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2006 J. Phys.: Condens. Matter 18 7393

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# Fitting of crystal structure parameters of InAs under high pressure: quantitative XANES analysis using a multidimensional interpolation approach

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Received 31 December 2005, in final form 15 May 2006

Published 21 July 2006

Online at [stacks.iop.org/JPhysCM/18/7393](http://stacks.iop.org/JPhysCM/18/7393)

## Abstract

A first application of the multidimensional interpolation approach to a crystalline system, namely for the determination of the structural parameters of the high-pressure *Cmcm* phase of InAs, is reported. The method of local three-dimensional (3D) geometry investigation is based on the fitting of the experimental x-ray absorption near edge structure (XANES) data using a multidimensional interpolation of spectra as a function of structural parameters and full multiple scattering (MS) calculations. The procedure is divided into the following steps: the construction of an interpolation polynomial, the calculation of its energy-dependent coefficients using multiple scattering theory, and the minimization of the discrepancy between interpolated and experimental data varying structural parameters. Additionally, the method of XANES calculations has been tested for the reference phase of InAs (with *Fm3m* symmetry) with well-known structure. To achieve a higher sensitivity of the method on the structural parameters and to exclude the influence of non-structural factors on the results of the fitting, we have analysed the differences between spectra corresponding to the different crystal phases. The best-fit geometry with the cell parameters  $a = c = 5.366 \text{ \AA}$  and  $b = 5.411 \text{ \AA}$  and the internal cell parameter (which corresponds to the displacement of atoms in the *y* direction)  $\delta = 0.025$ , has been found for InAs at 19 GPa.

## 1. Introduction

X-ray absorption spectroscopy yields atomic site and electron orbital moment selective information on the electronic and local structure in the close environment of the absorber atom. There are now several approaches [1–4] that allow, through nonlinear minimization techniques, to extract quantitative information from the high-energy part of the absorption

spectrum (approximately  $\geq 50$  eV from the absorption edge), the so-called extended x-ray absorption fine structure (EXAFS). Unfortunately, due to the disorder effects and to the small value of mean free path of the photoelectron, the information content relative to the higher-order multiple scattering paths, which yield the details of the local 3D geometry and electronic structure, is washed out in this region of the spectra. Only in rather specific cases it is possible to extract information about bond angles, taking into account the limited number of multiple scattering paths of photoelectrons during EXAFS fitting [5]. More often, combination of x-ray diffraction for the determination of cell constants and EXAFS to probe first coordination is used [6, 7] and it often gives valuable information. In principle, complete information on the local geometry and coordination around the x-ray absorbing atom could be obtained from the low-energy region of the x-ray absorption spectrum covering the first few tens of eV from the absorption edge: the x-ray absorption near edge spectra (XANES). However, the quantitative analysis of this region presents difficulties, mainly related to the theoretical approximation in the treatment of the potential and the need for heavily time-consuming ‘*ab initio*’ algorithms to calculate the absorption cross section. Therefore, XANES is used mostly qualitatively (in finger-print mode) to choose the best structural model on the basis of theoretical calculations for several model structures [8] or comparing experimental spectra of model compounds [9]. Two approaches have been developed recently for quantitative fitting of the XANES region: MXAN [10] and FitIt [11]. In the present study, we applied, for the first time, the FitIt code to extract quantitative structural information from the XANES region in crystalline systems, where the unknown fitted variables are lattice constants and internal unit cell parameters. Namely, the multidimensional interpolation approach was used for clarification of the local structure in the high-pressure phases of the III–V semiconductor InAs.

The high-pressure behaviour of InAs has been studied previously both experimentally and theoretically (for a review, see [12, 13]). But such an important feature as short-range chemical ordering is still under debate. A recent angle-dispersive x-ray diffraction study (ADXRD) in the pressure range up to 46 GPa has supposed that the structural sequence as a function of pressure is  $F\bar{4}3m \rightarrow Fm\bar{3}m \rightarrow Cmcm \rightarrow Pmma$  [14]. The first phase transition is of first order, with a large volume collapse, while in the latter transitions there are no obvious volume discontinuities. In particular, the *Cmcm* phase is obtained from the *Fm $\bar{3}$ m* phase through an orthorhombic distortion and displacements of the internal atomic positions in the unit cell. Although XRD studies have allowed the determination of the symmetries of the different phases, it was not possible using XRD alone to have direct access to information on the local chemical order, as diffraction techniques probe only average values over a large number of unit cells. Nonetheless, local structure information is crucial to validate theoretical methods, yielding the construction of the interatomic potentials. It was shown that EXAFS investigations have been able to give complementary information on the local structure of InAs at high pressure [14, 15]. Because of the limited number of structural parameters that could be varied simultaneously, the model used for the EXAFS analysis of the *Cmcm* phase was that of the structurally disordered NaCl phase, and only the number and distance of atoms in a single ‘average’ coordination shell was obtained. The aim of the current work is to extract more precise information on the local structure around As in the high-pressure *Cmcm* phase of InAs by quantitative XANES analysis using a multidimensional interpolation approach. We then compare our results with those obtained by EXAFS [15] and by XRD analysis [18].

## 2. Method of calculation

It is well known that two main sets of factors influence the calculation of XANES: (i) non-structural parameters such as crystal potential parameters, cluster size for multiple scattering

(MS) calculations and broadening of the spectra, and (ii) structural parameters, namely, for crystalline samples, the unit cell parameters and internal positions of the atoms. To exclude the influence of non-structural parameters on the results of geometry determination, we have chosen their values for the InAs phase with well-known structure and then fixed them in all subsequent calculations.

To determine the structure on the basis of the XANES fitting, a novel method of multidimensional interpolation of spectra as a function of structural parameters implemented in the FitIt software [11] has been used. A detailed description of the method can be found elsewhere [11]. It is based on an expansion of the absorption coefficient in multivariable Taylor series:

$$\begin{aligned} \mu_i(E, p_1 + \delta p_1, p_2 + \delta p_2, \dots, p_n + \delta p_n) = & \mu(E, p_1, p_2, \dots, p_n) + \sum_n A_n(E) \delta p_n \\ & + \sum_{m,n} B_{mn}(E) \delta p_m \delta p_n + \dots \end{aligned} \quad (1)$$

where  $\vec{p}^0 = (p_1, p_2, \dots, p_n)$  is a starting set of structural parameters and  $\delta p_n$  is a deviation of parameter  $p_n$  from the starting value,  $\mu(E)$  is the result of multiple scattering calculations of XANES,  $\mu_i(E)$  is the interpolated spectrum, and  $A_n(E)$ ,  $B_{mn}(E)$ , ... are energy-dependent coefficients.

A crucial point is to calculate the energy-dependent coefficients and to find the minimum number of terms, which are necessary to interpolate the spectrum correctly. The coefficients can be deduced from the results of multiple scattering calculations for certain sets of structural parameters  $\vec{p}^k$  solving the linear system of equations:

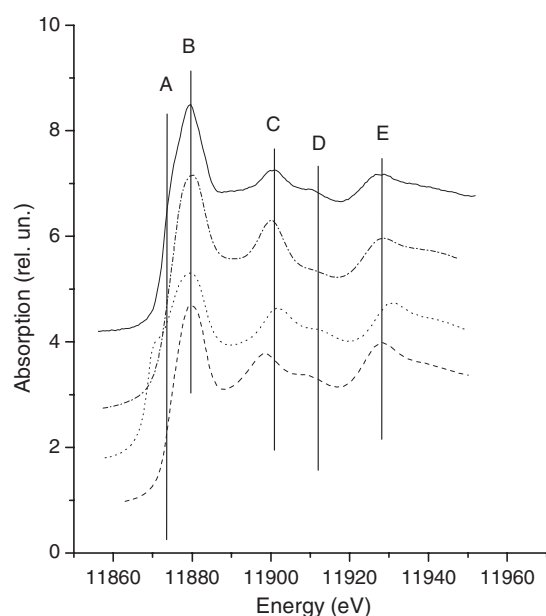
$$\mu_i(E, \vec{p}^k) = \mu(E, \vec{p}^k). \quad (2)$$

We will call these sets of parameters  $\vec{p}^k$  'interpolation nodes'. In these nodes, the MS calculated and interpolated spectra are exactly equal. The required MS calculations were performed using the FDMNES code [16]. For comparison purposes, we also performed calculations of the spectra using the self-consistent MS FEFF8.2 [17] package.

The polynomial construction consists of a step-by-step procedure, with successive testing and correction of the polynomial. Starting with the simplest polynomial, the discrepancies between the interpolated and the MS calculated spectra are checked for certain sets of structural parameters, which we will call 'control points'. They are selected so that the influence of the tested term of the polynomial is maximal for this set of parameters. If the modulus of maximal discrepancy between the interpolated and the MS calculated spectra exceeds 10% of the difference between the MS calculations for the control set of parameters (control point) and the spectrum calculated for the initial set of parameters ( $\delta p_i = 0$  ( $i = 1, \dots, n$ )), then one has to include the corresponding term into the constructed interpolation polynomial. To calculate the energy-dependent coefficient for this term, a new equation corresponding to this control point is added into the system (2). The next control points are tested using this improved polynomial. If it is found that any term is negligible in the polynomial, then it is possible to reduce the number of more complex terms which have to be tested on subsequent steps, and thus reduce the number of control points and correspondingly reduce the required MS calculations time.

### 3. Results and discussion

The first step of the analysis is the choice of optimal values of the non-structural parameters to use in the simulations: the size of the atomic cluster around the x-ray absorbing ion and the type and parameters of the crystal potential for the calculation of the photoelectron phase shifts.

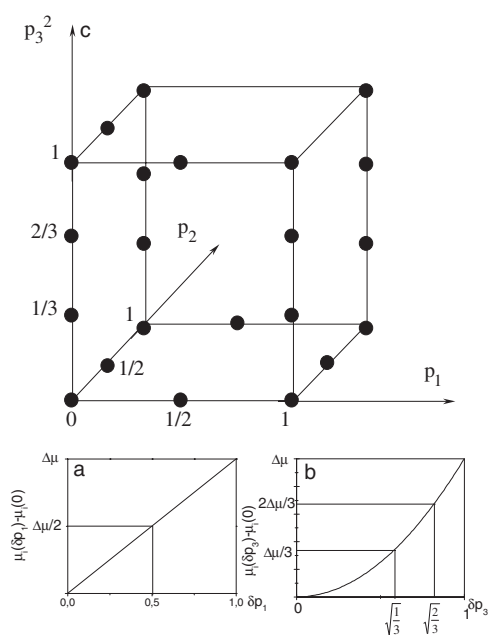


**Figure 1.** Experimental (solid curve) and theoretical As K-edge XANES of InAs in the  $Fm\bar{3}m$  high-pressure phase (14 GPa). Calculations were performed for different approximations of exchange potential using FEFF8.2 and FDMNES codes: Hedini-Lunqvist (FEFF8.2) (dashed curve), Dirac-Hara (FEFF8.2) (dotted curve) and  $X\alpha$  (FDMNES) (dash-dotted curve).

These parameters are evaluated by comparing the results of simulations and experimental XANES data for a reference phase with a well-known crystal structure. We used the  $Fm\bar{3}m$  structure of InAs as the reference phase to determine the non-structural parameters. The atomic cluster was constructed using the cell parameters  $a = b = c = 5.396 \text{ \AA}$  obtained from the Rietveld refinement of diffraction data [18]. We found that a spherical cluster with a radius of  $8.3 \text{ \AA}$  is sufficient to reproduce all features of the spectrum, and an increase of this parameter does not lead to appreciable changes.

With the FEFF8.2 code, several exchange potentials may be used (Hedini-Lunqvist, Dirac-Hara, Dirac-Hara with the imaginary part of the Hedini-Lunqvist potential). In figure 1 we show theoretical XANES calculated using a self-consistent potential with Hedini-Lunqvist and Dirac-Hara exchange potentials. One can see that both these potentials allow us to reproduce the main features of the spectrum, but the agreement in the energy positions of the peaks is not perfect in either case. In particular, peak C is shifted to lower energies when Hedini-Lunqvist exchange is used, while peak E is shifted to higher energies for the Dirac-Hara potential. To overcome this issue, we have used a non-self-consistent potential with  $X\alpha$  exchange [19], which is used in the MS scheme of the FDMNES code, and varied the exchange constant  $\alpha$  as a free parameter. The best agreement between the theoretical and experimental spectra in the energy positions of peaks was obtained for this case with  $\alpha = 0.4$ . For all subsequent calculations relative to the  $Cmcm$  structure of InAs, we fixed these optimal values found in the known  $Fm\bar{3}m$  structure.

The  $Cmcm$  structure can be seen as an orthorhombic distortion of the  $Fm\bar{3}m$  structure. It has two atomic positions at  $(0, y_1, 1/4)$  and  $(0, y_2, 1/4)$ . If  $a = b = c$  and  $y_1 = 3/4$  and  $y_2 = 1/4$ , then the structure is identical to NaCl. The two distortions from NaCl are a shift of the atoms in  $x$ - $y$  planes along the  $y$  direction and a smaller zigzag distortion along the  $x$  direction that arises when  $y = y_1 - y_2 \neq 1/2$ . On the basis of the Rietveld refinement of ADXRD data [18], the cell parameters are found to be close to a tetragonal condition at least up to 25 GPa with  $a \sim c \neq b$ . For this reason, in a first approximation, three structural parameters  $p_1$ ,  $p_2$  and  $p_3$  are necessary to describe InAs in the  $Cmcm$  phase below 25 GPa, corresponding



**Figure 2.** Illustration of the choice of interpolation nodes. For one-parameter interpolation, the absorption coefficient for the fixed energy as a function of parameter deviation is shown. Panel (a)—linear first approximation. Panel (b)—second-order first approximation. For variation of all parameters, interpolation nodes in the space of structural parameters are shown as full circles (panel (c)).

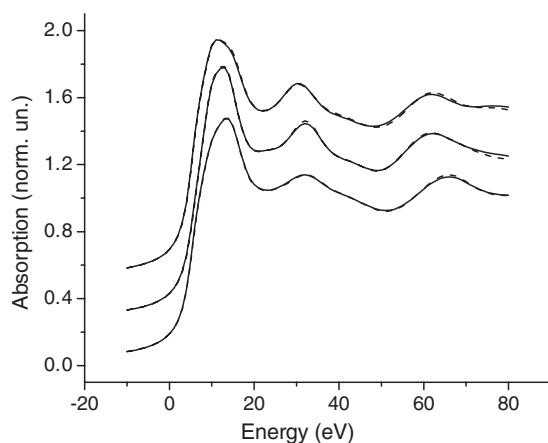
respectively to cell parameters  $a = c$  and  $b$ , and the internal parameter  $\delta$ , which corresponds to the displacement of atoms in the  $y$  direction:  $y_1 = 3/4 - \delta$ ,  $y_2 = 1/4 - \delta$ .

We have analysed XANES data at 19 GPa. In our calculations, the limits of variation for the three parameters were [5.396–5.096 Å] for  $p_1$ , [5.396–5.696 Å] for  $p_2$  and [0–0.1] for  $p_3$ . The limitations in the variation range of the  $p_1$ ,  $p_2$  and  $p_3$  parameters guarantee that the  $Cmcm$  symmetry is conserved.

The next step of the proposed method for the structure determination is devoted to the construction of the interpolation polynomial with the energy-dependent coefficients, which allows one to obtain a good agreement between the interpolated and MS calculated spectra for all the values of parameters within the selected limits. We start by fixing all parameters to the initial value, except for one, say  $p_1$ . We then find the minimal number of terms in the polynomial (1), which allow the interpolated spectrum to reproduce correctly the MS calculated spectra, allowing only for variations of  $p_1$ . Then we repeat this procedure for the other parameters. From symmetry, it is clear that positive and negative values of the parameter  $\delta$  correspond to the same structure. Therefore, only even powers of parameter  $p_3$  were taken into account in the polynomial (including all cross terms with other parameters).

We have found that two terms are necessary to interpolate the spectrum as a function of  $p_1$  and  $p_2$  and three terms are necessary for  $p_3$ . Interpolation nodes were selected so that, within the first approximation (the linear term for  $p_1$  and  $p_2$  parameters and square term for  $p_3$ ), the differences between the interpolated spectra corresponding to the closest interpolation nodes are equal. Schematically, this is shown in figures 2(a) and (b). In the case of a linear first approximation (for instance, for parameter  $p_1$ ) and two interpolation nodes, this leads to the choice of nodes (0, 0, 0), (0.5, 0, 0) and (1, 0, 0), whereas, in the case of second-order first approximation (for parameter  $p_3$ ) and three interpolation nodes, this leads to the choice of nodes (0, 0, 0), (0, 0,  $\sqrt{1/3}$ ), (0, 0,  $\sqrt{2/3}$ ), and (0, 0, 1).

Here and below, we use the relative units for deviations of parameters ((0, 0, 0) corresponds to the  $Fm3m$  structure with  $a = b = c = 5.396$  Å; (1, 0, 0) corresponds to the cell



**Figure 3.** Interpolated (solid) and MS calculated (dash) As K-edge XANES spectra of InAs in the *Cmc* phase corresponding to different geometrical parameters: (0.85, 0.9, 0.6)—bottom, (0.15, 0.85, 0.3)—middle, and (0.25, 0.25, 0.85)—top. Solid and dashed curves are so close that it is difficult to resolve them by eye.

with parameters  $a = c = 5.096 \text{ \AA}$ ,  $b = 5.396 \text{ \AA}$  and  $\delta = 0$ , where  $p_1$  is set at the value corresponding to the chosen limit of variability).

During the subsequent analysis, in the same way as described in detail in [11] we identify the following important terms:

- the first and second power terms of  $p_1$  and  $p_2$ ;
- the cross terms between  $p_1$  and  $p_2$ :  $p_1 p_2$ ,  $p_1^2 p_2$  and  $p_1 p_2^2$ ;
- all the terms, including  $p_3$  in the second, fourth and sixth powers and parameters  $p_1$  and  $p_2$  in the first power.

Thus we have constructed the following interpolation polynomial:

$$\begin{aligned} \mu_i(E, p_1 + \delta p_1, p_2 + \delta p_2, p_3 + \delta p_3) = & \sum_{\substack{k=0,1 \\ l=0,1 \\ m=0,\dots,3}} A_{klm}(E) \delta p_1^k \delta p_2^l \delta p_3^{2m} + \sum_{\substack{k=0,1 \\ i=1,2}} B_{ki}(E) \delta p_i^2 \delta p_3^{2k} \\ & + \sum_{i=1,2} C_i(E) \delta p_1 \delta p_2 \delta p_i \end{aligned}$$

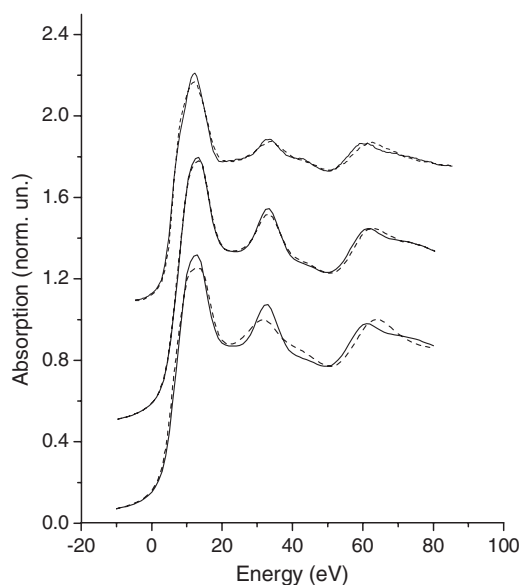
with the interpolation nodes shown schematically in figure 2(c).

To demonstrate that the interpolation approximation is quite accurate within the selected limits of variations, in figure 3 we have compared the interpolated and the MS calculated spectra for three random sets of parameters: (0.25, 0.25, 0.85), (0.15, 0.85, 0.3) and (0.85, 0.9, 0.6). Good agreement between the spectra is obtained in all the cases.

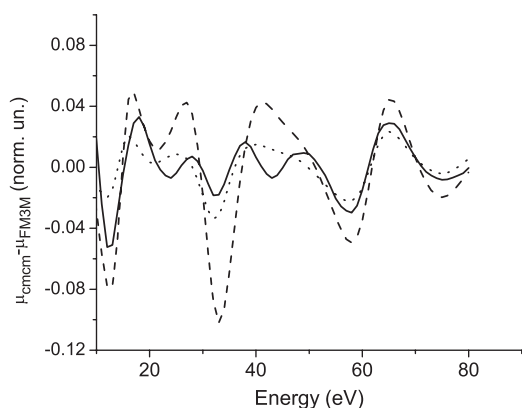
Figure 4 shows that experimental spectra corresponding to InAs at different pressures are all very similar (top). Differences are found to be rather small with respect to the discrepancy observed between the experiment and theory for the reference phase (figure 1).

Therefore, during the procedure of minimization of the discrepancy between experiment and theory, uncertainties can appear related to the fact that the structural parameters may wander away from real ‘physical’ values in the attempt to compensate for differences that are not of structural origin (because they appear in the simulation of the reference structure). To increase the sensitivity of the method, instead of working directly on the minimization of the discrepancy between measured and calculated spectra, we have minimized the discrepancy between differences in spectra at different pressures, i.e. between spectra corresponding to the *Cmc* and *Fm3m* phases. Thus, we used the following criterion to find the best fit:

$$\min \left( \frac{1}{E_2 - E_1} \int_{E_1}^{E_2} \left[ \left( \mu_{\text{exp}}^{FM3M} - \mu_{\text{exp}}^{CMCM} \right) - \left( \mu_{\text{theor}}^{FM3M} - \mu_{\text{theor}}^{CMCM} \right) \right]^2 dE \right).$$



**Figure 4.** Top: the experimental As K-edge XANES spectra of InAs in the reference *Fm3m* phase at 14 GPa (solid line) with that in the high-pressure (19 GPa) *Cmcm* phase (dashed line). Middle: simulation for the *Fm3m* phase at 14 GPa (solid line) compared to the simulation using the best-fit geometry for the *Cmcm* phase (dashed line). Bottom: simulation for the *Fm3m* phase at 14 GPa (solid line) compared to the simulation using 20 GPa x-ray diffraction data (dashed line).



**Figure 5.** Differences between As K-edge XANES spectra of InAs in *Cmcm* and *Fm3m* high-pressure phases: dots—experimental data; solid line—calculations for XANES best-fit geometry in the *Cmcm* phase; dashed line—calculations using 20 GPa x-ray diffraction data.

To find all the best-fit structures, we have used a gradient search of minima from 20 random points. Interpolation is very fast and therefore the optimization of the strategy of the multidimensional minima search is not very important. For the data at 19 GPa, the best-fit geometry with the following parameters has been found:  $a = c = 5.366 \pm 0.025 \text{ \AA}$ ,  $b = 5.411 \pm 0.025 \text{ \AA}$  and  $\delta = 0.025 \pm 0.005$ . This structure leads to a local environment of As composed of six In atoms at distances in the interval between 2.68 and 2.71  $\text{\AA}$ .

This picture agrees well with that obtained performing a complete EXAFS data analysis, using a simplified model for the *Cmcm* phase based on a distorted NaCl structure. EXAFS analysis [15] shows, for data at 19 GPa, that As in the *Cmcm* phase is coordinated with a structurally disordered shell of six In atoms at an average distance of  $2.69 \pm 0.01 \text{ \AA}$ .

In figure 5 we compare the differences between the *Fm3m* and the *Cmcm* phases corresponding to the curves shown in figure 4. This figure shows that the agreement with experiment is much better for the simulation using the best-fit geometry than for the simulation using XRD-derived parameters [18]. Whereas the values of cell constants are in reasonable agreement with diffraction data at 20 GPa ( $a = 5.314 \text{ \AA}$ ,  $b = 5.428 \text{ \AA}$  and  $c = 5.285 \text{ \AA}$ ),



XANES analysis yields a smaller value for the internal parameter ( $\delta = 0.025$  from XANES and  $\delta = 0.06$  from XRD). We believe that the determination of a cell-internal parameter, such as  $\delta$ , from XANES is more precise than that obtained from a Rietveld refinement of high-pressure XRD data, affected by uncertainties related to peak widening due to poor hydrostatic conditions within the sample volume.

To conclude, we have shown that quantitative XANES fitting using a multidimensional interpolation approach can be used to extract reliable structural 3D information on the local structure. The minimization of discrepancies between differences in spectra, corresponding in our case to two different high-pressure phases in InAs, instead of a direct comparison between theoretical and experimental spectra, allows us to obtain higher sensitivity in the determination of the values of structural parameters.

### Acknowledgment

We wish to thank the European Synchrotron Radiation Facility for the invitation of Grigory Smolentsev as a Visiting Scientist.

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