , which demonstrates that these modes are due to adsorbed nitrogen oxides. For example, the mode at  $1255\text{ cm}^{-1}$  shifts down by  $10\text{ cm}^{-1}$  when using  $^{15}\text{NO}_2$  and  $25\text{ cm}^{-1}$  when  $\text{N}^{18}\text{O}_2$  is used.

When we compare the frequencies of these modes with those associated with  $\text{NO}_2$  in the gas phase,<sup>33</sup>  $\text{NO}_2$  adsorbed on Pt(111) (Ref. 34) or Au(111),<sup>35</sup> or with those associated with bridging or N-bonded nitro complexes,<sup>36</sup> we find no satisfactory agreement. On the other hand, we note that  $\text{NO}_2$  has a substantial dimer-bond strength [ $D(\text{O}_2\text{N--NO}_2) \sim 13\text{ kcal/mol}$ ],<sup>37</sup> and that the symmetric and asymmetric stretch frequencies of gaseous  $\text{N}_2\text{O}_4$ , which are  $1261$  and  $1748\text{ cm}^{-1}$ ,<sup>38</sup> almost perfectly match the experimentally observed values. Hence we assign these modes to the vibrational modes of dimerized  $\text{NO}_2$  on the GaAs(110) surface. The occurrence of multiple peak structures at  $1255$  and  $1760\text{ cm}^{-1}$  may be due to the formation of different dimer configurations of  $\text{N}_2\text{O}_4$ .  $\text{N}_2\text{O}_4$  is known to form a variety of different dimers in the gas phase. We suggest that the dimerization of  $\text{NO}_2$  far below monolayer coverage occurs as a consequence of the confinement of adsorbed  $\text{NO}_2$ . We report elsewhere<sup>4</sup> evidence indicating that the barrier for surface diffusion is very high for this system, suggesting that on GaAs(110) the adsorbed  $\text{NO}_2$  may be thought of as confined predominantly to one dimension. Only occasionally do we observe weak modes at  $1190$  and  $1255\text{ cm}^{-1}$  at very low exposures (0.15 ML) which might be related to nondimerized  $\text{NO}_2$ .

In Fig. 7 we show the resulting spectra upon exposure

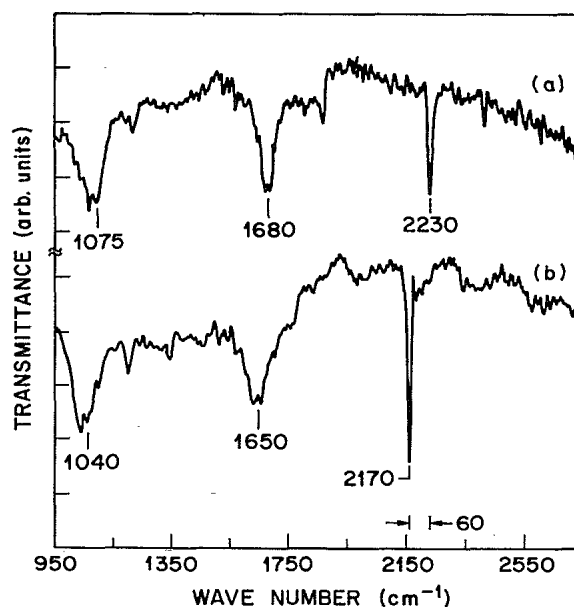


FIG. 7. ir spectra of GaAs(110) exposed to (a) 2.1 L NO and (b) 2.3 L  $^{15}\text{NO}$  at 94 K.

to NO at a surface temperature  $T_s = 94$  K. A more detailed account of the infrared spectroscopy associated with NO on GaAs(110) at low temperatures is published elsewhere.<sup>39</sup> Here we describe those principal features as to distinguish the results of NO adsorption with the possible products of NO<sub>2</sub> adsorption. Two broad absorption bands, at 1075 and 1680 cm<sup>-1</sup>, develop after exposure to ~2.1 L NO. A third sharp absorption appears at 2230 cm<sup>-1</sup>. We note that the mode at 1680 cm<sup>-1</sup> decreases in strength with time, after cessation of the exposure, whereas the 2230-cm<sup>-1</sup> mode becomes stronger.

All of these modes in Fig. 7(a) shifted when a clean sample was exposed to 2.3 L of <sup>15</sup>NO. The isotopic shift of the 1075-cm<sup>-1</sup> mode is consistent with the assumption of atomic N adsorbed on the surface. Based on the vibrational frequency observed for the diatomic molecule AsN (1068 cm<sup>-1</sup>),<sup>40</sup> we interpret this mode as due to atomic nitrogen bonded to As on the surface. The vibration at 1680 cm<sup>-1</sup> we assign to molecularly adsorbed NO on GaAs(110) in accordance with the observed isotopic shift (30 cm<sup>-1</sup>). An absorption at 1680 cm<sup>-1</sup> has also been observed in ir studies of NO on Pt(111) and assigned to molecularly adsorbed NO.<sup>41</sup> Finally, we note that the mode at 2230 cm<sup>-1</sup> has been assigned, in a previous study of NO adsorption on GaAs(110), to the N—N vibration of N<sub>2</sub>O molecules.<sup>42</sup> In that report it was stated that NO adsorbs molecularly at 90 K on GaAs(110) with partial reaction to form N<sub>2</sub>O. This assignment is in accord with the isotopic shift (60 cm<sup>-1</sup>) and the observed increase in strength of the 2230-cm<sup>-1</sup> mode (N<sub>2</sub>O) at the expense of the 1680-cm<sup>-1</sup> mode (NO). We suggest that a fraction of the adsorbed NO dissociates to form As—N bonds (and Ga—O bonds), and that the atomic N subsequently reacts with undissociated NO to form N<sub>2</sub>O. A comparison of the results of the NO and NO<sub>2</sub> experiments shows no absorption features in common. The observations described above provide evidence that upon dissociating, NO<sub>2</sub> does not build up a substantial coverage of physisorbed NO even at 100 K. It is likely that NO<sub>2</sub> displaces the NO dissociation product.

### C. Oxygen exposure

Extensive O<sub>2</sub> exposures (~10<sup>5</sup> L) at 300 K (100 K) without a hot filament resulted in only a weak absorption at 765 cm<sup>-1</sup> (782 cm<sup>-1</sup>), which has been discussed in Sec. III A. This finding is in accord with the results of several studies which have deduced that the sticking probability of molecular oxygen is very low, of the order of 10<sup>-5</sup>–10<sup>-9</sup> at room temperature.<sup>12,13</sup> These low values, and the associated scatter in oxygen-sticking probability, suggest that molecular oxygen does not dissociate on GaAs(110) unless special sites (steps or defects) are present, the density of which is low and varies from sample to sample. Further, at these very low sticking probabilities one cannot eliminate the role of oxygen-containing impurities such as water vapor.

In Fig. 8 we show two curves representing the change of the ir transmittance upon exposure of the sample to <sup>16</sup>O<sub>2</sub> and the isotope <sup>18</sup>O<sub>2</sub> in the presence of a hot fila-

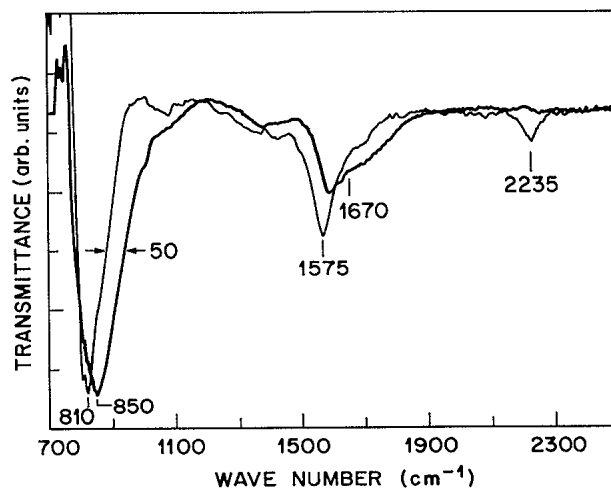


FIG. 8. ir spectra of GaAs(110) exposed to <sup>16</sup>O<sub>2</sub> (1.2 × 10<sup>5</sup> L, solid line) and <sup>18</sup>O<sub>2</sub> (0.6 × 10<sup>5</sup> L, thin line) at room temperature.

ment. These exposures were carried out at  $T_s = 300$  K in order to minimize surface contamination. Dissociation of a small fraction of the exposed O<sub>2</sub> was achieved by the hot filament ( $T > 2000$  K) of the Bayard-Alpert gauge located ~7 cm from the sample.

Two prominent absorption features are observed, one at 850 cm<sup>-1</sup> and the other one in the region 1600 cm<sup>-1</sup>. The detector for this experiment had low sensitivity in the low-wave-number region. Consequently, we could not assign the exact position or extract the FWHM of the first broad absorption, which maximizes near 850 and 810 cm<sup>-1</sup> for <sup>16</sup>O and <sup>18</sup>O, respectively. We used the half-height value of the high-wave-number side of the absorption band to estimate an isotope shift of 50 cm<sup>-1</sup>. The second strong absorption feature, located at ~1600 cm<sup>-1</sup>, is strongly asymmetric in the case of <sup>16</sup>O<sub>2</sub> exposure. We believe this asymmetry is due to the superposition of two features, one located at 1585 cm<sup>-1</sup>, the other at around 1670 cm<sup>-1</sup>. The former is coincident with the scissors mode of water,<sup>28</sup> which we observed in spectra of GaAs(110) exposed to H<sub>2</sub>O. This assignment is corroborated by the presence of the H<sub>2</sub>O stretching vibration at ~3200 cm<sup>-1</sup> (not shown). The absorption at around 1670 cm<sup>-1</sup> is broad. It shifts when using the isotope and overlaps more strongly with the scissors mode of H<sub>2</sub>O, which has shifted to 1575 cm<sup>-1</sup>. It is important to note that the features at 850 cm<sup>-1</sup> (810 cm<sup>-1</sup>) and at 1670 cm<sup>-1</sup> (1575 cm<sup>-1</sup>) are of comparable width, that their wave-number ratio is close to 2.0, and that they exhibit the same relative isotopic shift. This is consistent with the assumption that they are both due to oxygen atoms adsorbed on the surface (the presence of OH groups on the surface cannot be excluded, which would generate a similar isotope shift). We were not able to record spectra devoid of the vibrational modes of water due to the large oxygen exposures required, even with the hot filament operating. QMS after exposure showed an increased background level of OH and H<sub>2</sub>O (or <sup>18</sup>OH, H <sup>16</sup>O <sup>18</sup>O, and H<sub>2</sub> <sup>18</sup>O when using the isotope). The shift of 10 cm<sup>-1</sup>

of the H<sub>2</sub>O scissors mode in Fig. 8 is also consistent with the assumption of adsorbed H<sub>2</sub><sup>18</sup>O on the surface after <sup>18</sup>O<sub>2</sub> exposure. Adsorbed water has a broad absorption band below 900 cm<sup>-1</sup>, which prevented us from investigating the effect of oxygen-atom exposure in this low-wave-number region. It is interesting to note that a broad absorption at 850 cm<sup>-1</sup> occurs after oxygen-atom exposure, while a sharp mode at 782 cm<sup>-1</sup> appears as a result of NO<sub>2</sub> dissociation. Although we cannot definitively assign this mode, we mention two possible explanations. The absorption at 850 cm<sup>-1</sup> may result from substantial broadening and shifting from the mode originating at 782 cm<sup>-1</sup>. The source of this broadening may be bonding inhomogeneity, adsorbate interactions, or lattice disruption. We note that the mechanism for oxygen-atom deposition from NO<sub>2</sub> dissociation is very different than that for atoms incident from the gas phase. The sticking probability associated with the small fraction of atoms originating from the hot filament should be unity and the energy release per atom ~3 eV. This makes a heterogeneous O-atom adsorption site distribution and lattice disruption much more likely than that resulting from the nearly energy-neutral NO<sub>2</sub> dissociation. Because of this exothermicity, it is also imaginable that at least part of the adsorbing oxygen ends up in subsurface sites rather than in sites on the surface. Recently, it was reported that a vibrational mode at 845 cm<sup>-1</sup> is associated with oxygen interstitials in a GaAs bridge bonded between Ga and As atoms.<sup>32</sup>

Based on the appropriate shifts of the two main absorption bands at 850 cm<sup>-1</sup> and that near 1670 cm<sup>-1</sup>, their comparable widths, and the ratio of their vibrational frequencies (~2.0), we conclude that the 1670-cm<sup>-1</sup> absorption is the overtone of the fundamental at 850 cm<sup>-1</sup>. The observation of a strong overtone indicates a strong anharmonicity of the binding potential of oxygen (or OH) adsorbed on the GaAs(110) surface.

Although we are nominally dosing the surface with oxygen, we have assigned the mode at ~2235 cm<sup>-1</sup> to the reaction product N<sub>2</sub>O as we have discussed in Sec. III B. We do not think that this mode is a second oxygen overtone as it is not reproduced in all spectra. We have observed that atomic oxygen displaces adsorbed species (such as H<sub>2</sub>O or remnant NO<sub>2</sub>) from the chamber walls. We postulate that this peak is of the same origin as the one observed after NO exposure. Similarly, we do not assign the features at ~1100 and 1390 cm<sup>-1</sup>, which we find not to be reproducible.

#### D. Transmittance in the high-wave-number region

Oxidation of GaAs results in a considerable change in the broad ir transmission spectrum above ~3200 cm<sup>-1</sup>, as shown in Fig. 9. In Fig. 9(a) we show the decrease in the transmittance after exposure to NO<sub>2</sub> at 100 K. In contrast, exposing the sample to oxygen (with the hot filament) at 300 K (or NO<sub>2</sub> at 300 K) resulted in an increase in transmittance in this region, as shown in Fig. 9(b). Moreover, after a previous exposure to NO<sub>2</sub> at 100 K, annealing the sample above 140 K resulted in a dramatic increase in transmittance above 3200 cm<sup>-1</sup>

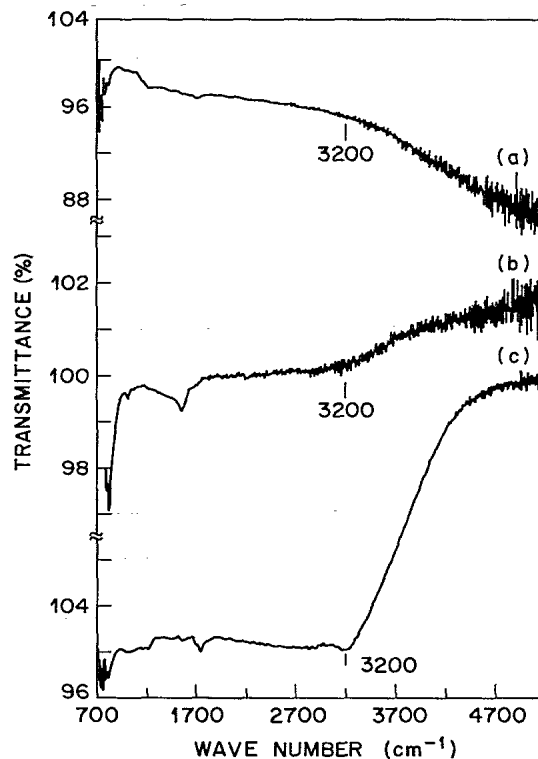


FIG. 9. ir spectra of GaAs(110) exposed to (a) 0.5 L of <sup>15</sup>NO<sub>2</sub> at 100 K, (b) 2 × 10<sup>4</sup> L of <sup>18</sup>O<sub>2</sub> at 300 K, and (c) ir spectrum at 100 K after exposure to 4.5 L of the isotopic mixture N<sup>16,18</sup>O<sub>2</sub> at 100 K and annealed above 140 K.

(~0.4 eV), as shown in Fig. 9(c). Finally, the sample was much more transparent at 300 K than at 100 K in the high-wave-number region (no figure). It is relevant to note that this effect was much less pronounced when we used the intrinsic (not defect-compensated) GaAs(100).

#### IV. DISCUSSION

GaAs(110) is relatively efficiently oxidized by NO<sub>2</sub>. The average low-coverage dissociative adsorption probability is approximately 0.03 at 300 K and increases to 0.14 at 100 K. At 300 K the dissociation product NO quickly leaves the surface (<1 ms) at all coverages, as does any undissociated adsorbed NO<sub>2</sub>. The oxidation efficiency falls markedly as the oxygen coverage approaches 0.15 and apparently saturates between 0.2 and 0.4, in which coverage range we postulate that the NO<sub>2</sub> dissociative adsorption may become endothermic. We do not know if this value is a true saturation or simply a very slow rate-limited process of diffusion away from defects (steps). The increase in the dissociative adsorption probability as the temperature is reduced is characteristic of competitive rate processes with different activation energies, in this case the competition between desorption and diffusion of NO<sub>2</sub> to dissociation sites (defects).<sup>4</sup>

In contrast to NO<sub>2</sub> the oxidation by O<sub>2</sub> is very inefficient (<10<sup>-5</sup>) to the point that it is difficult to distinguish between O<sub>2</sub> dissociation and the presumably

more efficient oxidation by a small oxygen-containing impurity such as H<sub>2</sub>O. The increase in the dissociative adsorption probability for NO<sub>2</sub> at low temperature, the variation from sample to sample, and the correlation of this probability with saturation O coverage all implicate steps and other defects as sites for dissociation. More compelling evidence will be published subsequently.<sup>4</sup>

At moderate exposures to NO<sub>2</sub> at 100 K, we see the evolution of a sharp mode at 782 cm<sup>-1</sup>, which we have assigned to O bonded to Ga atoms. In contrast, oxidation by dissociated O<sub>2</sub> (hot filament) produces a very broad adsorption apparently centered around 850 cm<sup>-1</sup>. We assign this to heterogeneously adsorbed oxygen atoms. In contrast to NO<sub>2</sub> dissociation, the heat of adsorption of atomic oxygen is very large (~3 eV). Thus oxygen-atom surface collisions can result in a very heterogeneous distribution of site occupation as well as significant lattice disruption in the adsorption (bonding) process. We note that the oxygen-atom deposition leads to considerably higher saturation coverages than NO<sub>2</sub> dissociation.

At higher exposures at T<sub>s</sub> = 100 K, NO<sub>2</sub> begins to build up after saturation of adsorbed O. We think the form of NO<sub>2</sub> near the onset of this buildup is the dimer N<sub>2</sub>O<sub>4</sub>.

A weaker mode, which develops at 715 cm<sup>-1</sup> at low NO<sub>2</sub> exposure, has been previously assigned to O atoms on As vacancies in the bulk of GaAs. We interpret the occurrence of this mode as a clear indication that O has penetrated into the bulk of the semiconductor. Using the values for the integrated optical absorption versus defect density,<sup>43</sup> we estimate that ~10<sup>13</sup> oxygen atoms have penetrated into the bulk. This is the source of the continuing evolution of the bulk conductance and carrier lifetime after the surface oxidation is complete. In addition, complex but large reproducible changes occur in the infrared absorption at high wave numbers, starting at about 3200 cm<sup>-1</sup>.

We interpret these results in terms of an impurity electronic level in the band gap of GaAs due to the introduction of a bulk oxygen defect and the associated optical transitions from that level to the conduction-band continuum. This conclusion is based on the following arguments: (i) The transmittance above 3200 cm<sup>-1</sup> simply changes with temperature for a clean surface, indicating that the effect is of bulk origin. (ii) The same effects are observed upon exposure of the sample either to dissociated O<sub>2</sub> or NO<sub>2</sub>, i.e., by oxidation of the surface. (iii) Upon exposure to dissociated O<sub>2</sub> or NO<sub>2</sub>, a mode at 715 cm<sup>-1</sup> occurs,<sup>32</sup> which indicates that oxygen atoms have diffused

into the bulk of GaAs. We have associated this bulk oxygen atom with the new electronic level. (iv) The relaxation of the conductance after cessation of the exposure (Fig. 1) takes place over the course of minutes, i.e., with a time constant inconsistent with a simple electronic process, but consistent with an activated atomic process such as diffusion. (v) There is a low-frequency threshold at ~3200 cm<sup>-1</sup>, but apparently no high-frequency limit, which suggests the existence of an electronic level about 0.4 eV away from either the valence- or conduction-band continuum. (vi) In a recent study on the nature of oxygen impurities in the bulk of GaAs and their relation to the EL2 defects,<sup>43</sup> it was confirmed that oxygen gives rise to a deep donor level 0.43 eV below the conduction band in accordance with our observation (v). In the same study it was reported that the oxygen-related defect exchanges charge with the EL2 defect, unless the latter is bleached,<sup>4,44</sup> by the presence of light below 140 K. Hence our observation of a change in transmittance after annealing through 140 K is in accord with the metastability of the oxygen-EL2 defect interaction<sup>5</sup> (this interpretation is also consistent with the observation that the transmittance changes were found to be much less pronounced using intrinsic GaAs, i.e., with a much lower EL2 density). The compensated material we used was reported to have 1.5 × 10<sup>16</sup> cm<sup>-3</sup> EL2 defects and an initial oxygen-impurity concentration of about 3 × 10<sup>15</sup> cm<sup>-3</sup>.

Although the mechanism of charge exchange between the EL2 defect and the oxygen-related defect level are not yet understood, it seems clear that the observed high-wave-number transmittance changes are due to changes in the density or the occupancy of the oxygen-related defect level. This picture is corroborated in Paper II, by measurements of the minority-carrier lifetime during and after cessation of the exposure to NO<sub>2</sub>. There we show that relaxation of the conductance observed after cessation of NO<sub>2</sub> exposure is of an electronic origin, starting with the onset of NO<sub>2</sub> exposure. Thus the nonlinear increase of the conductance shown in Fig. 1 results from the superposition of two effects: changing of the surface potential due to the oxidation of the surface and the additional electronic response due to the creation of a defect level upon diffusion of oxygen atoms into the bulk.

In summary, we have assigned vibrational modes of adsorbed oxygen and nitrogen oxides on GaAs(110). Of particular relevance to the following paper<sup>1</sup> is the observation of bulk oxygen atoms which have penetrated the surface along with the broadband changes in the transparency of the crystal to infrared radiation.

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<sup>3</sup>We define one monolayer (100% coverage) as one O atom per

surface unit cell. The precision of the O coverage is based on He-scattering attenuation. The absolute accuracy is discussed below.

<sup>4</sup>The very-low-coverage NO<sub>2</sub> dissociation probability is ~1. This quickly falls to an average value ~0.03 after a few percent O coverage. A. vom Felde, C. C. Bahr, and M. J. Cardillo (unpublished).

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- <sup>23</sup>The oxygen-atom source used in the molecular-beam apparatus consisted of a hot tungsten filament placed near the crystal. The filament was operated at 2700 K where O<sub>2</sub> dissociation is nearly complete [P. O. Schissel and J. Trulsson, *J. Chem. Phys.* **43**, 737 (1965)]. The O-atom flux to the sample has been calculated from the partial oxygen pressure in the chamber and the geometrical parameters of the source. We estimate the accuracy to be  $\pm 30\%$ .
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