VENUS: a 3D Visualization System for Crystal Structures and Electron/Nuclear Densities

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Despite the availability of many structure-drawing programs, cross-platform free software to visualize both crystal and electronic structures in three dimensions are relatively few. We should understand structural details and space distribution of various physical quantities not two-dimensionally but three-dimensionally. No whole picture of the complex space distribution is obtainable from contour maps that are often plotted.

To improve such a situation, we developed our own software package VENUS (**V**isualization of **E**lectron/**NU**clear densities and **S**tructures). We designed, from the ground up, two graphics programs taking full advantage of the OpenGL technology. These two bear the bell in three-dimensional (3D) visualization, rendering, and manipulation of crystal structures and electron/nuclear densities determined not only by X-ray/neutron diffraction but also by electronic-structure calculations. With VENUS, visualization of electrostatic potentials and wave functions calculated with part of these programs is also possible.

Further, VENUS includes two programs for **M**aximum-**E**ntropy **M**ethods (MEM). They allow us to determine electron/nuclear densities and Patterson functions, which are readily visualized as described above.

1. Four components of VENUS

The VENUS package comprises four independent programs:

VICS: **VI**sualization of **C**rystal **S**tructures
VEND: **V**isualization of **E**lectron/**N**uclear **D**ensities
PRIMA: **PR**actice **I**terative **M**EM **A**nalyses
ALBA: **A**fter **L**e **B**ail **A**nalysis

VICS and VEND visualize crystal structures and electron/nuclear densities, respectively. They have been written in ANSI C for cross-platform portability, which enabled us to port them from Microsoft Windows to UNIX/Linux. Their Graphical User Interface (GUI) was constructed with a combination of GLUT and GLUI. They can output 10 kinds of image files such as TIFF, EPS (including pixel or vector data), JPEG, and JPEG 2000.

With VICS and VEND, objects are rotated, expanded, shrunken, and translated fast in three dimensions, particularly in the presence of video cards accelerating the OpenGL API, *e.g.*, those powered by GeForce and RADEON graphic processing units. Four different modes of rotating objects are supported: drag, push, click, and automatic. In addition to crystallographic and electronic-state studies and education, we will take pleasure in manipulating 3D objects on personal computers (PC's).

PRIMA is a MEM analysis program to calculate electron densities from X-ray diffraction data and nuclear densities from neutron diffraction data [1]. It was designed with **M**EM-based **P**attern **F**itting (MPF) [1–3] in mind, as can be inferred from its name. ALBA is a program for the **M**aximum-**E**ntropy **P**atterson (MEP) method [4], whereby Patterson functions in the unit cell can be determined from observed integrated intensities resulting from Le Bail analysis [5].

The VENUS package is distributed free of charge on a Web site http://homepage.mac.com/fujioizumi/ .

2. VICS

VICS can read in 23 kinds of crystal data files such as CIF, PDB, and ICSD. Users of a multi-purpose pattern-fitting system RIETAN-2000 [6] will be pleased to learn that VICS can read and write standard input files, *.ins, of RIETAN-2000. After Rietveld analysis using RIETAN-2000, it updates lattice and structure parameters in an input file, *.vcs, with the VICS format if *.vcs shares the same folder with *.ins.

Crystal structures are represented by ball-and-stick, space-filling, polyhedral, wireframe, stick, dot-surface, and thermal-ellipsoid models. Ball-and-stick and stick models may be enclosed in dot-surface spheres of van der Waals radii. With translucent coordination polyhedra, atoms and bonds inside them are visible. Needless to say, VICS expresses anisotropic thermal motion by 3D graphics (Fig. 1) whereas ORTEP-III [7] has no 3D-graphics capability.

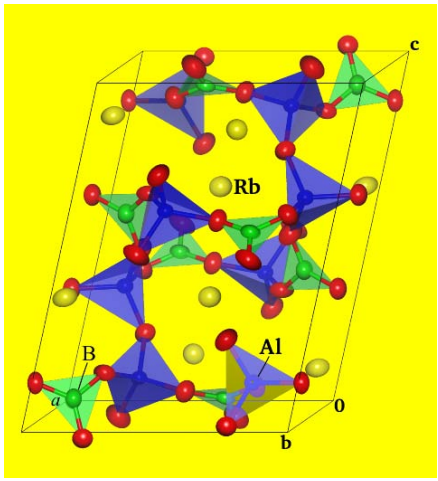

Fig. 1: *Monoclinic unit cell of $Rb_2Al_2B_2O_7$ drawn with VICS. Its structure consists of Rb^+ ions, AlO_4 tetrahedra, and BO_3 triangles.*

VICS supports automatic atom search on the basis of bond specifications including minimum and maximum bond lengths. Boundaries for drawing structures can be specified in sophisticated ways similar to convoluting and reiterative-convoluting spheres in ORTEP-III. For example, we can readily find all the atoms in a molecule, starting from only one atom inside it.

Selection of objects (atoms, bonds, and coordination polyhedra) makes it possible to obtain fractional coordinates, symmetry operations, translation vectors, interatomic distances, bond angles, torsion angles, and

information on coordination polyhedra including volumes, Baur's distortion indices [8], quadratic elongations [9], bond angle variances [9], bond valence sums [10] of central metals, and bond lengths expected from bond valence parameters [10] (Fig. 2).

```
   2     Mn2 Mn  0.00000  0.00000  0.50000  (-1, 0,-1)+ -x+1,-y+1/2,z+1
-------------------------------------------------------------------------------
   3      O1  O  0.22220  0.25000 -0.50890  (-1, 0, 0)+ y+3/4,-x+1/4,-z+3/4
   3      O1  O  0.00000  0.02780  0.25890  (-1, 0,-1)+ -x+1,-y+1/2,z+1
   3      O1  O  0.00000  0.97220 -0.25890  (-1,-1, 0)+ -x+1,y+1/2,-z+1
   3      O1  O -1.22220  0.25000 -0.50890  ( 0, 0, 0)+ -y+1/4,-x+1/4,-z+3/4
   3      O1  O -1.22220  0.75000 -0.49110  ( 0,-1, 0)+ -y+1/4,x+3/4,z+1/4
   3      O1  O  0.22220  0.75000 -0.49110  (-1,-1, 0)+ y+3/4,x+3/4,z+1/4
-------------------------------------------------------------------------------

l(Mn2-O1) =  1.9301(8) Angstrom
l(Mn2-O1) =  2.282(2) Angstrom
l(Mn2-O1) =  2.282(2) Angstrom
l(Mn2-O1) =  1.9301(8) Angstrom
l(Mn2-O1) =  1.9301(8) Angstrom
l(Mn2-O1) =  1.9301(8) Angstrom
---------------------------------------
Average bond length =  2.0474 Angstrom

Polyhedral volume = 11.1616 Angstrom^3
Distortion index (bond length) = 0.07642
Quadratic elongation =  1.0234
Bond angle variance =  39.0014 deg^2
-----------------------------------------
Input a bond valence parameter: 1.76
Bond valence sum = 3.014
Input an oxidation number [0 for quit]: 3
Expected bond length = 2.016 Angstrom
```

Fig. 2: *Parts of the Output Window of VICS when selecting an MnO_6 octahedron in Mn_3O_4 (space group $I4_1/amd$; a = 5.765 Å and c = 9.442 Å) and calculating a bond valence sum. Jahn-Teller distortion in the MnO_6 octahedron with Mn^{3+} as the central cation can be quantitatively understood.*

Other features include (a) addition of arrows indicating magnetic moments or positional shifts to any selected atoms, (b) displaying X−H···Y hydrogen bonds, and (c) insertion of lattice planes whose transparency and translation with a mouse are possible.

3. VEND

VEND can read in files storing 3D mesh data recorded with 11 formats. Files output by SCAT [11], WIEN2k [12], ABINIT [13], VASP, Gaussian, GAMESS, *etc*. can be input directly or indirectly. VEND can also input 3D density files, *.pri, created by PRIMA. In principle, VEND is capable of visualizing any physical quantities in parallelepipeds, *e.g*., Patterson functions determined from powder diffraction data with ALBA and Laplacians of electron densities.

M. Mizuno developed a Fortran program, contrd, to convert binary files, F09 and F39, output by SCAT into text files storing 3D data. He has recently written its extended version called contrwd. With a script wien2venus.py coded by M. Arai in Python, 3D electron densities calculated with WIEN2k are convertible into a text file, which is in turn input by VEND to display electron-density distribution in three dimensions. In addition, Cut3D in the ABINIT package can convert binary files output by ABINIT into text files with the XCrySDen XSF format. VEND is capable of reading all of these text files.

With VEND, electron/nuclear densities as well as wave functions and electrostatic potentials obtained by molecular-orbital methods are visualized as isosurfaces (Fig. 3), bird's-eye views, and two-dimensional maps to learn the nature of chemical bonds. Isosurfaces can be expressed in three different ways: smooth shading, wire-frame, and dot surface. Isosurfaces for positive and negative values, *e.g*., wave functions, electrostatic potentials, and coherent-scattering lengths, b_c, in neutron diffraction, are drawn with two different colors (Fig. 3a).

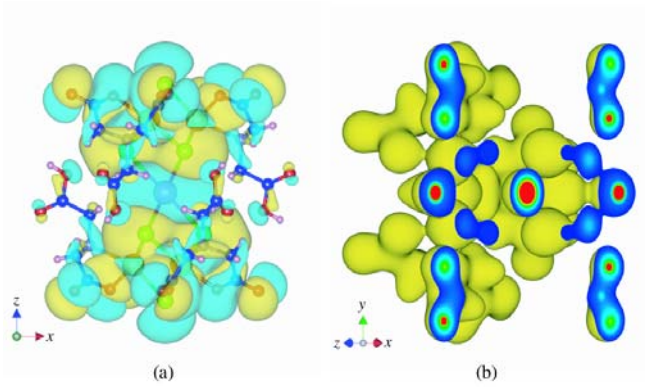

Fig. 3: *Isosurfaces of (a) the wave function of HOMO and (b) electron densities calculated for the $[Cd\{S_4Mo_3(Hnta)_3\}_2]^{4-}$ ion with SCAT. Isosurface levels: (a) $\pm 0.002a_0^{-3/2}$ and (b) $0.08a_0^{-3}$, where a_0 denotes the Bohr radius.*

VEND also has a feature of surface colorization to show the electrostatic potential value at each point on isosurfaces. Isosurfaces can be smoothed by spline interpolation. Clicking a [More] button doubles pixel numbers along *a*, *b*, and *c* directions whereas clicking a [Less] button half them. One of great advantages of VEND over other visualization tools is a feature to overlap translucent isosurfaces as well as slices with ball-and-stick and stick models drawn with VICS (Fig. 3a).

Drawing boundaries are specified using the numbers of unit cells along *a*, *b*, and *c* directions as well as a pair of cross sections inside a unit cell. Unit-cell edges and/or cross sections are colorized according to values of physical quantities on them to learn their distribution inside isosurfaces (Fig. 3b).

As Fig. 4 shows, we can insert up to three slices, *i.e*., planes colorized with an equation relating values to colors.

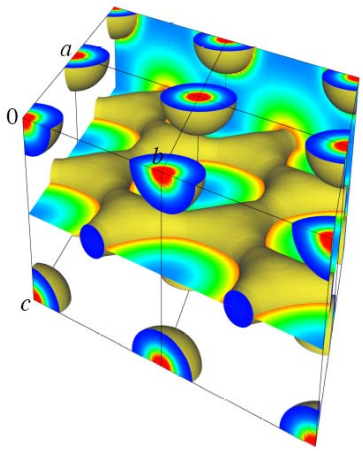

Fig. 4: *Isosurfaces of electron densities (density level: 0.7/Å^3) calculated for a superconductor MgB_2 by an augmented plane wave method with WIEN2k. (100) and*

(002) planes, where Mg and B atoms are located, are inserted as slices.

4. PRIMA and its use in MPF (Maximum-entropy methods-based Pattern Fitting)

MPF is an alternative to a classical approach, *i.e.*, Rietveld analysis, to structure refinement from powder diffraction data [1–3]. Crystal structures are represented not by structure parameters in Rietveld analysis but by electron/nuclear densities in MPF. A fast MEM analysis program is desired in MPF where whole-pattern fitting (w.p.f.) and MEM analysis are alternately iterated until convergence (refer to Fig. 1 in Ref. 2).

Before the development of PRIMA, we had been utilizing MEED [14] for the MEM analysis of observed structure factors, F_o, obtained from X-ray and neutron diffraction data. After making every effort to speed up MEM analysis, we completed our own program PRIMA. It executes MEM analysis several-tens times faster than MEED. MEED is now obsolete because of its sluggish speed and serious bug, where the total number of electrons (total of b_c values) in the unit cell deviates more or less during MEM iterations.

PRIMA was written from the ground up in Fortran 95, which enables us to create storage for allocatable arrays dynamically. It is thoroughly optimized for PC's equipped with Intel Pentium 4 processors and operated with Windows. Nonlinear single-pixel approximation, full use of space-group symmetry, and adjustment of Lagrangian multipliers further accelerate MEM analysis. PRIMA is applicable to MEM analysis from neutron diffraction data of compounds containing elements whose b_c's are negative, *e.g.*, H, Li, Ti, and Mn. The algorithm of MEM in PRIMA is described in a document PRIMA.pdf in the archive file of VENUS.

PRIMA makes it easier to modify a structural model during Rietveld analysis. In a user input file, *.ins, set NMODE at 0 and NMEM at 1, and input various parameters, *e.g.*, numbers of pixels along *a*, *b*, and *c* axes, for MEM analysis. Then, execute Rietveld analysis with RIETAN-2000 [6] to create a MEM data set file, *.fos. F_o(Rietveld) data, *viz.*, $|F_o|$'s and phases, recorded in this file are analyzed by PRIMA, which creates a 3D density file, *.pri, and a feedback data file, *.fba, storing structure factors, F_c(MEM)'s, obtained by the MEM analysis. VEND serves to input *.pri to visualize 3D electron/nuclear-density distribution. By linking RIETAN-2000 with VENUS in such a manner, the structural model may be rebuilt after close checking of the density image, if necessary (so-called MEM/Rietveld method [15]).

MEM gives only nonnegative electron densities (X-ray diffraction), estimates F_c(MEM)'s for reflections whose intensities have not been measured, and improve F_c(MEM)'s for overlapped reflections. Thanks to these advantages of MEM, it affords much clearer density distribution with high S/N ratios than Fourier synthesis from F_o(Rietveld) data. Thus, we now regard PRIMA as a must-have item for Rietveld analysis using RIETAN-2000.
The MEM/Rietveld method is a halfway approach to determination of electron/nuclear densities from X-ray/neutron powder diffraction data because the F_o(Rietveld)'s are more or less biased toward the structural model in the Rietveld analysis. For this purpose, MPF is far superior to the MEM/Rietveld method.

Nothing is so difficult as MPF. At first, w.p.f. is carried out from the F_c(MEM) data in *.fba. Simply set NMODE at 2 and NMEM at 1 in *.ins, and then run RIETAN-2000. Note that all the structure parameters in *.ins must have been updated on the analysis of X-ray diffraction data because contributions of anomalous scattering to structure factors need to be calculated from them. On repartition of observed diffraction intensities after w.p.f., the improvement of structure factors for the overlapped reflections effectively reduces the bias toward the structural model in the Rietveld analysis. F_o(w.p.f.) data in the resultant file, *.fos, are analyzed by PRIMA to get *.fba as well as *.pri.

In such a way, w.p.f. and MEM analysis are alternately repeated until *R* factors (usually R_{wp}) in the former no longer decrease (REMEDY cycles). The bias to the structural model reduces with increasing number of cycles. Throughout the REMEDY cycles, the total number of electrons (X-ray diffraction) or the total of b_c values (neutron diffraction) in the unit cell is fixed at that evaluated from the chemical formula and *Z*. Thus, electron/nuclear-density distribution affording the best fit to the observed diffraction pattern can be determined by MPF.

5. Application of MPF to a superconducting Co oxide hydrate

Takada *et al.* [16] prepared a layered compound $Na_{0.343}(H_3O)_{0.237}CoO_2{\cdot}1.19H_2O$ (space group: $P6_3/mmc$; a = 2.8114 Å and c = 11.2111 Å) *via* soft-chemical processing and discovered that it is a superconductor with a T_c of 5 K. Intercalation of H_3O^+ ions was overlooked at first but evidenced later by Raman spectroscopy [17]. This Co oxide has aroused interest widely because it is the first superconductor where first-row transition metal and oxygen atoms form layers. It is interesting to note that the host in this compound is a famous thermoelectric material Na_xCoO_2.

To elucidate the arrangement of the guests (H_2O, H_3O^+, and Na^+) sandwiched between two CoO_2 layers, MPF analysis from synchrotron X-ray powder diffraction data with the combination of RIETAN-2000–PRIMA and 3D visualization with VEND were very effective [17]. Because MEM is, *per se*, model-free, we could successfully find sites occupied by the guests, getting rid of any preconceived ideas. Fortunately, this noteworthy structure refinement was the first application of PRIMA to a novel material.

Figure 5 illustrates isosurfaces drawn with VEND for electron densities in three unit cells. Highly covalent Co–O bonds are clearly visible. In Rietveld analysis preceding MPF, we assumed that H_3O^+ and Na^+ ions statistically occupy M1 (2/3, 1/3, 1/4) and M2 (0, 0, 0.2413) sites. Because M2 is slightly displaced from the ideal 2*b* site (0, 0, 1/4), isosurfaces corresponding to M2 atoms are elongated along the *c* axis. H_2O molecules are disordered on $z \approx 0.17$ and $z \approx 0.33$ planes, encompassing the M1 and M2 sites.

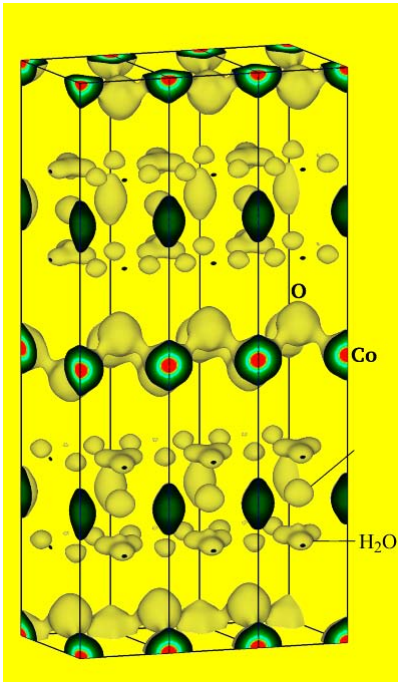

Fig. 5: *Electron-density distribution (density level: 1 Å^{-3}) determined by MPF from synchrotron X-ray powder diffraction data of $Na_{0.343}(H_3O)_{0.237}CoO_2{\cdot}1.19H_2O$.*

Furthermore, MPF has successfully been used in other studies including dynamic disordering of Cu^+ ions in the superionic conductor $Rb_4Cu_{16}I_{7.2}Cl_{12.8}$ [3, 18], the conduction path and disorder in the oxide-ion conductor $(La_{0.8}Sr_{0.2})(Ga_{0.8}Mg_{0.15}Co_{0.05})O_{2.8}$ [19], and the migration path of Li^+ ions in the Li-ion conductor $La_{0.62}Li_{0.16}TiO_3$ [20].

6. ALBA

ALBA is a Fortran 95 program for the MEP analysis of $|F_o|^2$'s estimated by the Le Bail method [5] from powder diffraction data and determined from single-crystal diffraction data. The name of the program originates from the most significant feature of the program; that is, MEP analysis is carried out **A**fter **L**e **B**ail **A**nalysis using RIETAN-2000.

Only one program for MEP analysis from $|F_o|$'s obtained by the Pawley method has hitherto been developed [4]. To our knowledge, no MEP analysis program has yet been distributed on the Web. We, therefore, built a powerful MEM engine into ALBA, making alterations to that of PRIMA. Thus, ultra-fast MEP analysis is possible with ALBA. The algorithm of the MEP method in ALBA is described in a document ALBA_manual.pdf in the archive file of VENUS.

Integrated intensities of overlapped reflections in powder diffraction data are, more or less, improved by the sophisticated MEP method, which is favorable for *ab initio* structure analysis from powder diffraction data.

ALBA is used in combination with RIETAN-2000 [6] or EXPO2004 [21] for *ab initio* structure analysis from powder diffraction data by a direct method (Fig. 6). Such a collaborative analysis is particularly effective for deriving initial structural models for compounds containing relatively heavy atoms.

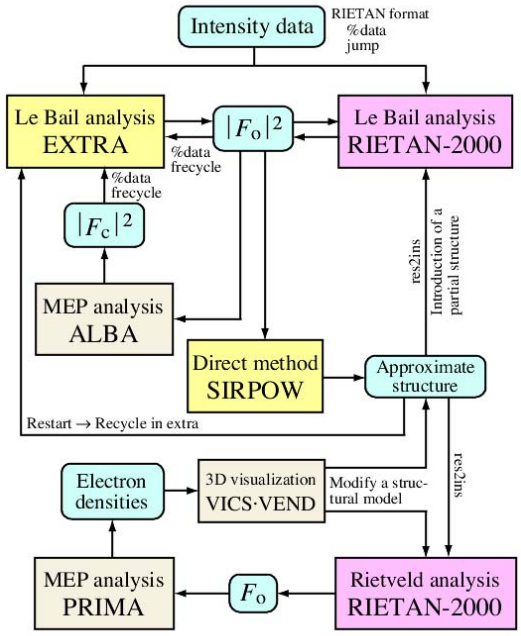

Fig. 6: *Flow chart of ab initio structure analysis with RIETAN-2000—EXPO2004—VENUS*

ALBA outputs a binary file, *.pri, storing 3D Patterson functions, which are, in turn, visualized with VEND (refer to Sect. 3). The resulting 3D images in the unit cell serve for construction of an initial structural model by the heavy-atom method. However, the direct method is preferred to the heavy-atom method because the number of experts in the latter is decreasing more and more.

Most Rietveld-analysis programs have the feature of Le Bail analysis because of the ease with which it can be implemented in this type of software. ALBA allows us to improve $|F_o|$'s of overlapped reflections, adding value to them.

Ikeda and Itabashi [22] have recently determined the structure of a new zeolite RMA-3 from X-ray powder diffraction data measured with Cu $K\alpha_1$ radiation. Integrated intensities resulting from Le Bail analysis with RIETAN-2000 were improved with ALBA and analyzed by the direct method using EXPO to give an initial structure model. Subsequent Rietveld and MPF analyses based on this model revealed a novel framework topology containing two eight-membered ring pore-openings with dimensions of 4.9 × 0.37 Å and 3.4 × 3.8 Å.

7. Concluding remarks

The development of VENUS was motivated by a desire to present the poor with the advanced graphics software; neither expensive graphics workstations nor commercial programs are now necessary for 3D visualization. As described above, VENUS has superior features compared with existing commercial software. VENUS will contribute to a wide variety of studies as a tool for understanding the crystal and electronic structures of materials three-

dimensionally to enhance the creativity of researchers. VENUS may be able to prevent 'phase separation' between experimental and theoretical approaches. Because VENUS is free software, it is ideal for education of crystal and electronic structures for various compounds.

Now, the GUI in GLUT and GLUI is rather old-fashioned because none of them have been updated for quite a long time. K. Momma and one of the authors (F.I.) have been developing successors to VICS and VEND, using wxWidgets as a C++ GUI framework. The new software has tabbed multiwindow browsing as the most pronounced feature. A β version of the structure-drawing program, VICS-II, is available for download on http://www.geocities.jp/kmo_mma/crystal/en/vics.html. This next-generation 3D visualization software will be reported elsewhere.

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