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1. Introduction

The behaviour of Li in Si and Ge has been studied extensively, both due to an interest in the fundamental properties of Li in semiconductors and the widespread use of Li-passivated Si(Li) and Ge(Li) radiation detectors. An overview of the basic properties of Li in Si and Ge is contained in ref. [1]. In both materials Li is known as a positively charged fast diffusing donor which easily forms complexes with acceptors such as B^-, Al^-, Ga^- or In^-, but also with electrically neutral impurities, e.g. O. In Si, the lattice site of isolated Li and Li within the complexes (Li^+B^-) and $(LiO)^+$ could be concluded from EPR [2], IR excitation [3] and local vibrational mode spectroscopy [4] to be the tetrahedral interstitial (T) site. While the high Li diffusivity in Ge [$D=2.5\leftrightarrow10^{-3}$ cm^2 s^{-1} exp(-0.512 eV/kT)] [1] and especially its small pressure dependence [5] is a clear indicator of the interstitial character of Li, no direct measurement of the lattice sites of Li in Ge exists. Similarities in the IR excitation spectra of Li in Si and Ge [3, 6, 7] suggest that isolated Li in Ge also occupies T sites. For $(LiO)^+$ in Ge two competing models exist [8], which explain experimental observations, one based on a tunneling behaviour of Li and the other on the occupation of low-symmetry interstitial sites.

A direct method for the lattice site determination of radioactive atoms in single crystals is the emission channeling and blocking technique, see e.g. ref. [9]. We have recently applied this technique to radioactive ^{8}Li ions implanted into high-purity Si, and established that Li occupies tetrahedral interstitital sites after implantations in the temperature regime 50-300 K, and bond-centered sites at slightly higher implantation temperatures (T=400-475 K) [10]. The incorporation on BC sites is due to short-range diffusion of Li in Si and its capture at certain defects which could, for example, be divacancies created during implantation. In this paper we present results of recent measurements on the lattice sites of ^{8}Li in moderately Ga-doped Ge and some new developments in the analysis of two-dimensional channeling spectra from foreign atoms in Si and Ge.

2. Experimental

The isotope ^{8}Li ($t_{1/2}$=838 ms) decays via β^- emission into an excited state of ^{8}Be which immediately breaks up into two α particles with energies distributed around 1.6 MeV. Within a single crystal, these α particles experience channeling or blocking effects along crystal axes and planes, leading to an anisotropic emission yield from the surface which depends in a characteristic way on the lattice sites of ^{8}Li prior to decay. The α emission yield in the vicinity of major crystallographic directions is conveniently measured using a two-dimensional position-sensitive Si detector. Details of our experimental setup at the ISOLDE facility [11] at CERN have been published earlier [9, 10, 12]. The *p*-Ge crystal used in the experiment was Ga-doped (0.03 Ωcm, corresponding to [Ga]=10^{17} cm^{-3}) and of <100> surface orientation.

3. Results and discussion

Figs. 1a and 1b show the normalized α-emission yield χ_{ex} within about $\pm$2.5° around the <100> and <211> axes of the Ge crystal observed after 60 keV implantation of ^{8}Li at T=300 K. As indicated in the figure, the <100> axis, and the {100} and {110} planes show blocking effects while the <211> axis, and {111} and {311} planes exhibit emission channeling effects, which is clearly evidence that the majority of Li atoms occupy tetrahedral interstitial sites [10].

Because of the Lindhard reciprocity theorem [13], the interpretation of α-emission channeling and blocking spectra is analogous to experiments where one would monitor the close encounter probability of an external alpha beam with Li atoms within the crystal. An important consequence of the reciprocity theorem is that direct quantitative information on the fraction of emitter atoms on distinct lattice sites can be obtained by fitting the results of Monte Carlo ion beam channeling simulations to the emission channeling and blocking data [10]. As a new approach to extracting the maximum information from our measurements, we have chosen to fit complete two-dimensional spectra, as is outlined in the following. Flux density distributions of α particles were calculated as a function of polar and azimuthal incidence angle towards <100> and <211> directions using the ion beam simulation program FLUX [14]. As input we used a Debye temperature of 374 K for Ge [15] and depth profiles corresponding to 60 keV implantation of ^{8}Li as obtained from TRIM 91 [16]. The angular range of $\pm$2° was considered in steps of 0.125° (the experimental angular resolution was σ=0.18°). Depending on the symmetry properties of the corresponding axis, 289 respectively 561 different angular

positions were treated, requiring typically either 1 or 2 weeks computing time on an HP 700 workstation. Once the flux density distributions have been calculated, the close encounter probability for every lattice site in the unit cell of the crystal structure is conveniently obtained for a given vibrational amplitude of foreign atoms [14], yielding characteristic two-dimensional patterns χ_{theo}. Theoretical patterns were fitted to experimental spectra χ_{ex} according to

$$\chi_{ex}(\theta,\phi) = S\,[f_1\chi_1(\theta,\phi) + f_2\chi_2(\theta,\phi) + 1-(f_1+f_2)]$$

using non-linear least square fitting routines [17]. f_1 and f_2 are the fractions of ^{8}Li atoms on two sites labeled 1 and 2, respectively, $\chi_1(\theta,\phi)$ and $\chi_2(\theta,\phi)$ are the theoretical count rates corresponding to these sites, S is a scaling factor common to all angles in one pattern, and f_R=1-(f_1+f_2) accounts for a fraction of emitter atoms which produce no anisotropies in the emission yield ("random fraction"). Up to six fitting parameters were simultaneously optimized: the quantities f_1, f_2 and S, and, within reasonable limits, the relative orientation of the experimental and theoretical patterns as a whole, which is accounted for by introducing translational (x_0,y_0) and rotational ϕ_0 degrees of freedom in the fit. Keeping f_2=0 fixed, good and consistent fit results were obtained for 60(10)% of ^{8}Li atoms on tetrahedral lattice sites with vibrational amplitudes $u_1(^8\text{Li})$=0.18(5) Å, and the rest on random sites, as shown in Figs. 1c and 1d. Except for the region directly along the <211> axis, where the theoretical yield is 5-6% lower, the agreement with the experimental data is good and within the limits of the counting statistics. The reason for the discrepancy along <211> is not clear at present. Additionally, we also considered static displacements *d* of ^{8}Li atoms while keeping the vibration amplitude at $u_1(^8\text{Li})$=0.076 Å, which corresponds to a Debye temperature of $T_D(^8\text{Li}) = 1127\ \text{K} = (72.6/8)^{1/2}\ T_D(^{72.6}\text{Ge})$. In this case best fits were obtained for $d(^8\text{Li})$=0.27(8) Å rather independent on the direction of displacement, the quality of fit being comparable to the best fits when varying the thermal vibration amplitude. These results illustrate that the channeling and blocking effect is usually unable to discriminate between dynamic or static displacements which are on the same order of magnitude [18]. Allowing for fractions of ^{8}Li on additional lattice sites (substitutional S, bond center BC, antibonding AB, hexagonal H, Split-<100>, and so-called C and Y sites, see e.g. Ref. [19]) did not improve the quality of fit significantly. However, a fraction of up to 10-15% on BC sites would still be in agreement with the statistical uncertainty of the experiment, while the main error in determining the tetrahedral fraction comes from the uncertainty in the rms displacement of Li.

Figs. 2a and 2b show the experimental α-emission patterns observed after ^{8}Li implantation into Ge at T=392 K which are distinctively different compared to room temperature implantation. Apart from an overall decrease in the intensity of the angular anisotropies, the most pronounced differences are in the {111} and {100} planes, where the effects have changed from channeling to blocking and blocking to channeling, respectively, and in the <100> axis, which now shows channeling instead of blocking, indicating different lattice sites of ^{8}Li at the two temperatures. Using the fitting procedure described above, best results were obtained for placing 30-45% of ^{8}Li atoms on or close to bond center sites, and the rest on random sites. The chi square of the fit became substantially worse if sites further away than 0.4 Å from BC sites were considered, but showed a rather broad minimum within these limits. This behaviour is due to the fact that gradients of the α flux density are small close to the BC site, causing less accuracy of the lattice location than, e.g. in the case of S or T sites. Consequently, it made not much sense to vary the vibration amplitude of bond-

centered Li and a fixed value of 0.083 Å, corresponding to $T_D(^8Li)$=1127 K, was used in the analysis. Introducing fractions of ^{8}Li on additional lattice sites did not give significant improvements in fit quality.

At a first glance it may appear surprising that we identify Li on BC sites in Ge and Si [10] despite the fact that in our measurements the normalized yield along {111} planes was below unity. Since BC sites are located in the middle of the interstitial region between {111} planes, geometric arguments suggest that emitter atoms occupying these sites cause strong emission channeling effects. However, this does not take dechanneling into account, which is especially pronounced for particles moving within the tight pairs of {111} planes in Si and Ge. The atomic {111} planes of the diamond structure are arranged in pairs with an interplanar spacing of 3/12 d_0 within a pair, but 3/4 d_0 towards the nearest plane within the next pair, d_0 being the lattice constant. With respect to a specific {111} planar direction (e.g. one which leads to the crystal surface) three out of four BC sites lie between tight neighbouring {111} planes, but only one BC site in the wide open interstitial region, where, e.g., all T sites are located. To illustrate the dechanneling for the case of Si, we have calculated the emission yield from foreign atoms on bond-center sites at T=425 K for several homogeneous depth profiles, assuming an angular resolution of σ=0.125°, a foreign atom vibration amplitude of u_1=0.10 Å and an α-particle energy distribution corresponding to the decay of ^{8}Li [12]. An azimuthal scan around the <110> direction (fig. 3) reveals that most low-index planes keep their channeling or blocking characteristics with respect to BC sites, with the exception of the {111} plane, where the flux peaking from BC sites has almost disappeared already after 1000 Å. Thus, under these conditions foreign atoms that occupy BC sites and have a shallow depth profile ($<\sim$2000 Å) will cause a maximum of the emission yield along {111} planes, whereas for deeper lying profiles strong dechanneling and a normalized yield below unity is observed. The effect was also found in Ge and in simulations where the angle was chosen much further away from the <110> direction, e.g. 5°, and for other projectile species and energies, e.g. ^{3}He at 670 keV, which are often used particles for the detection of deuterium through the d(^{3}He, ^{4}He)p reaction. The strong {111} dechanneling may also be partly responsible for some inconsistencies between several ion beam channeling studies on the lattice location of hydrogen in Si, as reviewed in Ref. [20]. It is now generally accepted that isolated H and H in (H-B) pairs occupy bond-center sites in Si. However, rather large differences in d(^{3}He, ^{4}He)p yields along {111} planes were observed in some experiments, apart from beam-induced damage probably due to different deuterium depth profiles, measuring temperatures and angular resolution. Low temperatures and good angular resolution, however, are essential. For example, in Si at 50 K and using an angular resolution of σ=0.05°, the flux density of 670 keV ^{3}He at BC sites should still be 1.18 if averaged over the depth range 0-5000 Å, but will nevertheless drop to 0.98 if the depth range 0-10000 Å is considered.

In our analysis we used Gaussian depth profiles extracted from TRIM 91 simulations for 60 keV implantation of ^{8}Li into Si and Ge. Taking into account that due to the on-line geometry of our measurements the implantation of ^{8}Li and the detection of emitted α particles are done under different angles towards the surface normal, the calculated effective ^{8}Li depth profiles are 2460 Å (FWHM 2400 Å) for <100>, 3350 Å (FWHM 2820 Å) for <211>, and 4250 Å (FWHM 4140 Å) for <111> spectra. For radioactive nuclei with narrow line widths, the measured α-energy spectrum gives directly the energy loss of the emitted particles within the source material and hence reflects the depth distribution of emitter atoms. In the case of the isotope

$^{8}Li/^{8}Be^{*}$ the large natural line-width of the α decay (Γ=1.50 MeV) does not permit such a detailed derivation of the depth distribution. However, the relative position of the maxima of different spectra can be easily obtained with a precision of a few keV through fitting procedures, and the comparison of energy spectra recorded for different implantation and emission geometries then allows to make reasonable estimates on the mean emitter depth. The maxima of the Ge <211> and <111> spectra were shifted by -40(5) keV and -80(5) keV with respect to the <100> spectrum which compares to calculated values of -30 keV and -61 keV, respectively, using an energy loss of 34eV/Å for 1.6 MeV α particles in Ge [16] and differences in the mean path length of emitted particles as given above. Therefore, the observed relative shifts in α energy would be well understandable if the mean implantation depth of Li would be som 30% larger than predicted by TRIM. For the case of Si, it is known from experiment that the maxima in the implantation profiles of Li are rather well described by TRIM, while due to channeling tails the Li concentration deeper in the sample is usually higher than predicted [21-23]. Though we tried to avoid to do implantations under channeling conditions, such effects can never be excluded completely. Note that an about 1000 Å deeper profile of Li would merely increase the derived fractions of bond-centered Li by a few per cent but not at all influence the quantitative identification of these lattice sites in our case.

We also checked for temperature-dependent shifts in α energy. Such shifts may indicate long-range diffusion of ^{8}Li and diffusion widths of a few thousand Å are clearly visible [24]. Since in the Ge experiment less than 5 keV shift occured in all spectra, we conclude that the mean depth was not shifted by more than a few hundred Å up to the maximum measuring temperature of 440 K. Hence a major redistribution of ^{8}Li due to long-range diffusion did not occur.

4. Conclusions

The present measurements are the first direct lattice location study of Li in Ge. Unambiguous identification of the preferred lattice sites, even in the case of low-symmetry sites such as BC sites, was achieved by fitting the results of Monte Carlo simulations to the recorded two-dimensional α-emission spectra. Simulation parameters, however, especially the Li depth profile, have to be carefully chosen in order to model the experiment. For room temperature implantation, we have found the tetrahedral site to be the favoured Li site in moderately Ga-doped Ge, while for higher temperatures (330 K to at least 440 K) BC sites were increasingly occupied. This behaviour is similar to our findings in low-doped Si [10, 25] where the BC sites were favoured at slightly higher temperatures (400-475K). The physical processes leading to the occupation of these lattice sites in Ge, however, remain open at present. Projected mean diffusion widths $(2D\tau)^{1/2}$ of ^{8}Li during its lifetime of τ=1.21 s would be 390 Å at 300 K, 3820 Å at 390 K, and 9080 Å at 440 K, using the diffusion coefficient given above. The absence of such long-range diffusion up to 440 K suggests that at least the bond-centered Li is rather strongly bound to defects. Clearly the Ga doping of the Ge sample (10^{17} cm^{-3}) was high enough so that (LiGa) pairs could have formed already at room temperature. However, the diffusivity of Li in Ge is so high that we believe that the concentration of defects is of minor relevance compared to their binding

energy for Li. Since the occupancy of BC sites was recently also detected in high-purity Ge [25], these sites seem to be related to implantation induced defects.

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Figure Captions

Fig. 1: Normalized α-emission yield from ^{8}Li in *p*-Ge:Ga at 300 K around <100> and <211> axes; c) and d) are theoretical patterns for the indicated site fractions after fitting to the experimental results shown in a) and b) as described in the text.

Fig. 2: Normalized α-emission yield from ^{8}Li in *p*-Ge:Ga at 390 K. Note that apart from the angular range, which is slightly different, the same axes as in fig. 1 are shown.

Fig. 3: Normalized emission yields from bond center sites in Si for different homogeneous depth profiles of ^{8}Li atoms. Shown are azimuthal scans which intersect all major low-index planes.

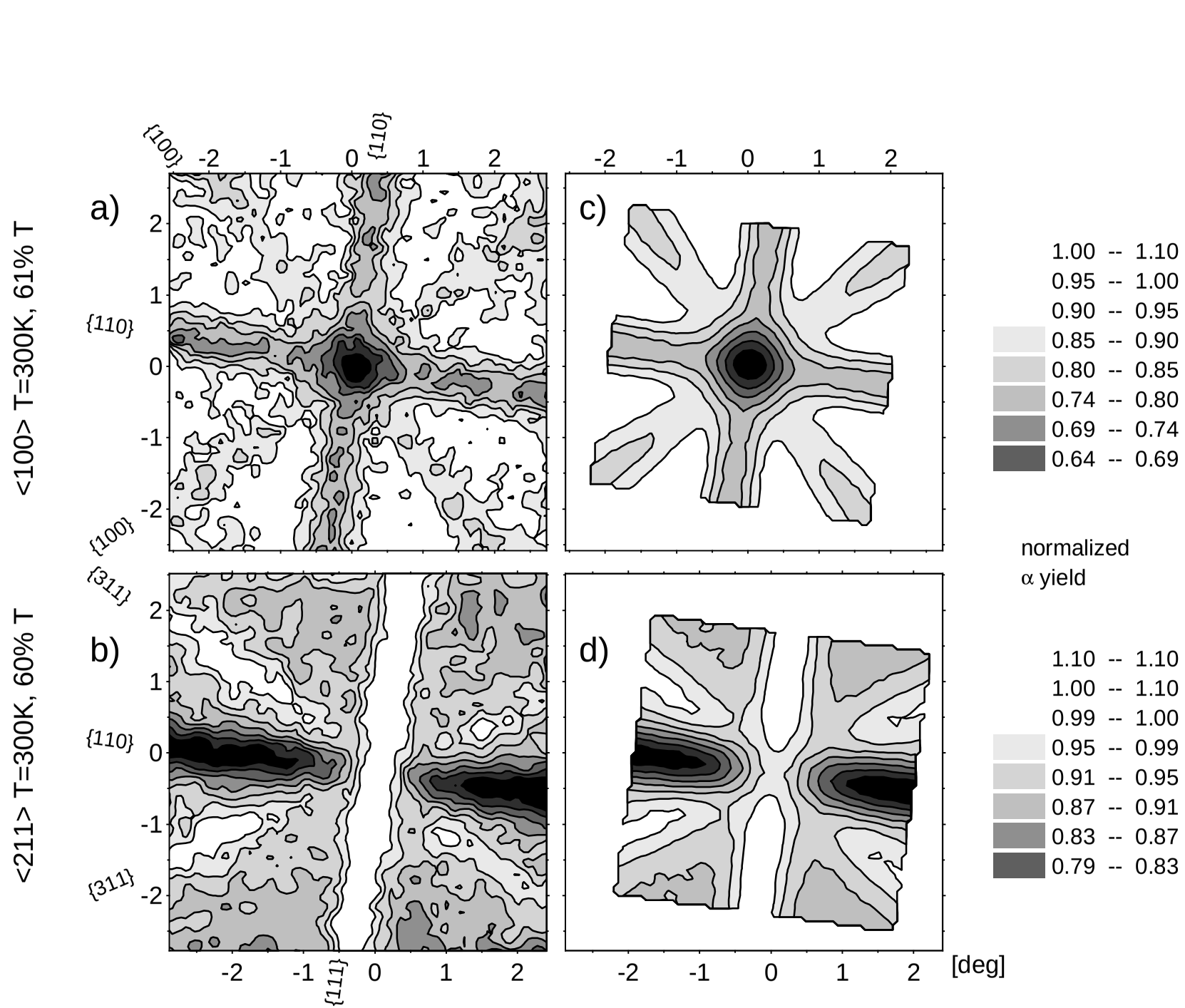
a)
b)
c)
d)
{100}
{110}
{311}
{111}
-2
-1
0
1
2
[deg]
<100> T=300K, 61% T
<211> T=300K, 60% T
normalized
α yield
1.00 -- 1.10
0.95 -- 1.00
0.90 -- 0.95
0.85 -- 0.90
0.80 -- 0.85
0.74 -- 0.80
0.69 -- 0.74
0.64 -- 0.69
1.10 -- 1.10
1.00 -- 1.10
0.99 -- 1.00
0.95 -- 0.99
0.91 -- 0.95
0.87 -- 0.91
0.83 -- 0.87
0.79 -- 0.83

Fig. 1

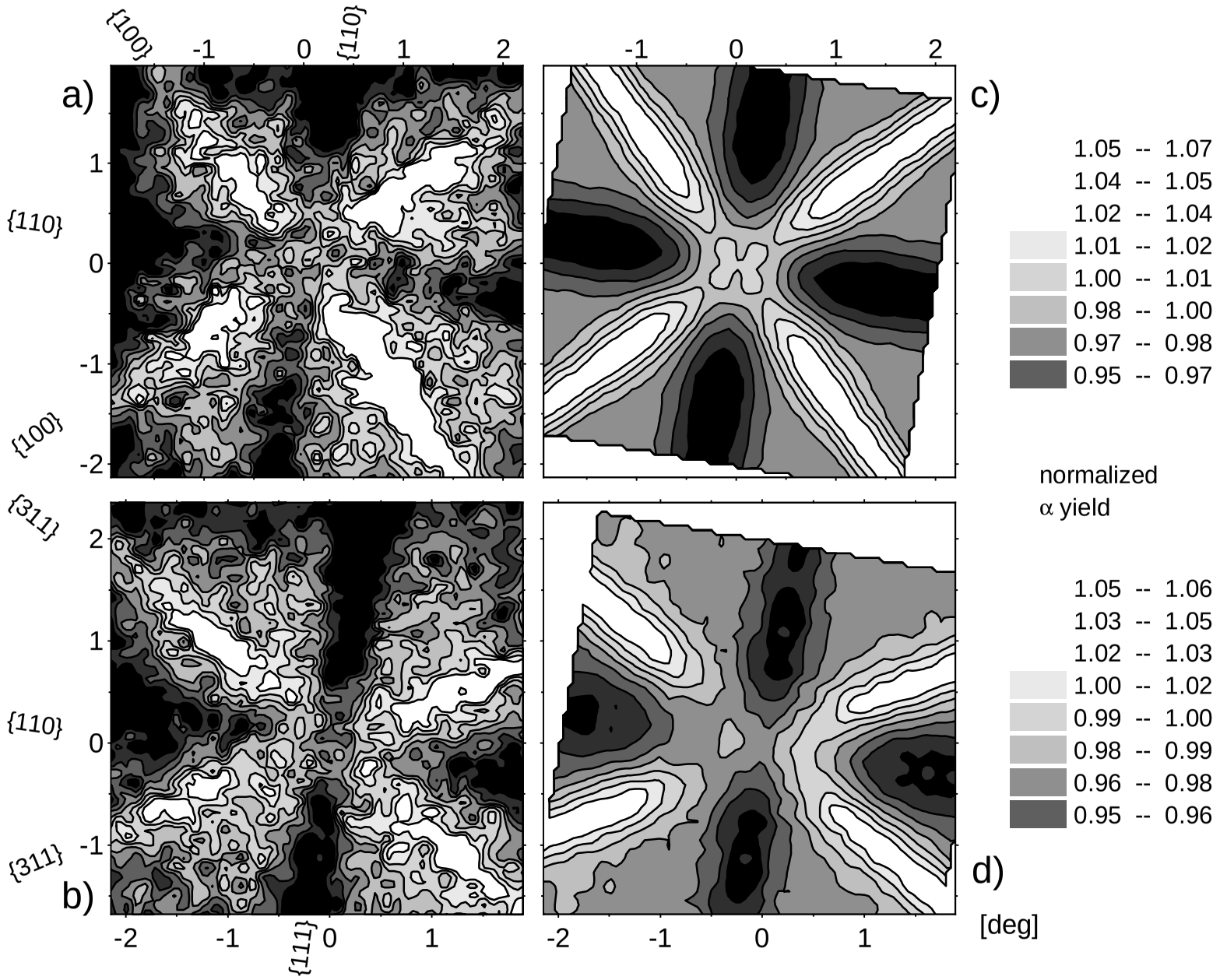
a)
b)
c)
d)
{100}
{110}
{111}
{311}
-1
0
1
2
-2
1.05 -- 1.07
1.04 -- 1.05
1.02 -- 1.04
1.01 -- 1.02
1.00 -- 1.01
0.98 -- 1.00
0.97 -- 0.98
0.95 -- 0.97
normalized
α yield
1.05 -- 1.06
1.03 -- 1.05
1.02 -- 1.03
1.00 -- 1.02
0.99 -- 1.00
0.98 -- 0.99
0.96 -- 0.98
0.95 -- 0.96
[deg]

Fig. 2

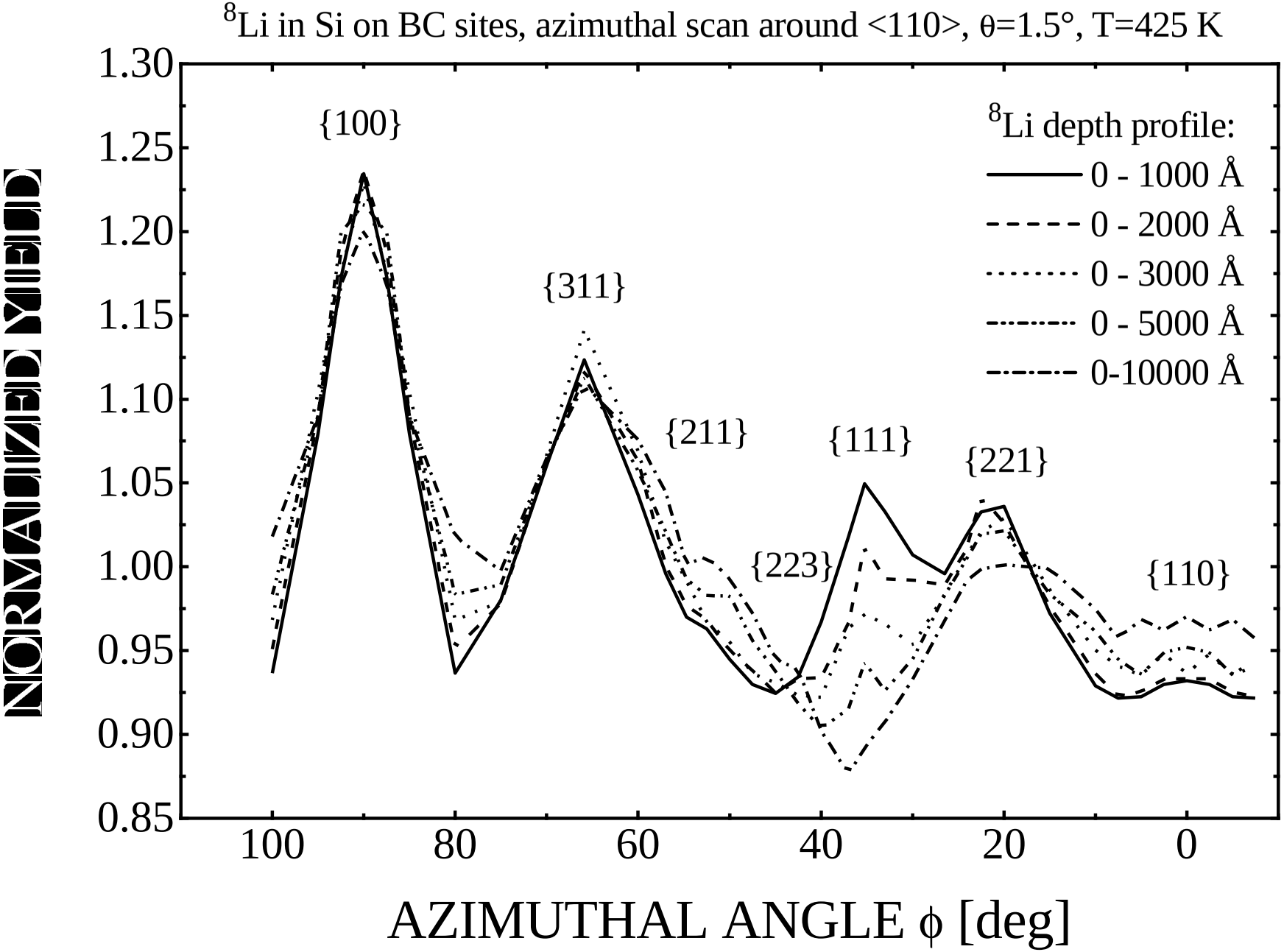
^{8}Li in Si on BC sites, azimuthal scan around <110>, θ=1.5°, T=425 K
NORMALIZED YIELD
1.30
1.25
1.20
1.15
1.10
1.05
1.00
0.95
0.90
0.85
{100}
{311}
{211}
{223}
{111}
{221}
{110}
^{8}Li depth profile:
0 - 1000 Å
0 - 2000 Å
0 - 3000 Å
0 - 5000 Å
0-10000 Å
100
80
60
40
20
0
AZIMUTHAL ANGLE ϕ [deg]

Fig. 3