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High-temperature X-ray standing wave study: Application to melting of monolayers of Pb on Ge(111) surfaces

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Abstract

The effect of a substrate temperature of about twice the Debye temperature on the x-ray standing wave fields has been explored. An atomic scattering amplitude modified by the Debye-Waller factor appears to be adequate for the description of the standing wave fields. The high-temperature standing wave method has been applied to study the temperature dependence of Pb monolayers on Ge(111) surfaces. We obtain evidence that the high-temperature (1x1) phase of the reversible phase transition $\sqrt{3}\times\sqrt{3}R30^{\circ}\rightarrow 1\times 1$ is not consistent with a model of a two-dimensional isotropic liquid Pb layer. Rather it appears to be composed of small islands of the original $\sqrt{3}\times\sqrt{3}$ R30° crystalline overlayer.

X-ray standing waves (XSW) are generated inside a perfect crystal under the condition of Bragg diffraction [1]. The spatial periodicity and the phase tunability of such standing wave fields have been exploited to determine the location of atoms both inside the crystal [2,3] and on crystal surfaces [4-11]. An XSW experiment is performed by Bragg reflecting a plane wave x-ray beam from the sample and rocking the sample or the monochromator crystal over the reflection region. The width of the reflection range depends on wavelength, crystal structure factor and reflection order. The actual width one has to operate with in a particular experiment is determined by the scientific problem and by instrumental considerations, and is typically only tens of microradians. In such a situation even a slight mechanical disturbance or a small variation in room temperature can change the crystal alignment. These problems have been overcome by using analog feed-back systems for angle control [12]. Obviously a high-temperature experiment becomes more difficult because of the stringent requirement of temperature stability. The second problem at high temperature is more fundamental - the effect of thermal vibration on the standing wave field. The present high temperature experiment was performed at a temperature of nearly twice the Debye temperature of the substrate (Θ_D = 291 K for Ge). An analysis incorporating the thermal effect through a Debye-Waller factor on the atomic scattering amplitude: $f = f_o e^{-M}$, where f_o is the free--atom form factor and e^{-M} is the Debye-Waller factor, appears to be adequate.

We have applied the high temperature XSW method to study a subject of current interest, namely, two-dimensional melting. Melting of lead overlayers on germanium (111) surfaces has been reported in the literature [13]. For a Pb coverage of 4/3 monolayers (ML), the Ge(111)-Pb system shows a reversible transition in low energy electron diffraction

(LEED) patterns: $\sqrt{3}x\sqrt{3}R30^{o} \rightleftarrows 1x1$, at about 470 K. We have studied the nature of the high temperature (HT) 1x1 phase. Our observations are consistent with some features of dislocation-mediated melting (DMM) theory [14,15]. From the reflection high energy electron diffraction (RHEED) experiments Ichikawa [13] attributed the high temperature 1x1 phase to the presence of a 2-D isotropic liquid Pb layer, which is not under the strong influence of the Ge(111) substrate. Our XSW results for the high temperature 1x1 phase show a high degree of order in contrast to a complete disordering expected for an isotropic liquid Pb layer.

We first illustrate how the presence of a 2-D isotropic liquid overlayer on a crystal surface can be detected with XSW. By using the phase tunability and the periodicity of the x-ray standing wave fields, generated by an (hkl) Bragg diffraction from a perfect crystal substrate, the (hkl) Fourier component (F.C.) of the adsorbate atom density distribution is measured. The phase (Φ) and the amplitude (f) of the F.C. are closely related to the distance(s) of the adatoms from the substrate surface in the [hkl] direction, and the fraction of the adatoms at that distance(s), respectively. If a 2-D isotropic liquid layer is present on the $(h_1k_1l_1)$ surface of the substrate, planar diffusion of the overlayer atoms will not change their distance in the $[h_1k_1l_1]$ direction. However, in another direction $[h_2k_2l_2]$, inclined with $[h_1k_1l_1]$, the distance distribution will be random giving rise to an F.C. with zero amplitude (f = 0). These situations are illustrated in Fig. 1.

The XSW experiments were performed at the wiggler beamline (W1) in the Hamburg Synchrotron Radiation Laboratory (HASYLAB). The (111) surfaces of germanium samples were sputter cleaned by argon ion

bombardment, annealed at 1000 K and characterized with LEED and photoemission. 4/3 ML of Pb were evaporated in an MBE system onto a clean Ge(111)2x8 surface. The coverage was determined with a quartz crystal microbalance and was checked by measuring the relative intensities of the Pb 5d and Ge 3d core levels in soft x-ray photoemission measurements on the sample. An independent check on the coverage was made by the analysis of surface x-ray diffraction experiments on the sample [16]. Upon Pb deposition the reconstruction changed into a $\sqrt{3}x\sqrt{3}R30^{o}$ pattern, which upon heating and cooling passed through a reversible transition: $\sqrt{3}x\sqrt{3}\ R30^{o} \rightleftarrows 1x1$ at = 470 K. It should be noted that the exact transition temperature depends strongly on the Pb coverage [13].The sample heating was provided by passing a direct current through the sample. No temperature reading was available during the XSW measurement. We calibrated the current corresponding to the transition observed by LEED and surface x-ray diffraction measurements. XSW measurements were made on both the room temperature (RT) $\sqrt{3}x\sqrt{3}R30^{o}$ and the high temperature (HT) 1x1 phases. During the in-situ measurements the pressure in the small transportable UHV chamber was maintained at better than 10^{-7} Pa. The experimental set-up has been described in Ref. [17].

The quality of the substrate crystal is crucial for XSW measurements. The strain patterns left and introduced from sputtering and annealing during sample preparation and the subsequent direct heating of the sample to above the transition temperature were revealed by double crystal topography [18] measurements on the samples before each XSW measurement. A strainfree region down to an area of ≈ 0.2 mm^2 was selected with a slit system for the XSW measurements.

The results of an XSW measurement on the HT 1x1 phase using a (111) bulk reflection are shown in Fig. 2. The measured values of f and Φ, obtained by a least-squares fit of the normalized Pb L-fluorescence yield using the dynamical theory of x-ray diffraction, are 0.48 ± 0.04 and 0.96 ± 0.02, respectively. These values are the same, within the experimental errors, as those for the RT $\sqrt{3}x\sqrt{3}R30^{\circ}$ phase [f=0.50±0.05, Φ=0.96±0.03]. The results of a measurement on the HT 1x1 phase with a (220) reflection are shown in Fig. 3. The measured values of f and Φ are 0.60 ± 0.10 and 1.23 ± 0.01, respectively, while the expected value of f for a 2-D isotropic liquid overlayer, as explained before, is 0. The fluorescence yield profile corresponding to f = 0, that is, for a liquid layer, is also shown in Fig. 3 (curve marked "LIQUID"). Clearly, our results do not support the presence of a 2-D isotropic liquid Pb layer on the surface. In fact the HT results are the same, within the experimental error, as the corresponding results for the RT $\sqrt{3}x\sqrt{3}R30^{\circ}$ phase [f=0.64±0.12, Φ=1.23±0.02] [19].

The next question is: if the Pb atoms are not in a random distribution in the form of a 2-D isotropic liquid, what other possible structure(s) could give rise to the 1x1 LEED pattern of the HT phase.

One possibility is that the HT phase is an ordered phase which leads to the 1x1 LEED pattern. (In a previous LEED, Auger and desorption study on the Ge(111)-Pb system for a Pb coverage of 1 ML Metois and Le Lay [20] observed a similar reversible transition at somewhat higher temperature, and the HT 1x1 phase was attributed to an ordered Pb overlayer). However, it would be a coincidence if the new distribution of the Pb atoms in the ordered 1x1 structure maintains practically the same (111) and (220) Fourier components as those for the $\sqrt{3}x\sqrt{3}$ $R30^{\circ}$ phase, as observed in the present experiments.

The second possible explanation can be given by noting that the XSW method is not sensitive to long range order. A large value of f is an indication of strong local order, that is, preferential bonding of the overlayer atoms to the surface atoms. Thus the 1x1 LEED pattern of the HT phase could arise from $\sqrt{3}x\sqrt{3}$ $R30^{\circ}$ domains which would still have the same local geometry as in the RT phase. In this case the F.C.'s would remain practically unchanged as observed in the present study. This is consistent with the DMM theory [14,15] which predicts that regions smaller than the correlation length retain solidlike properties in the "liquid" phase. In the $\sqrt{3}x\sqrt{3}$ $R30^{\circ}$ structure, there are three equivalent ways of placing the overlayer atoms on the surface. These are referred to sublattices. In each of these sublattices an overlayer atom has the same local geometry. Presence of domains of these sublattices in the overlayer will have an effect of destructive interference in all diffraction experiments. This would wipe out the fractional order spot due to the overlayer and the 1x1 diffraction pattern due to the substrate underneath will be left. The disappearance of the overlayer fractional diffraction spots in a diffraction experiment may be associated with a disordered overlayer, but the actual nature of disorder remains unknown. The ambiguity in the nature of the 1x1 phase is conspicuous even in an elaborate LEED study of the reversible transition Si(111)7x7 $\rightleftarrows$ 1x1 at 1140 K by Bennett and Webb [21]. Though they frequently referred to a lattice gas model for the HT 1x1 phase they could not rule out the possibilities of a disordered 7x7 or a true melted surface layer. On the basis of dynamical LEED analysis Zehner et al. [22] concluded that laser annealed Si(111)1x1 surface is essentially bulk like, i.e. ordered. Zehner et al. [23] later concluded, using photoemission spectroscopy, that the 1x1 surface is not ordered, but a disordered 7x7, possibly mixed with 2x1 structure. Tromp et al. [24] showed, using ion channeling and blocking technique, that the laser annealed 1x1 surface is a disordered 7x7 surface. These examples show the complexities in the analysis of diffraction data from a system that produces 1x1 diffraction pattern.

The XSW method uses diffraction only from the substrate crystal to set up the standing wave field. Then via the detection of an inelastic signal, characteristic of the overlayer atoms, it determines the Fourier components of the overlayer atomic distribution, which need not have long range order. The study of local order can shed light on the nature of disorder in a system, as has been demonstrated in the present study.

In a recent quasielastic and inelastic neutron scattering study [25] of dynamical response of the 2-D system, the melting of intercalated alkali-metal layers have been investigated. These experiments show that the 2-D melting process exhibits coexisting solidlike and liquidlike dynamical behaviour over a wide range of temperature. Just at the melting point, defined by the softening of the layer shear elastic constant, the diffusion is not very significant. At higher temperatures the diffusive motion of the alkali-metal atoms becomes more dominant and the alkali-metal layers transform into a rotationally isotropic 2-D liquid. Whether this is the case for the Ge(111)-Pb system remains to be investigated. An increasing diffusive motion of the Pb atoms should be reflected in the amplitude (f) of the F.C. for the (220) measurement. In principle, a diffusion coefficient could be derived, which would open up the possibility of the application of XSW to the study of dynamical response.

In conclusion, we have made high temperature x-ray standing wave measurements at a temperature of approximately twice the Debye temperature of the substrate. In the dynamical theory an atomic form factor modified by the Debye-Waller factor appears to be adequate for an accurate description of the standing wave field. By the application of the high temperature x-ray standing wave method to the Ge(111)-Pb system we obtain evidence that the high temperature (1x1) phase is not produced by a true two-dimensional liquid, rather it appears to be composed of small islands of the original crystalline layer.

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19. The details of the structure of the $\sqrt{3}x\sqrt{3}$ R30° phase for a Pb coverage of 4/3 ML will be presented elsewhere. Basically the Pb atoms are incorporated at two different heights in the [111] direction - 1/3 ML at a height of 1.55 Å and the remaining 1 ML at a height of 2.85 Å from the ideal surface atomic plane. The Pb atoms in the lower layer (1/3 ML) are at the threefold hollow (H_3) site and those in the higher layer (1 ML) are between the atop (T_1) and the threefold eclipsed site (T_4). The structure of this system projected onto the surface plane has been shown in Ref. 16. The two different heights along with some spreading due to thermal vibration of the Pb atoms accounts for the observed amplitude and phase of the (111) F.C. This distribution of the Pb atoms corresponds to three different heights in the [220] direction and is consistent with the observed amplitude and phase of the (220) F.C.
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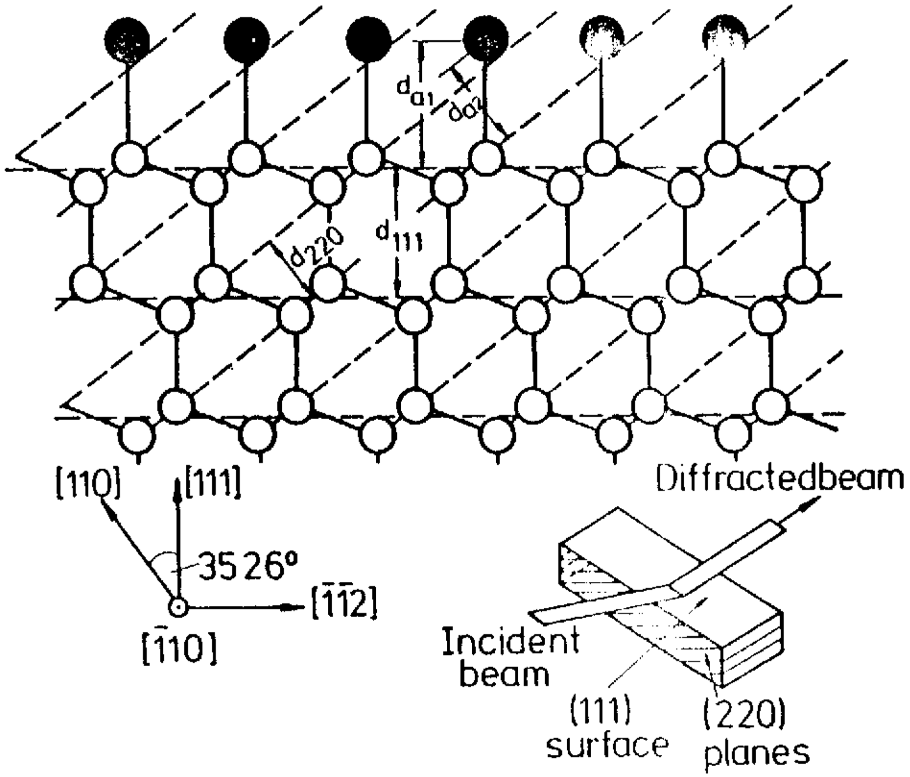
Figure captions:

Fig. 1 (a) A two-dimensional solid overlayer. Here the adatoms are adsorbed on the (111) surface of a diamond type lattice. All the adatoms are shown to be at the same distance in the [111] direction as well as in the [220] direction. d_{111} and d_{220} are the planar distances for the (111) and (220) reflections respectively. (b) A 2-D isotropic liquid overlayer. All the adatoms are still at the same distance in the [111] direction, but not any more in the [220] direction. This random distribution of distances in the [220] direction will reduce the (220) Fourier component of this distribution to zero.

Fig. 2 Measured (+) and calculated (---) reflectivities for Ge(111) reflection and the corresponding Pb L-fluorescence yields (●,—) as a function of wavelength of the incident x-rays. λ_B is the wavelength corresponding to E_γ = 15.5 keV and satisfies the Bragg condition: $2d\sin\theta = \lambda_B$.

Fig. 3 Measured (+) and calculated (---) reflectivities for Ge(220) reflection and the corresponding Pb L-fluorescence yields (●,—) as a function of wavelength of the incident x-rays. The fluorescence yield expected from a 2-D isotropic liquid Pb layer is shown by the curve marked 'LIQUID'.



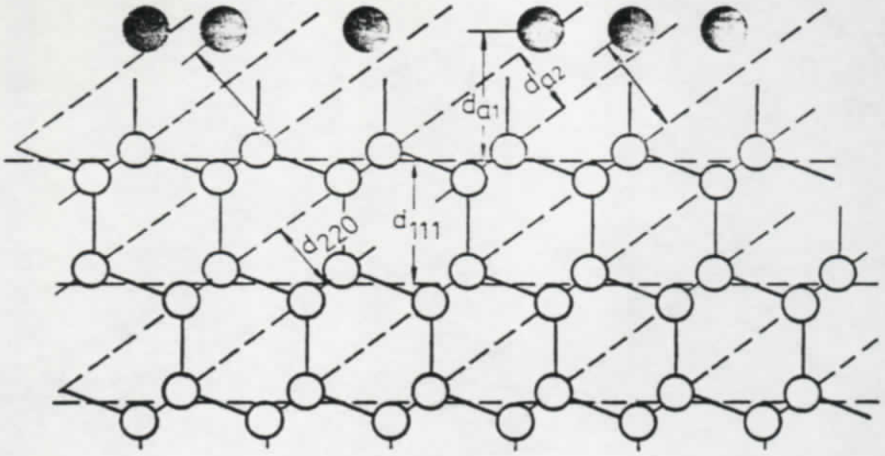
● Adatoms

○ Substrate atoms in the diamond structure (such as Si, Ge)

d_{a1} = adatom distance component in the [111] direction

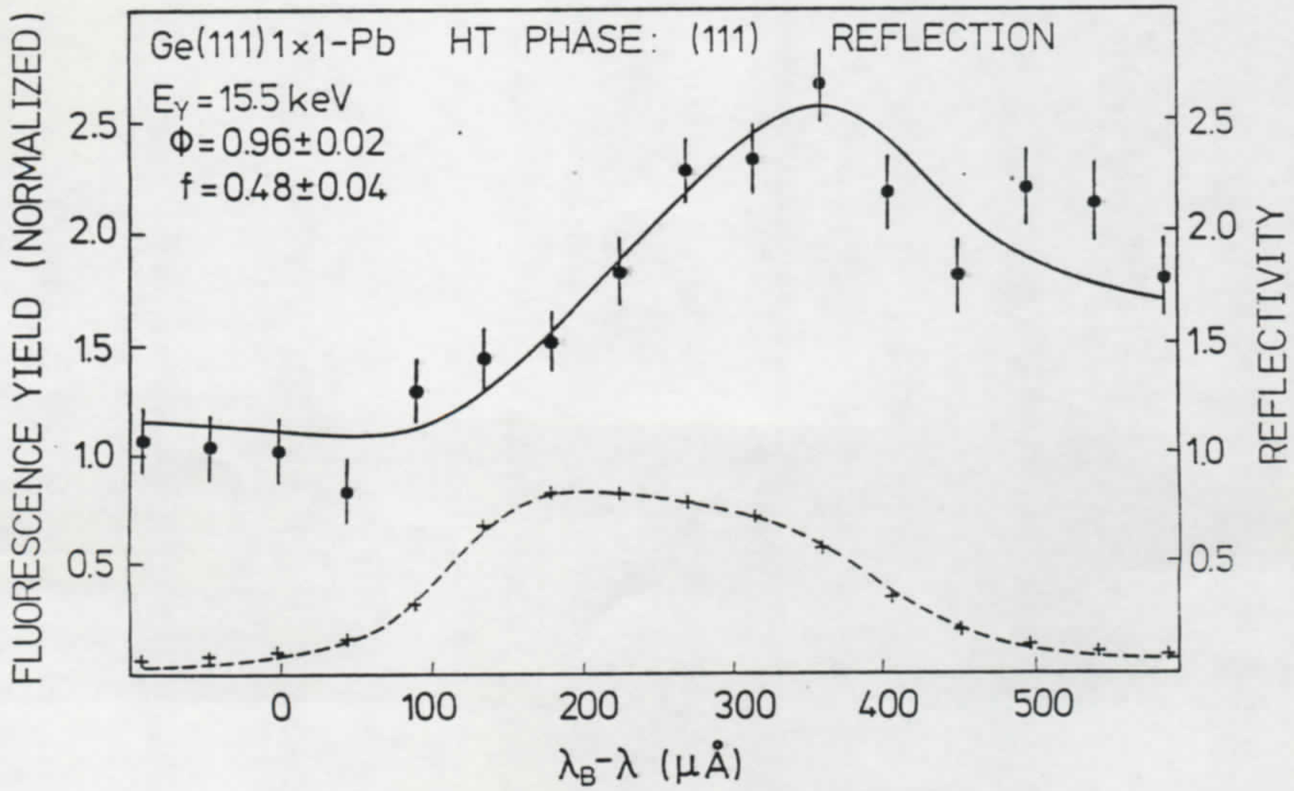
d_{a2} = adatom distance component in the [220] direction

Fig. 1(a)



d_{a1}
d_{a2}
d_{220}
d_{111}

Fig. 1(b)



Ge(111)1×1-Pb HT PHASE: (111) REFLECTION
$E_\gamma = 15.5$ keV
$\Phi = 0.96 \pm 0.02$
$f = 0.48 \pm 0.04$
FLUORESCENCE YIELD (NORMALIZED)
REFLECTIVITY
0.5
1.0
1.5
2.0
2.5
0
100
200
300
400
500
$\lambda_B - \lambda$ (μÅ)

Fig. 2

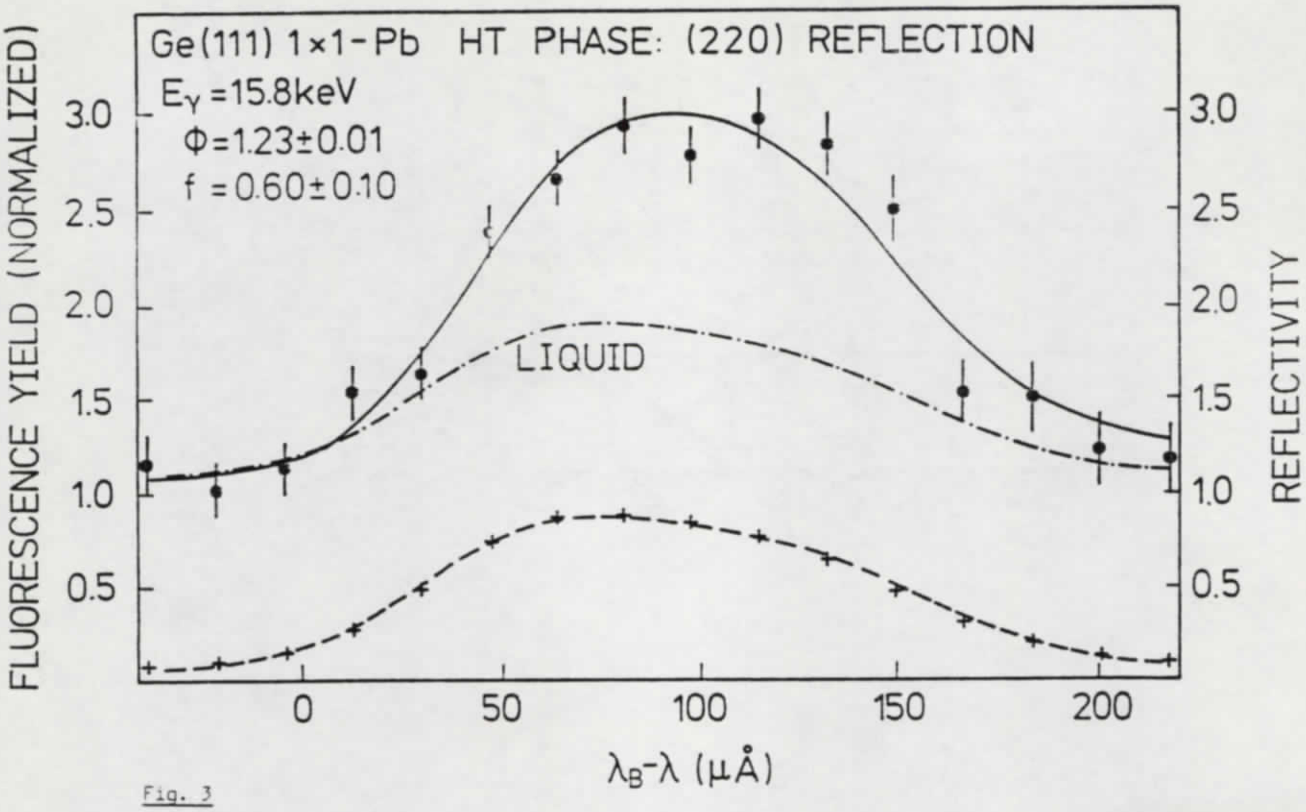

Ge(111) 1×1-Pb HT PHASE: (220) REFLECTION
E_γ=15.8keV
Φ=1.23±0.01
f =0.60±0.10
LIQUID
FLUORESCENCE YIELD (NORMALIZED)
REFLECTIVITY
λ_B-λ (μÅ)
0
50
100
150
200
0.5
1.0
1.5
2.0
2.5
3.0

Fig. 3