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Splitting of electron paramagnetic resonance lines of lithium–oxygen centers in isotopically enriched ^{28}Si single crystals

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ABSTRACT

A significant narrowing of the electron paramagnetic resonance (EPR) and additional hyperfine structures of lithium–oxygen (Li–O) centers was observed in isotopically enriched ^{28}Si single crystals. Unexpected splitting was found, reflecting the principal axis of the formally assigned trigonal g-tensors being tilted 3° from the ⟨111⟩ crystal axis, i.e., the g-tensor of the Li–O center actually has a monoclinic symmetry. Furthermore the splitting of the ^{7}Li hyperfine lines into four components was observed at a temperature of 3.5 K.

1. Introduction

The recent availability of isotopically engineered silicon [1,2] has stimulated many optical and magnetic resonance investigations of these materials [3–12]. The interest in the shallow donor centers of silicon has been extended recently to employing them as quantum bits (qubits) for silicon-based quantum computation [13,14]. While phosphorus was the first donor to be proposed for such applications [13], an isolated lithium interstitial shallow donor was also proposed to be an attractive candidate for a qubit in silicon [15,16]. However, it is not experimentally straightforward to introduce lithium atoms exclusively into isolated interstitial sites. Instead Li–O complexes that involve residual oxygen impurities are easily formed. The Li–O complexes in silicon are also shallow donors with the ionization energy 39.41 meV [17,18]. Therefore, it is important to understand the magnetic properties of Li–O centers especially in silicon that are depleted of ^{29}Si nuclear spins, e.g., in isotopically enriched ^{28}Si single crystals, since most silicon-based quantum computer schemes require host silicon substrates that are depleted of ^{29}Si nuclear spins.

An electron paramagnetic resonance (EPR) spectrum of isolated lithium interstitial donors (Li^0), reported previously, exhibited rather complex structures in the absence of externally applied stress but became very simple upon the application of external uniaxial stress [19]. Under the stress the isolated Li donors showed a g-tensor of tetragonal symmetry with $g_{\parallel} = g_{[100]} = 1.9997$ and $g_{\perp} = 1.9987$. Another EPR signal having trigonal symmetry with the g-factors $g_{\parallel} = g_{[111]} = 1.9978$ and $g_{\perp} = 1.9992$ was found and attributed to lithium–oxygen (Li–O) complexes [20]. With an EPR frequency (ν_e) of 9 GHz, the Li–O complex center gave a broad unresolved line whereas an EPR frequency (ν_e) of 22.7 GHz allowed to resolve fine structures for the determination of the symmetry of the Li–O g-tensor and for electron nuclear double resonance (ENDOR) spectroscopy to determine the hyperfine constants of ^{6}Li and ^{7}Li as $A(^{6}\text{Li}) = 0.316$ MHz and $A(^{7}\text{Li}) = 0.845$ MHz, respectively [20]. More recently, the narrowing of the Li–O complex EPR line in isotopically enriched ^{28}Si and the observation of hyperfine structures due to ^{7}Li nuclei were reported [21]. In this paper we report the EPR study of the Li related centers in a ^{28}Si enriched silicon single crystal to demonstrate additional splitting in hyperfine EPR lines that has never been reported before. We show that the symmetry of Li–O g-tensors in silicon is intrinsically monoclinic in contrast to the previously reported trigonal symmetry [21].

2. Experimental

The present experiments were performed with a ^{28}Si single crystal of 99.991% isotopic enrichment and a naturally available

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silicon (^{nat}Si) single crystal with an isotopic composition of 92.2% ^{28}Si, 4.7% ^{29}Si, and 3.1% ^{30}Si. Each crystal was cut into a shape of approximately $3 \times 8 \times 1$ mm^3. After the mechanical polishing with 1900 slurry of both sides of the 3×8 surfaces of each sample, Li deposition to one side was performed in a vacuum followed by diffusion annealing without breaking the same vacuum at 420 °C for 15 min. A ^{28}Si sample prepared in this manner is labeled ^{28}Si:Li. Some of the ^{28}Si and ^{nat}Si were taken out from the deposition and annealing chamber, sealed in vacuumed ampoules, and annealed further at 450 °C for 45 min in a resistive annealing furnace. The samples prepared in this manner are referred to as ^{28}Si:Li–O and ^{nat}Si:Li–O.

The EPR spectra were recorded with *X*-band continuous-wave JEOL (JES-RE3X) and Bruker (E500) EPR spectrometers. The temperature of the sample was controlled by an Oxford Instruments He gas flow cryostat in the range of 3.0–50 K. Illumination by a 100 W halogen lamp was performed during some of the EPR measurements in order to enhance the relaxation of electrons bound to the paramagnetic centers to increase the EPR intensity. The optimal illumination intensity that depended on the sample and temperature was tuned for each experiment.

3. Results and discussion

Very similarly to the EPR of ^{nat}Si:Li which we reported recently [22], EPR signals by isolated lithium interstitial donors (Li^0) and lithium–oxygen complexes (Li–O) are observed clearly in ^{28}Si:Li without the application of external stress and illumination. The EPR intensity increases with decreasing temperature down to 3.1 K in ^{28}Si:Li in accordance with the temperature dependence observed for ^{nat}Si:Li [22]. The intensity of the Li^0 EPR spectrum decreases under illumination. However, the first derivative EPR linewidth of Li^0 detected along different crystalline orientations of ^{28}Si:Li was only ∼0.025 mT which is significantly narrower than the 0.05–0.13 mT which was found for ^{nat}Si:Li. No hyperfine structure of Li^0 in ^{28}Si:Li was observed. The previous ENDOR investigation found that the hyperfine interaction $A(^7\text{Li})$ for Li^0 varied with temperature from 0.07 MHz at 3 K to 0.1 MHz at 4 K corresponding to hyperfine splitting from 0.0025 to 0.0036 mT, respectively [19]. Such hyperfine splitting was not detectable in the present study since it was at least one order of magnitude smaller than the EPR linewidth.

In the temperature range 8–14 K another EPR signal of "trigonal symmetry" attributed to Li–O complexes [20] with a well resolved ^{7}Li hyperfine structure is observed in ^{28}Si:Li. The maximum Li–O EPR intensity in the dark is achieved at around 10–12 K. At lower temperatures, due to the increase of the spin lattice relaxation time with decreasing temperature (up to 10^2 s below 3.1 K [20]), the Li–O EPR intensity decreases in the dark. Here the illumination of above band gap light is found to be effective in decreasing the spin lattice relaxation time enough to enhance the EPR signal [23,24] in combination with the low microwave power (∼12 μW) to avoid the saturation of the EPR transition. The Li–O EPR spectra detected in ^{28}Si:Li–O and ^{nat}Si:Li–O are shown in Fig. 1 to show the striking difference between the two. The spectrum of ^{28}Si:Li–O shows a significant reduction in inhomogeneous broadening to show hyperfine structures similar to the case of the EPR of ^{28}Si:P and ^{28}Si:B [11,12]. The intensities of the Li^0 and Li–O EPR signals in ^{28}Si:Li–O are 1:5 and 4:1 of those in ^{28}Si:Li, respectively.

The hyperfine interaction due to the ^{7}Li isotope (nuclear spin $I = 3/2$, natural abundance 92.41%) is $A(^7\text{Li}) = 0.845$ MHz [20] corresponding to splitting of ∼0.03 mT. This splitting is isotropic within our experimental error leading to the appearance of four equidistant hyperfine lines marked as high-field in Fig. 1. The four lines appear by the usual relation $2I + 1$ of the Li–O centers oriented along one of the four equivalent ⟨111⟩ orientations that is parallel to the direction of *B*. The EPR signal marked as low-field in Fig. 1 consists of twelve overlapping lines due to the slight misorientation of the sample with respect to the *B* direction employed in the EPR measurements, otherwise four hyperfine lines would have been expected.

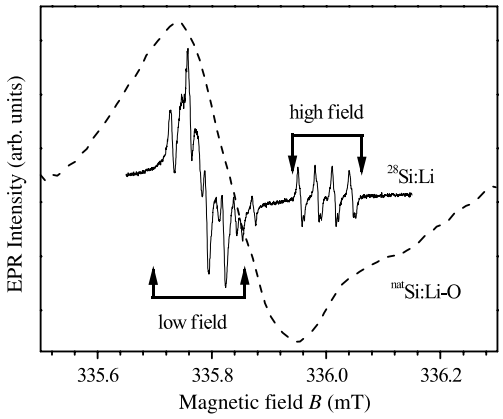

Fig. 1. The Li–O EPR spectra recorded with ^{28}Si:Li and ^{nat}Si:Li–O under illumination at 4.2 K, $B \parallel \langle 111 \rangle$, and $\nu_e = 9.3973$ GHz. The low-field group is composed of twelve overlapping ^{7}Li hyperfine structures oriented along three equivalent directions along ⟨111⟩ that are not parallel to *B*. The high-field group is composed of four ^{7}Li hyperfine structures originating from the centers oriented along one of the four ⟨111⟩ directions that is parallel to *B*.

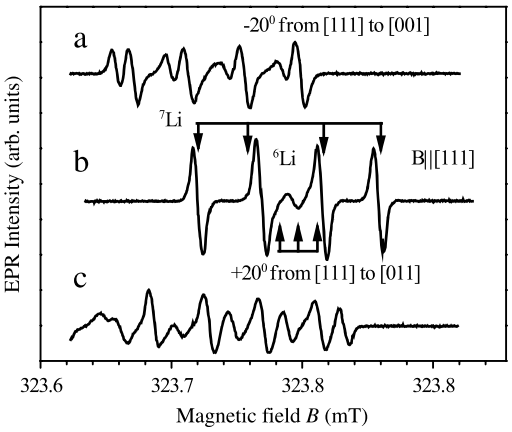

Fig. 2. The high-field group of the EPR spectra detected under illumination of ^{28}Si:Li–O in three different orientations (a) *B* along −20° from [111] towards [001] (b) *B* along [111] (c) *B* along +20° from [111] towards [011]. $T = 4.2$ K and $\nu_e = 9.0512$ GHz. The high-field group of lines is hyperfine due to ^{7}Li (4 lines) and ^{6}Li (3 lines) isotopes.

Fig. 2 shows the unexpected splitting of the high-field group of four lines at different angles of magnetic field directions around the ⟨111⟩ axis. The weak line in the center of the spectrum shown in Fig. 2 originates from the hyperfine structure due to the ^{6}Li isotope (spin $I = 1$, abundance 7.59%). This splitting cannot be explained by misorientation of the sample and/or the interaction of ^{7}Li nuclei quadrupole moments with the gradient of the electric field because such effects do not lead to the appearance of the forbidden EPR transition peak at an energy lower than the lowest energy allowed transition nor at an energy higher than the highest energy allowed transition as we observed in the present study [25]. Therefore, a reasonable explanation of the splitting of the high-field EPR lines under rotation is the symmetry of the centers being lower than trigonal symmetry. The angular dependence of the *g*-factors for the high-field part of EPR spectra is shown in Fig. 3. The solid lines are the calculated angular dependences with a ∼3° deviation of the [111] axial symmetry axis towards [011] in the $(1\bar{1}0)$ plane with $g_1 = g_2 = 1.9994$ and $g_3 = 1.9978$.

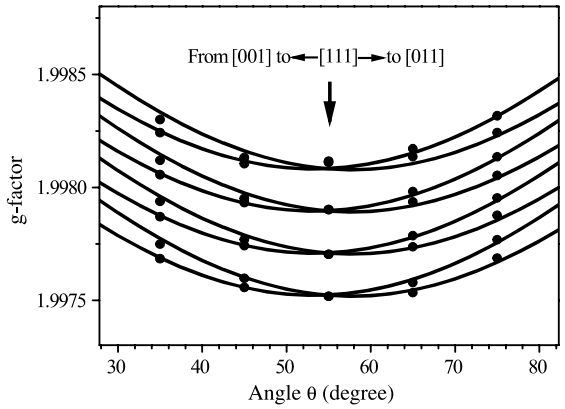

Fig. 3. The angular dependence of the Li–O g-factors recorded with ^{28}Si:Li–O under illumination at 4.2 K. The solid lines are the fitting of the experimental points (•) as described in the text.

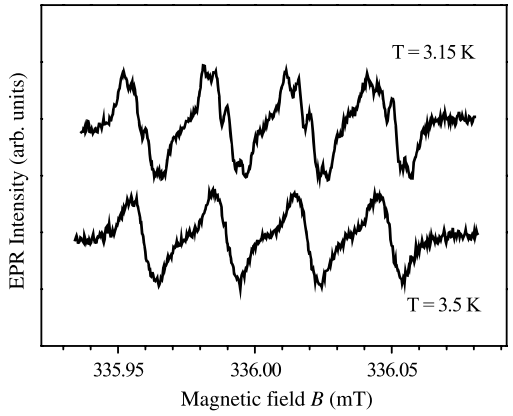

Fig. 4. An additional structure appearing among each ^{7}Li hyperfine line with an equal spacing of 0.004 mT only for temperatures below 3.5 K. Here $B \parallel \langle 111 \rangle$, the microwave field power = 12 μW, and ν_e = 9.39526 GHz. The spectrum taken at 3.15 K shows such fine structures while that taken at 3.5 K does not.

These g-tensor component values are close to those determined in Ref. [20]. This corresponds to the monoclinic symmetry of the g-tensor having the principal axis g_1 along $[1\bar{1}0]$, angle $\theta \approx 58°$ between the g_3 axis and [001] direction, and orthogonality $g_2 \perp g_1$, g_3. Such symmetry describes the experimentally observed splitting of the EPR lines into two components with an intensity ratio of 1:2 when B is exactly in the {110} plane and into three components with equal intensities under a small misorientation of the sample. Within the experimental accuracy these parameters describe very well the positions of all the EPR lines recorded at $B \parallel \langle 100 \rangle$ and $B \parallel \langle 110 \rangle$.

An additional structure in the Li–O EPR signal was found in ^{28}Si:Li at temperatures below 4 K with $B \parallel \langle 111 \rangle$ and illumination (Fig. 4). Each of four high-field ^{7}Li hyperfine EPR lines had four additional components separated by 0.004 mT. The structures became much more complicated for other B directions due to the increasing number of lines reflecting the monoclinic symmetry. Such an additional structure with four lines can arise from the hyperfine interaction with other distant ^{7}Li nuclei. However, an additional structure observed in the ^{7}Li ENDOR spectrum was attributed to the quadrupole interaction [25]. Further investigation is needed to identify the origin of this structure.

4. Conclusion

The isotope enrichment of a silicon host single crystal with a nuclear-spin-free ^{28}Si stable isotope removed the inhomogeneous broadening of EPR lines originating from isolated interstitial lithium (Li^0) donors and lithium–oxygen (Li–O) complex centers. The hyperfine structures normally hidden by inhomogeneous broadening are made visible. The analysis of such hyperfine structures reveals that the g-tensor of the Li–O complexes exhibits monoclinic symmetry. At temperatures below 3.5 K, additional splitting of the ^{7}Li EPR lines of Li–O is observed.

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