

ICSD-for-WWW, a crystallographic database on the WWW

Draft 20 June 2003

Alan Hewat,

Diffraction Group Leader, Institut Laue-Langevin (ILL), B.P. 156X Grenoble Cedex 9, FRANCE.

Tel: (33) 476.20.72.13; Fax: (33) 476.20.76.48 E-mail: hewat@ill.fr WWW: <http://www.ill.fr/dif/>

Peter Hewat,

Institut National de Recherche en Informatique et en Automatique (INRIA) ZIRST – 655 Avenue de l'Europe, 38330 Montbonnot Saint Martin, France.

Tel: (33) 6.2381.6283; E-mail: hewat@free.fr WWW: <http://hewat.free.fr/>

Since 1997 the ILL Grenoble has provided a WWW interface to the ICSD (Inorganic Crystal Structure Database), making it simpler to use. ICSD is a product of the [Fachinformationszentrum \(FIZ\) Karlsruhe](#), a non-profit organisation of the ILL's German Associate offering more than 200 electronic databases in almost every field of science and technology. FIZ already provided internet access to ICSD and other databases via their STN International service, but this was limited to a simple command-line interface. ICSD also existed at that time as a PC programme, with a rather primitive DOS interface.

ICSD now contains over 70,000 entries describing inorganic structures. The rate of adding new entries has greatly accelerated with the growth of electronic publishing, since journals can now submit the contents of their new issue directly to the database. A new database is issued twice a year, and the latest issue contained over 5000 new entries and corrected another 3000 entries. ICSD is not simply a collection of CIF coordinate files, but contains many other data fields containing information about the conditions of the measurement, the results of various tests for possible errors in the structure, links to electronic versions of the original papers and much more. All entries are checked and re-checked, not only for trivial syntactic errors, but more importantly for reasonable symmetry, bond lengths, coordination, temperature factors, valence sums etc.

[ICSD-for-WWW](#) made it possible for the first time for non-expert users to make complex searches for inorganic crystallographic structures over the internet, without the need to install any special software. Even crystallographers had found it difficult to remember the many commands needed to retrieve information from the old CRYSTIN fortran programme written by R. Hundt & R. Sievers. The WWW-interface generated the CRYSTIN commands from data such as author names and chemical formulae entered into 20 query boxes. Quite complex queries, involving symmetry, bond-lengths and coordination was possible.

Authors <input type="text"/>	Years <input type="text"/>	Remarks <input type="text"/>	S.String <input type="text"/>	Help Reset <input type="button" value="Go"/>
Elements <input type="text"/>	Ele.Count <input type="text"/>	Mineral N. <input type="text"/>	Jrnl Coden <input type="text"/>	ANX Form <input type="text"/>
Laue class any <input type="text"/>	System any <input type="text"/>	Space Gp. <input type="text"/>	Cell vol. <input type="text"/>	Pearson S. <input type="text"/>
Min.dist. <input type="text"/>	Dist.Select <input type="text"/>	Dist.Range <input type="text"/>	Co-ordin. <input type="text"/>	Expert Query For experts

For some years now, several countries have purchased national licenses for ICSD-for-WWW, allowing any scientist within that country unlimited access to the full database over the WWW. For example the Daresbury laboratory provides a national server for the whole of the UK, which services hundreds of users every week. Similar access is available in the Netherlands, Switzerland, Spain, Taiwan etc. Where national licences are not available, laboratory-wide licences have been purchased by, for example, ILL-ESRF, NIST, Oak Ridge, Los Alamos, Sandia, CalTech etc.

In 2001 it was decided to replace the original database with a modern SQL database, and a completely [new version of ICSD-for-WWW](#) was written using PHP-mysql. The new interface was designed to look familiar, but was improved in many ways. The old interface was written in simple HTML-Javascript, even though much of it was generated on-line by a perl CGI. The new interface is generated using the PHP Hypertext Preprocessor, which allows perl-like PHP instructions to be embedded within HTML. PHP is often associated with the popular [mysql database engine](#) which provides complex relational database queries and runs on all popular computer platforms from linux to Windows and Macintosh.

Authors Years Journal Title Help
Elements Element Count Mineral Name ANX Form Search Reset
System Laue Class Space Group Cell Volume Pearson Symbol
Remarks Min. Distance Distance Select Distance Range Density
Co-ordin.

ICSD Help (Close)

Example searches :

- Elements = "Cu O"
- Elements = "Y Ba2 Cu3 O"
- Elements = "Cu O", Title = "supercond"
- Authors = "Ahtee Hewat"
- Authors = "Hewat", Years = "1987-1997", Elements = "Y Ba2 Cu", Element Count = "3-5"
- Years = "1900-2100" (The total number of database entries).

Notes :

- Start by filling in only 2 or 3 boxes. If the number of results is too large, fill in more boxes.
- If your search is too specific, you may miss relevant entries.
- The most useful searches are on 'Elements', 'Element Count', 'Authors', 'Title', ...
- Once the compounds of interest are defined, searches on symmetry, coordination etc can be tried.

Although the new interface looks similar, it is much more powerful, and even easier to use. The titles to the query boxes again contain examples of the query required, but they are now much simpler and drop down beneath the query form when required. To learn to use the interface the user can simply click on these titles, click on an example query, and immediately see the result of that query. If necessary, additional queries can be added and the search repeated.


The user can then order the selected entries according to year, author name, formula, space group or mineral name, select those that appear of interest, and list these references. Direct links to PDF files of the original publication are provided in some cases, notably for IUCr journals. These references can also be exported to the [EndNote](#) personal reference database, which will automatically format them appropriate for citing in a particular journal. The *Details* button can be used to compare several entries, while the *Pattern* button produces postscript or PDF plots with [hkl] labels. Finally, the *Structure* button produces interactive 3D structure drawings in VRML or PDB/Chime format. Again entries can be compared by super-imposing diffraction patterns or structure drawings.

Authors	Years	Journal	Title	Help
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="button" value="Search"/> <input type="button" value="Reset"/>
Elements	Element Count	Mineral Name	ANX Form	Pearson Symbol
Cu+2 O	2	<input type="text"/>	<input type="text"/>	<input type="text"/>
System	Laue Class	Space Group	Cell Volume	Density
any	any	<input type="text"/>	<input type="text"/>	<input type="text"/>
Remarks	Min. Distance	Distance Select	Distance Range	Co-ordin.
<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>

Select All / None 22 Results

Year	Authors	Struct. Formula	sgr	Mineral Name
<input type="checkbox"/> 1922	Niggli, P.	Cu O	C12/C1	Tenorite
<input type="checkbox"/> 1935	Tunell, G.; Posnjak, E.; Ksanda, C.J.	Cu O	C12/C1	Tenorite
<input type="checkbox"/> 1968	Schmahl, N.G.; Eikerling, G.F.	Cu O	FM3-M	
<input type="checkbox"/> 1970	Asbrink, S.; Norrby, L.J.	Cu O	C12/C1	Tenorite
<input checked="" type="checkbox"/> 1978	O'Keeffe, M.; Bovin, J.O.	Cu ₄ O ₃	I41/AMDZ	Paramelaconite

Pages : [1] 2 3 4 5 (22 results) 5 results per page.


PHP/MySQL Interface Designed by Peter Hewat hewat@free.fr 

In the above example, we found 22 entries for copper oxide containing Cu^{2+} . Most are simply CuO of course, but ICSD also found the interesting compound Cu_4O_3 by O'Keeffe and Bovin (1978). The formal copper valence of this compound is 1.5 ! The details below confirm that indeed *Paramelaconite* appears to be a mixed valence compound containing Cu^{1+} on site (8c) and Cu^{2+} on (8d).

1 entry selected.

#49413	<input type="button" value="Pattern"/> <input type="button" value="Structure"/>
Title	The crystal structure of paramelaconite, Cu ₄ O ₃ .
Author(s)	O'Keeffe, M.; Bovin, J.O.
Reference	American Mineralogist (1978) 63 , 180-185
Formula	Cu ₄ O ₃ (Paramelaconite) Dicopper(i) dicopper oxide
Cell	(I41/AMDZ) 5.837(1), 5.837(1), 9.932(2), 90., 90., 90. (V=338.390000)
Refinement	R=0.035000 Remarks : : t PDF 33-480

Atom (site) Oxid.	x, y, z, B, Occupancy
Cu1 (8c) 1.000000	0, 0, 0, ,
Cu2 (8d) 2.000000	0, 0, 0.5, ,
O1 (8e) -2.000000	0, 0.25, 0.1173(9), 0.8(2),
O2 (4b) -2.000000	0, 0.25, 0.375, 0.7(3),

PHP/MySQL Interface Designed by Peter Hewat hewat@free.fr 

To investigate further, we click on the *Structure* button. The drawing of the crystal structure is completely automatic – we do not need to specify which atoms are bonded (although we can if we wish using the *Bonded Atoms* box). We have various other options to draw the structure, but generally we need only click on the *Display* button to obtain a 3D VRML drawing of *Paramelaconite* produced using xtal-3d.

1 entry selected.

Edit the CCSL data, select the **Atoms** and **Bonds** model, and click on **Display**. Choose 2 or more structures to compare them. You may need help with the **3D display** or with special **drawing options**. Most **problems** are due to the **Space Group** representation. **Please check the symmetry operations in the print-out !! (button below).**

```
N *Paramelaconite-Cu4 O3-[I41/AMDZ] O'Keeffe, M.; Bovin, J.O.(1978)
C 5.837000 5.837000 9.932000 90.000000 90.000000 90.000000
S GRUP I 41/A M D
A Cu1 0.000000 0.000000 0.000000 0.000000 0.000000
A Cu2 0.000000 0.000000 0.500000 0.000000 0.000000
A O1 0.000000 0.250000 0.117300 0.800000 0.000000
A O2 0.000000 0.250000 0.375000 0.700000 0.000000
T Cu1 4 0.006600 0.009300 0.002100 -0.002300 0.000000 0.000000
```

PDB/Chime VRML2 Cell At.Names Transparent Black B/G
 Perspective Axes Shaded Title Wireframe Gzip file

Blink time Atoms Bonds

Reference Plane

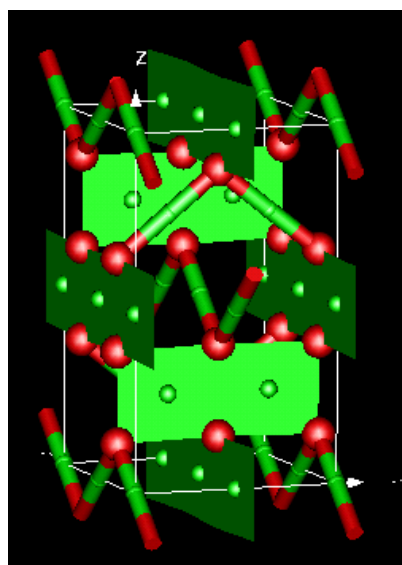
Multiple Cells: x: y: z:

Bonded atoms

Min Bond: Max Bond:

VRML drawing with **x_{tal}-3d** by **Marcus Hewat**.

ICSD shows us that there are indeed two very differently coordinated copper atoms (green) – one at the centre of a square of 4 oxygen atoms (red) and the other with only 2 oxygen neighbours. If we were to select the option to label the atoms we would see that Cu1 had two oxygen neighbours and Cu2 four.



But we can do better ! If we click the *Valence-Sum* button, ICSD displays the Brown-Shannon valence sum for the various Cu-O bonds. We see that the valence sum for Cu1 is indeed 1, while for Cu2 it is 1.51, somewhat less than 2.0. It is not unusual that the valence sum is not a simple integer for all atoms, since coordination is usually a compromise between the relative sizes of the different types of atoms and some bonds are strained. Xtal-3d, which did this calculation, had to automatically decide whether to use the bond-valence parameters R_0 and B for Cu^{1+} or for Cu^{2+} ; it did this by simply trying both and then finding that Cu2 was closer to Cu^{2+} .

Instead of using xtal-3d, we can generate PDB/Chime format, which displays as a simple space-filling model. In either case we must install the appropriate plug-ins to display on Windows or other computers.

```
***** Valence Sums for File=AGre41.ccl *****
Bond-valence sum for Cu1 is 1.00 assuming Ro=1.610 B=0.370 for Cu1+ to O -2
Bond-valence sum for Cu2 is 1.51 assuming Ro=1.679 B=0.370 for Cu2+ to O -2
```

This simple example shows that any scientist, not necessarily a crystallographer, would be able to use ICSD to find compounds containing copper in *mixed-valence* states, and to understand the structure of these compounds with a few clicks of the mouse-button. ICSD is designed not only for crystallographers ! If we have chosen the example of copper, it is because such mixed valence compounds are found as high temperature superconductors, as colossal magneto-resistive magnetites and as many other new materials with very interesting properties. The structures of these materials are often difficult to understand by many non-crystallographers working with them.

But returning to the crystallographers, we can also use ICSD to calculate the bond-lengths (with bond-angles and standard errors if required). Clicking on the *Bonds* button brings up a similar form containing the cell dimensions, space group and atom coordinates. Incidentally, the format used for both structure drawing and bond-length calculations is that of the [Cambridge Crystallographic Subroutine Library](#), which is used for these calculations. These forms can of course be edited to see the effect on the structure of adding or removing specific atoms, or displacing them. The list of Cu-O bonds again shows that Cu1 has only two oxygens at 1.87Å, while Cu2 has two at 1.97Å and another two at 1.92Å.

Bond Lengths and Angles

Edit the CCSL data, specify the bonds to calculate, and click on **Bondla**. Choose 2 or more structures to compare them. Most **problems** are due to the **Space Group** representation. **Please check the symmetry operations in the print-out !! (button below).**

```
N *Paramelaconite-Cu4 O3-[I41/AMDZ] O'Keeffe, M.; Bovin, J.O. (1978)
C 5.837000 5.837000 9.932000 90.000000 90.000000 90.000000
S GRUP I 41/A M D
A Cu1 0.000000 0.000000 0.000000 0.000000 0.000000
A Cu2 0.000000 0.000000 0.500000 0.000000 0.000000
A O1 0.000000 0.250000 0.117300 0.800000 0.000000
A O2 0.000000 0.250000 0.375000 0.700000 0.000000
```

Enter the **maximum** and **minimum** bond lengths and a pair of ions eg **Cu-O** (blank means all ion pairs) and click the **Bondla** button to calculate bond lengths (with angles if required).

Bonds from to Å between atoms with angles ->

PHP/MySQL Interface Designed by [Peter Hewat hewat@free.fr](mailto:hewat@free.fr)

ICSD

Paramelaconite-Cu4 O3-[I41/AMDZ] O'Keeffe, M.; Bovin, J.O.

	Atom1	Atom2	Atom3	Value	Error
Bond	Cu1	O1		1.8673	
Bond	Cu1	O1		1.8673	
Bond	Cu2	O1		1.9663	
Bond	Cu2	O1		1.9663	
Bond	Cu2	O2		1.9159	
Bond	Cu2	O2		1.9159	
Bond	O1	O2		2.5595	

Finally, for the crystallographer, and especially for the Rietveld refiner, ICSD can calculate the powder diffraction pattern for both X-rays and neutrons, or even compare powder patterns for different structures, labelling the [hkl] peaks if required.

1 entry selected.

Edit the data then click on **Plot** to see the pattern. You can plot up to **3 patterns** on the same axes. You may need help setting up to **view postscript files**. Most problems with the **data format** are due to an incorrect **Space Group**, but try switching off the **gzip option** if it is selected below. **Please check the symmetry operations in the print-out !! (button below)**.

```

TITLE *Paramelaconite-Cu4 O3-[I41/AMDZ] O'Keeffe, M.; Bovin, J.(1978)
CELL 5.837000 5.837000 9.932000 90.000000 90.000000 90.000000
SPCGRP I 41/A M D
ATOM CU 1 0.000000 0.000000 0.000000 0.000000 0.000000
ATOM CU 2 0.000000 0.000000 0.500000 0.000000 0.000000
ATOM O 1 0.000000 0.250000 0.117300 0.800000 0.000000
ATOM O 2 0.000000 0.250000 0.375000 0.700000 0.000000
END

```

Technique: X-Ray Diffractometer	Wavelength Custom	Custom Wave. 1.5418 Å
Width Parameters u 0.05 v -0.06 w 0.07	Plot Type 2Theta	2Th.Zero 0 Step 0.1 2Th.Range 0 to 40
<input type="checkbox"/> Labels <input type="checkbox"/> Dispers <input checked="" type="checkbox"/> PDF plot <input type="checkbox"/> Color <input checked="" type="checkbox"/> Gzip	Plots/Page 1	Defaults Plot

Re-plot or Copy the plot file, or Get the profile file, or Print-out the listing.
Postscript plotting using Klaus Yvon et al's **Lazy Pulverix** (Benjamin Nunes, MIT).

PHP/MySQL Interface Designed by Peter Hewat hewat@free.fr

ICSD

*Paramelaconite-Cu4 O3-[I41/AMDZ] O'Keeffe, M.; Bovin, J.(1978)

