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Role of Neutron Diffraction in Identifying Stoichiometry and Nonstoichiometry in the Compounds

Som Datta Kaushik and Anil Kumar Singh

Abstract

In this chapter we introduce stoichiometry and nonstoichiometry from crystal structure point of view along with some examples. We also discussed about the importance of nonstoichiometry in the application oriented research work and their use in the technological applications. We further discuss the ways to identify stoichiometry through various methods. We then introduce neutron diffraction and briefly describe how neutrons and X-ray interacts with matter and the difference in their interaction with matter. We then focus upon its (neutron) usability to identify nonstoichiometry by using some examples available in the literatures. High-temperature superconductivity-based research has seen the importance of neutron diffraction and scattering in identifying the structural modification which leads to superconductivity in the compounds.

Keywords: neutron, interaction with matter, neutron diffraction, neutron scattering, oxygen deficiency

1. Introduction

Stoichiometry in plane Google search is defined as “the relationship between the relative quantities of substances taking part in a reaction or forming a compound, typically a ratio of whole integers.” This points out that stoichiometry has something to do with the formation of a compound. Thus in order to define the stoichiometric compound, we can consider the compound in which the reactant or constituent elements of the compound are in integer numbers. It is usually proposed that stoichiometry follows the law of conservation of mass where the total mass of the reactant element is equal to the total mass of the product, thus leading us to believe that the relations among quantities of reactants and products typically form a ratio of positive integers. This means that if the amounts of the separate reactants are known, then the amount of the product can be calculated. If we take the example of water, the chemical formula of which is H_2O , thus the total mass of water molecule is the sum of the mass of two hydrogen atoms and one oxygen atom. Here, two molecules of hydrogen react with one molecule of oxygen gas to yield two molecules of water. This particular chemical equation is an example of complete reaction. Stoichiometry measures these quantitative relationships and is used to determine the amount of

products and reactants that are produced or needed in a given reaction. Defining quantitative relationships among substances as they participate in chemical reactions is known as reaction stoichiometry. In the example above, reaction stoichiometry measures the relationship between hydrogen and oxygen as they react to water.

We can further define that stoichiometric compounds are those compounds which maintain their stoichiometry or simply maintain the ratio in which they were formed. Here we must understand that stoichiometric compounds can still possess the defects which are termed as intrinsic point defects. As displayed in **Figure 1**, some of the well-known defects are called Schottky (originating due to cation and anion vacancies), Anti-Schottky (due to cation and anion interstitials), Frankel (cation vacancies and interstitials), Anti-Frenkel (anion vacancies and interstitials), and Anti-site defects (originating because of cation and anion swap).

Upon the aforementioned analogy, we can describe the nonstoichiometric compound as antithesis of stoichiometric compounds. Thus we can describe nonstoichiometric compounds as chemical compounds, having elemental composition whose proportions cannot be represented by integers; most often, in such materials, some small percentage of atoms are missing, or too many atoms are packed into an otherwise perfect lattice work. In order to define nonstoichiometry microscopically, a situation of array of atom (shown by the open circle in **Figure 1**) in two-dimensional primitive cubic crystal can be imagined. In such scenario the absence of the atom from the regular place will form vacancy (described as I), displacement of the atom will create Frenkel pair (described as II), and substitution of the atom by another smaller or larger atom (shown by closed circle) can be referred as nonstoichiometry. Nikolai Semenovich Kurnakov along with his students has worked quite significantly on stoichiometry. Kurnakov et al. suggested that the nonstoichiometric compound could be allocated in the categories of berthollides and daltonides depending upon the monotonicity in property and composition correlation. The term berthollide was

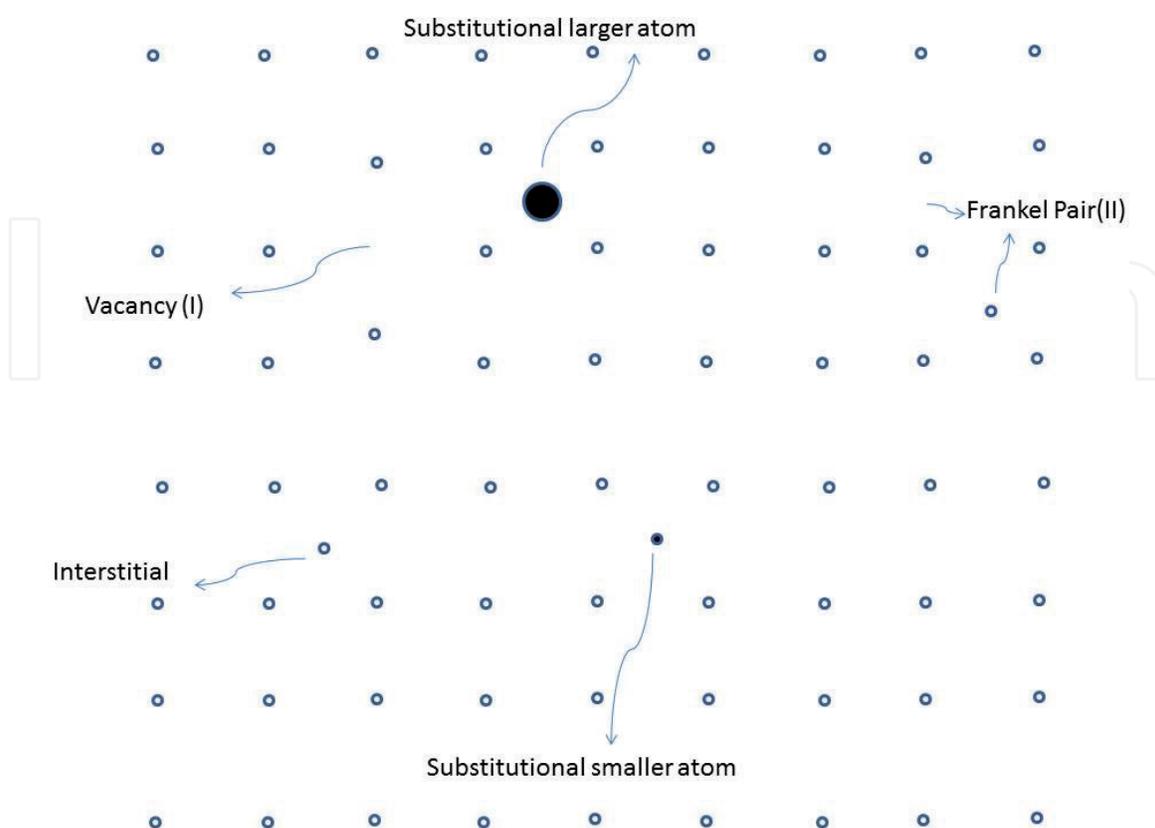


Figure 1.

A two-dimensional arrangement of atoms to describe nonstoichiometry.

recognized by the International Union of Pure and Applied Chemistry (IUPAC) [1]. The name “berthollide” was formed from combination of two well-known chemists of nineteenth century, Claude Louis Berthollet and John Dalton, who proposed the substance composition theories, albeit these theories were in opposite direction and later Dalton’s theory (Law of definite proportions) prevailed with significant exceptions [2]

2. Example of stoichiometric and nonstoichiometric materials and applications

Though it is generally said that nature loves symmetry, it can also be mentioned that stoichiometry is more like a concept in chemistry. In the real world, the naturally occurring stoichiometric materials are not often found. There are few examples of stoichiometric compounds including NaCl, MgO, Al₂O₃, etc. Most of stoichiometry compounds are man-made, while on the other hand in nonstoichiometric compounds, in order to maintain the overall electrical neutrality, the defects are compensated by alternation in the valence state of other atoms present in the solid or by replacing the atom with atom of some other elements with a suitable charge. Many oxides and sulfides of metals are examples of nonstoichiometric compounds; here a rarely found stoichiometric iron(II) oxide, having the formula FeO, is an example of stoichiometric compound; however the more common material is nonstoichiometric compound, having the formula Fe_{0.95}O. Here one should note that, in nonstoichiometric compounds, the type of equilibrium defects can vary with attendant variation, thus resulting in the variation in bulk properties of the material [3]. Sulfides of iron also known as pyrrhotite are also examples of a nonstoichiometric inorganic compound. They have a general formula Fe_{1-x}S (x = 0 to 0.2). The monosulfides of the transition metals (or better known as 3d elements) are often nonstoichiometric. The rare stoichiometric FeS end-member is known as the mineral troilite. Pyrrhotite is remarkable in that it has number of poly types, i.e., crystalline forms differing in symmetry (monoclinic or hexagonal) and composition (Fe₇S₈, Fe₉S₁₀, Fe₁₁S₁₂, and others). Most of the time, the aforementioned materials possess iron deficiency owing to the existence of lattice defects, mainly iron vacancies. In spite of the presence of these defects, the composition of these materials is normally expressed as a ratio of large numbers, and the crystals symmetry is reasonably high. This situation suggests that the iron vacancies in the materials are not randomly scattered over the crystal; rather it forms certain regular configurations. The vacancies significantly modify the magnetic properties of pyrrhotite: the magnetism gets enhanced with the concentration of vacancies and is absent for the stoichiometric FeS [4].

The presence of defects in nonstoichiometric compounds leads to display distinctive electrical or chemical properties; for example, when certain atoms are missing, electrons can travel through the solid more rapidly. Nonstoichiometric compounds are very useful in day-to-day life and found applications in various properties, viz., in ceramic and superconducting material, electrochemical (i.e., battery) system designs, and catalysis-based processing. Various valuable compounds can be produced by the reactions of hydrocarbons with oxygen in which a certain metal oxide acts as catalysis. Under this process transfer of “lattice” oxygen to the hydrocarbon substrate takes place, which temporarily generates a vacancy (or defect,) and subsequently, the missing oxygen is replenished by O₂. Such catalysts depend upon the ability of the metal oxide to form phases that are not stoichiometric [5]. Similar sequence of events describes other kinds of atom transfer reactions such as hydrogenation and hydride sulfurization catalyzed by solid catalysts. These considerations point out that stoichiometry is determined by the interior of crystals: the surfaces of crystals mostly do not follow stoichiometry of the bulk. The complex structures on surfaces are termed as “surface reconstruction.”

A very interesting aspect of nonstoichiometric compound has been seen in high-temperature superconductors (HTSC). Many such HTSC's are nonstoichiometric. For example, yttrium barium copper oxide (YBCO) arguably is the most notable high-temperature superconductor and is a nonstoichiometric solid with the formula $Y_xBa_2Cu_3O_{7-x}$. The critical temperature (often denoted as T_c , which determines the temperature under which compounds become superconductor) of the superconductor depends on the exact value of x . The stoichiometric species has the value of x as zero, but this value can be as high as one. In the subsequent section, we will also deal with such examples. Here it is interesting to note that the identification of stoichiometry/nonstoichiometry in itself is an interesting science.

3. Techniques to characterize stoichiometry and nonstoichiometry

In order to identify stoichiometry, one has to carefully identify the ratio of constituent elements. Previously wet chemical method was employed to identify stoichiometry, but nowadays several advanced techniques are available to ascertain stoichiometry or otherwise. Some of the prominent techniques include high-resolution transmission electron microscope (HRTEM), field emission surface electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDS), etc. Here we will discuss neutron diffraction, which broadly assists in identifying various types of stoichiometry in terms of oxygen deficiencies, anti-site disorder, and cation distribution. There are methods which can be used to estimate stoichiometry by studying the crystal structure as well. X-ray diffraction and neutron diffraction are two such methods. Here neutron diffraction is a more powerful technique than X-ray diffraction. We will try to understand it in terms of various examples explained in subsequent sections. Here before going further, it would be interesting to understand how the neutron interacts with the matter.

4. X-ray and neutron diffraction techniques and neutron interactions with matter

X-ray diffraction (XRD) has been a very popular technique to identify the crystal structure due to more accessibility in terms of various parameters such as economics, portability, and hassle-free operation and thus has more prominently been described in the materials science books than neutron diffraction. Basic principles of X-ray as well as neutron scattering and neutron diffraction along with its usage in characterization technique of materials have been the subject matter of several excellent books which can be consulted for details [6–15]. Broadly neutrons interaction with matter can be defined in variety of ways due to which neutron diffraction seems similar to and but different from X-ray diffraction. First of all a neutron is a chargeless particle. The chargeless state of neutron assists to penetrate deep into the material, approximately up to the atomic nuclei which looks like a point in the whole material. In this scenario nuclear scattering takes place at very short distances of close to 10^{-14} – 10^{-15} m; due to this scattering form, an ordered crystalline material yields coherent Bragg scattering. This Bragg scattering produces the intensity in the form of various Bragg's reflections corresponding either in single-crystal or in the powder diffraction pattern. These results are more or less similar to X-ray diffraction and provide essentially the same structural information. However, there is a point to be noted that the elemental scattering lengths for X-ray and neutron are distinctly different. The reason lies in the fact that X-ray diffraction results from scattering by the electrons; thus atoms of nearby atomic number exhibit

very similar scattering which make practically difficult to distinguish between the nearby atoms by X-ray diffraction. On the other hand, neutron scattering depends upon the nature of the scattering nuclide, and consequently, atoms of similar atomic number often have quite different neutron scattering lengths (Figure 2).

The difference in scattering length is also apparent in Table 1, for some of the important transition metals. In addition to this, it is also to be noted that for neutron scattering the integrated intensity is independent of scattering angle (θ), while for the X-ray scattering, it is highly dependent upon the scattering angle. This difference can be observed in the angular dependence of the form factor for the different scattering processes (Figure 3).

This can be observed in the peak intensity for X-ray diffraction and neutron diffraction pattern. For X-ray diffraction pattern peak, intensity gradually decreases as scattering angle increases, while for the neutron diffraction, it is not the case. This situation helps in extracting the comprehensive information post analysis of neutron diffraction data.

The major factor is the fact that the neutron possesses the magnetic moment, because of this, the neutron is also scattered as a result of interaction with magnetic ion (in ordered form) present within a material; thus in the resultant coherent scattering, the magnetic scattering is superimposed upon the nuclear scattering in such magnetic material, though this magnetic scattering may not certainly affect the orientation of spin of the neutron, but since the magnetic neutron scattering consists of interaction with spin and orbital components of the magnetic moments, thus resultant moments originate from all the unpaired valence electrons. Here one should note that the magnetic scattering has an angular dependence which is similar to that of X-ray scattering by electrons as shown in Figure 3. This situation is opposite to the nuclear scattering, where the nuclear scattering is independent of scattering angle as displayed in Figure 3 in which the typical angular dependence of the spin, orbital, and nuclear form factors for neutron scattering by chromium is shown, and for comparison, the form factor for X-ray scattering is also depicted. In order to identify the magnetic and nuclear neutron scattering, angular dependence

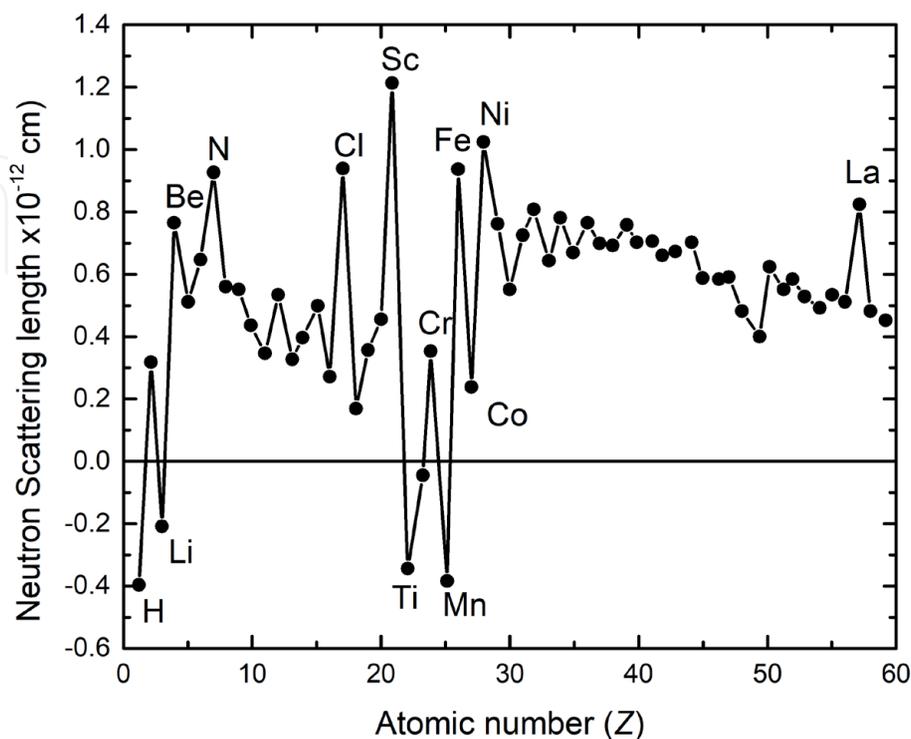


Figure 2.
The elemental scattering length behavior.

Element	Proton	Isotope	X-ray scattering ($10^{12}b_x/\text{cm}$)	Neutron scattering ($10^{12}b_{\text{coh}}/\text{cm}$)	Coherent cross section σ_{coh} (barn)	Incoherent cross section σ_{inc} (barn)	Absorption cross section σ_a (barn)
Hydrogen	1	1	0.282	-0.374	1.758	79.7, 80.27	0.33, 0.383
Hydrogen	1	2	0.282	0.667	5.592	2.0, 2.05	0.0005
Boron	5	Natural		0.530	3.54	1.70	767.0
Carbon	6	12	1.69	0.665	5.550	0.0, 0.001	0.0035, 0.004
Nitrogen	7	14	1.97	0.936, 0.940, 0.94	11.01	0.3, 0.5	1.9
Oxygen	8	16	2.16, 2.26	0.580, 0.58	4.232	0.0, 0.000	0.00019, 0.0002
Aluminum	13	Natural		0.345, 0.35	1.495	0.0, 0.008	0.23, 0.231
Silicon	14	Natural		0.42		0.0	0.17
Phosphorus	15	30	3.23	0.510			
Sulfur	16	32	4.51	0.280, 0.28			
Titanium	22	Natural		-0.344, -0.34	1.485	2.87, 3.0	6.09, 6.1
Vanadium	23	Natural		-0.038	0.018	5.07	5.08
Chromium	24	Natural		0.364	1.66	1.83	3.05
Manganese	25	55 (Natural)		-0.373	1.75	0.4	13.3
Iron	26	Natural		0.945, 0.95	11.22	0.4	2.56, 2.6
Nickel	28	Natural		1.03	13.3	5.2	4.49
Copper	29	Natural		0.772	7.485	0.55	3.78
Zirconium	40	Natural		0.716, 0.72	6.44	0.02, 0.3	0.18, 0.185
Niobium	41	93 (Natural)		0.7054	6.253	0.0024	1.15
Molybdenum	42	Natural		0.672	5.67	0.04	2.48
Cadmium	48	Natural		0.487	3.04	3.46	2520
Tin	50	Natural		0.623	4.87	0.022	0.626
Cerium	58	Natural		0.48		0.0	0.63
Gadolinium	64	Natural		0.65	29.3	151	49,700
Tantalum	73	Natural		0.691	6.00	0.01	20.6

Table 1.

Neutron scattering length and cross sections of certain elements along with their isotopes.

giving the indication is one way in which these can be distinctly identified. Other potential methods would be to study the magnetic scattering as a function of temperature or the use of polarized neutron scattering.

For certain nuclei the neutron actually interacts with the nuclide and forms a short-lived compound nucleus, which results in isotropic incoherent scattering with a negative scattering length; such interaction may potentially be associated with alteration in neutron spin. Neutron scattering by hydrogen atom falls in a special case where incoherent scattering is especially strong because the scattering proton can have either the same or opposite spin as compared to the scattered neutron [16].

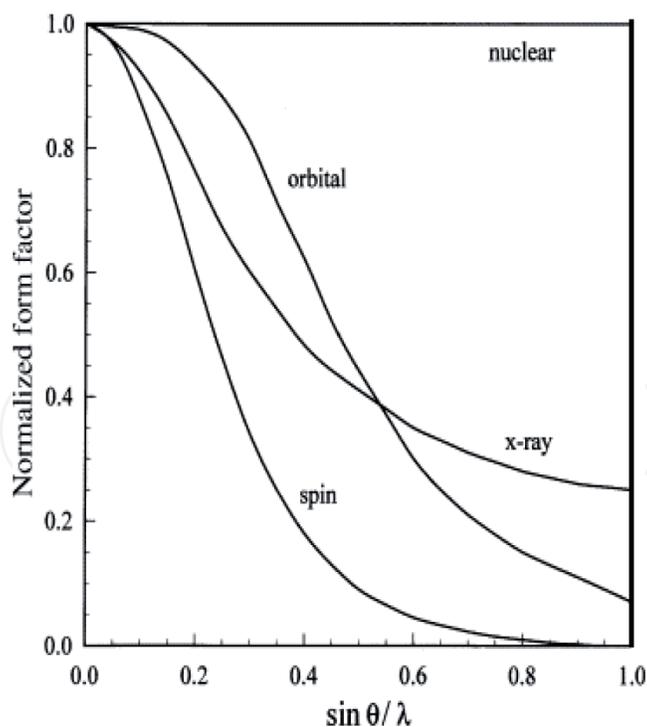


Figure 3.
The scattering length dependence on scattering angle.

These two different types, singlet or triplet scattering, lead to strong incoherent scattering by hydrogen. Interestingly, this does not apply to neutron scattering by deuterium (which is an isotope of hydrogen), and due to this reason, many neutron diffraction studies require the replacement of hydrogen by deuterium.

Another interesting aspect is pertaining to the isotope behavior; for most of the isotope atoms, the neutron scattering lengths and cross sections usually have different values as compared to their parent atom. This is in fact an added advantage which assists in understanding the compound with neutron-absorbing materials or getting the contrast in the intensity. Here we have reproduced the scattering lengths and cross section of some important atoms along with their isotopes in **Table 1**. In order to explain it, we have considered the case of nickel (Ni); the values for the different isotopes of nickel are given in **Table 1** along with that of natural abundance nickel. The differences in scattering lengths for nickel isotopes given in **Table 1** show that different but pure isotopes may be utilized to provide contrast with other elements in a compound, such contrast in the intensity is not possible to obtain with X-ray diffraction [16].

5. Neutron diffraction as probe in studying nonstoichiometry in superconductivity

The advent of cuprate-based superconductors in the late 1980s and early 1990s and the superconductivity in iron-based superconductors in the first decade of the twenty-first century created the flurry in the research in such compounds. In some of the superconducting series, the oxygen deficiencies created a significant role, and neutron diffraction played a significant role in identifying the extent of oxygen. Many superconductors are nonstoichiometric. One such example of yttrium barium copper oxide superconductor was described in earlier section.

In [17], Rupp et al. have mentioned the importance of neutron diffraction in cuprate superconductors. Their neutron diffraction data on YBCO revealed that on approaching toward low equilibrium oxygen concentrations, two different structural effects occur concurrently: first the Cu-O plane-chain bond length increases without

a significant alteration in the planes or significant vacancies on the O(1) apex atom site, and second the O(4) atoms point out toward large anisotropic vibrations perpendicular to the b-axis or large static displacements from the ideal position on the b-axis. It is also pointed out that the Cu-O planes does not get affected on approaching low oxygen concentrations; it was further emphasized that in YBCO, the whole coupled Cu-O plane-chain system is responsible for the superconducting properties.

In another study by Ohshima et al., on [18] $\text{TlSr}_2\text{CuO}_y$, they could model the crystal structure of $\text{TlSr}_2\text{CuO}_y$ as orthorhombic; they also found that oxygen vacancies are formed along the *a* direction in a CuO_{2-z} sheet, which is consistent with a superstructure of doubling of the subcell along the b-direction. It was also found out that the structure involves CuO_6 octahedra and CuO_4 square planes alternating along the b-direction by sharing their corners in accordance with TlO ordered oxygen vacancies in the CuO_{2-x} layer as has been presented in **Figure 4** as suggested by authors. An apical oxygen atom in the CuO_6 octahedron is closer to a TlO layer than an oxygen atom shared by a TlO_6 octahedron and the CuO_4 plane as has been depicted in **Figure 5** here. The oxidation state of Cu in $\text{TlSr}_2\text{CuO}_y$ was evaluated to be 2.12 from the neutron diffraction analysis.

In [19] the simultaneous addition of CaO and CuO along with Dy^{3+} substitution in nonsuperconducting $\text{La}_2\text{Ba}_2\text{Cu}_4\text{O}_z$ compound started showing the signature of superconductivity. Rayaprol et al. used room temperature neutron diffraction in this resultant compound $\text{La}_{2-x}\text{Dy}_x\text{Ca}_{2x}\text{Ba}_2\text{Cu}_{4+2x}\text{O}_z$ (or written as La 125 further in the text) and ascertained that the holes at La^{3+} sites are created by substitution of Ca^{2+} at La^{3+} which led to bring the two CuO_2 sheets and hence induced the superconductivity in the La-2125 compound. The typical obtained crystal structure is shown in **Figure 6**.

Tranquada et al. and reference therein in their current perspective on superconductivity, antiferromagnetism, and neutron scattering [20] have also emphasized the importance of neutron scattering in superconductors. They underlined the fact that the high-temperature superconductivity in both the copper oxide and the iron-pnictide/chalcogenide systems occurs in close proximity to antiferromagnetically ordered states. Neutron scattering has proven to be an essential technique for characterizing the spin correlations in the antiferromagnetic phases and for demonstrating how the spin fluctuations persist in the superconductors. While the nature of the spin correlations in the superconductors remains controversial, the neutron scattering measurements of magnetic excitations over broad ranges of energy and momentum transfers provide important constraints on the theoretical options.

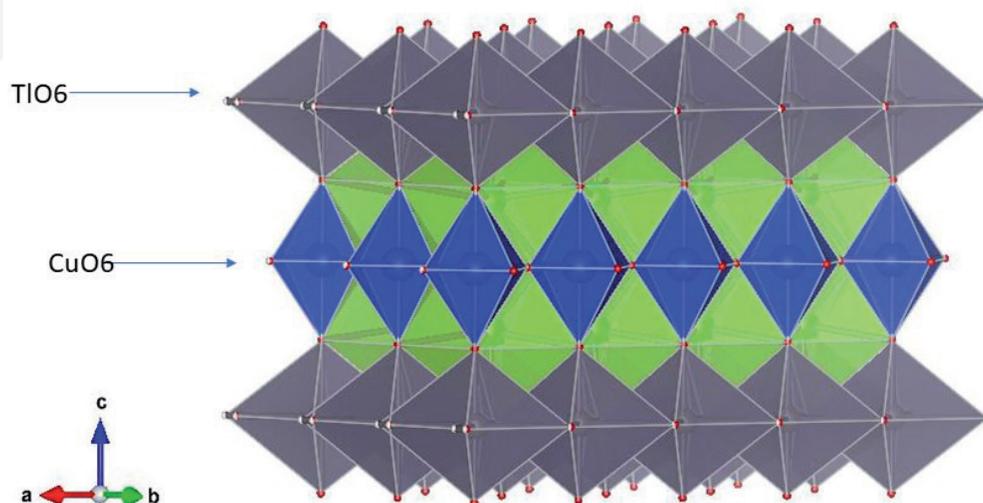


Figure 4.
Crystal structure of $\text{TlSr}_2\text{CuO}_y$.

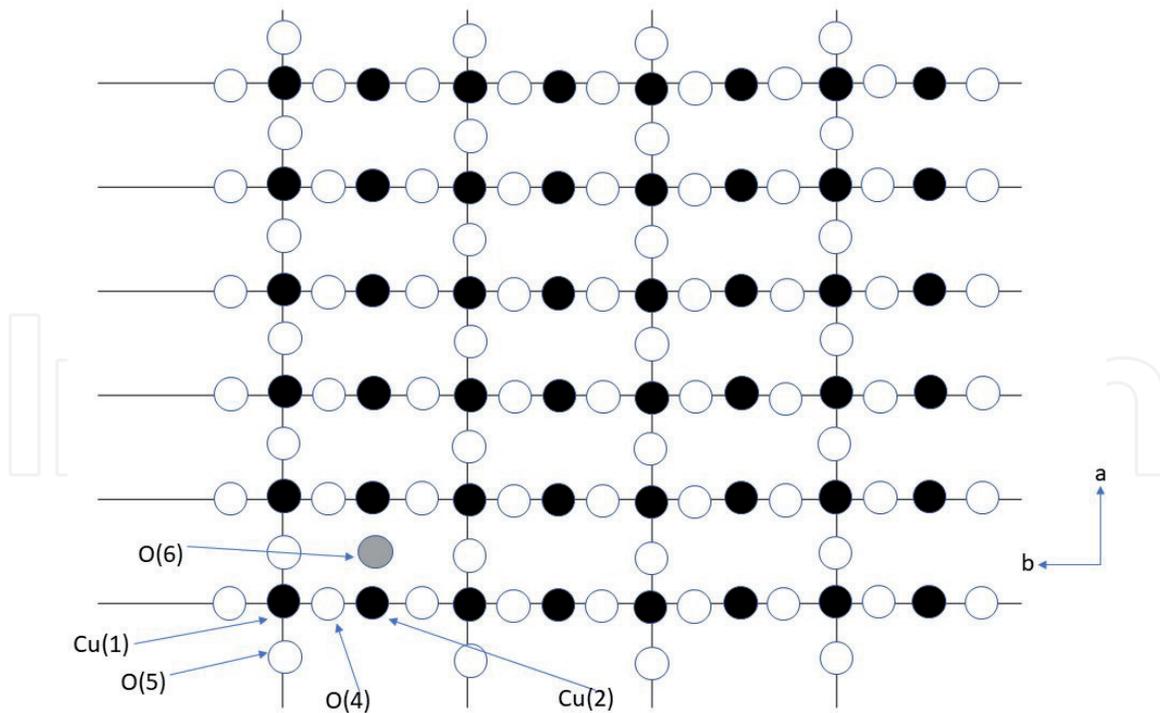


Figure 5.
 Copper and oxygen arrangement on CuO_{2-x} layer in $\text{TlSr}_2\text{CuO}_y$.

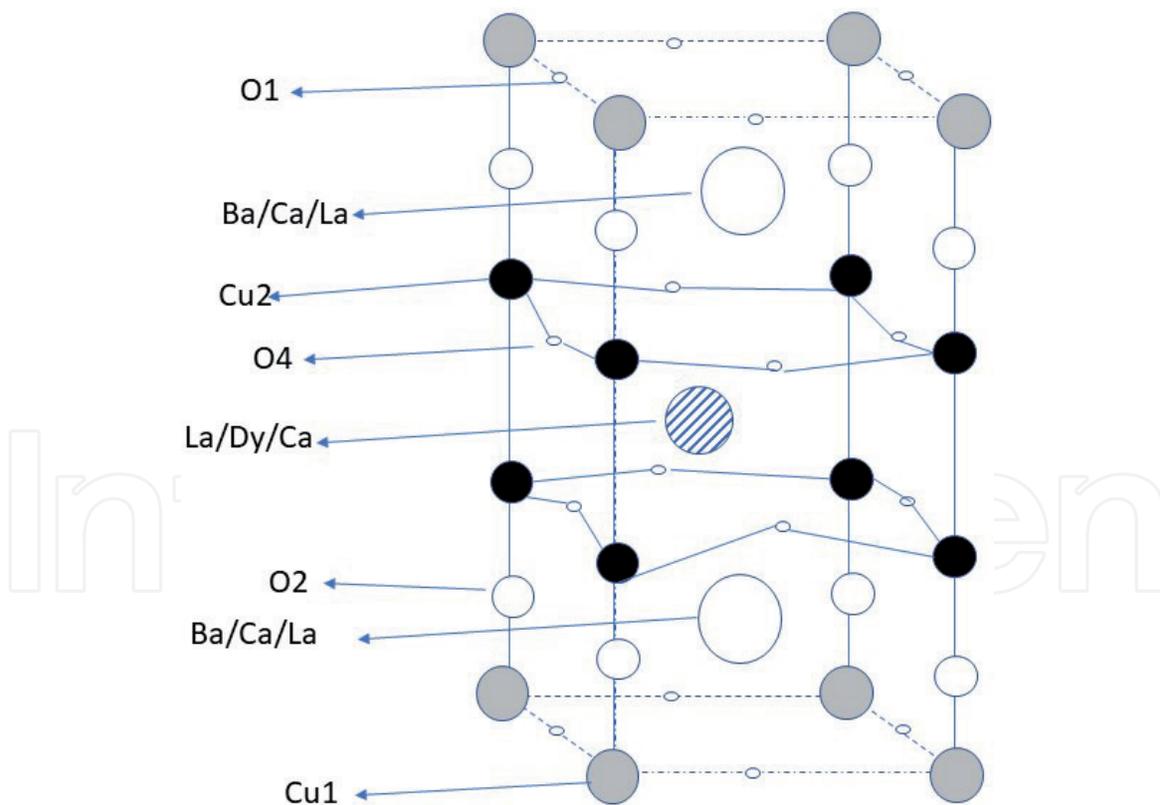


Figure 6.
 La-2125 unit cell showing the CuO layer and oxygen atom position.

In a recent study on iron-based superconductor, the parent LnOFeAs ($\text{Ln} = \text{La}, \text{Sm}, \text{Ce}, \text{Nd}$ and Gd) was found to show spin density wave below 150 K due to Fermi surface associated with tetragonal structure to transform into orthorhombic symmetry. Addition of the electron into $\text{Ln}(\text{O}, \text{F})\text{FeAs}$ or a hole in the $(\text{La}, \text{Sr})\text{OFeAs}$ layer modify the Fermi surface; thus superconductivity could be introduced.

The neutron scattering study helped in calculating the electron–phonon coupling in $\text{LaO}_{0.87}\text{F}_{0.13}\text{FeAs}$ sample; the spin density wave (SDW) could not be detected [21]. So with the help of neutron scattering experiment, it could be established that the order parameters pertaining to SDW and superconductivity are competing for itinerant holes and electrons on the Fermi surface in $\text{La}(\text{O},\text{F})\text{FeAs}$ compound.

Some more examples: The structure and chemical order of a Ni-Mn-Ga Heusler alloy of nonstoichiometric composition were studied using constant-wavelength (1.538 Å) neutron diffraction at 363 K, and the diffraction pattern was analyzed. At this temperature the structure is austenite (cubic) with Fm space group and lattice constant of $a = 5.83913(4)$ [Å]. The chemical order is of critical importance in these alloys, as Mn becomes antiferromagnetic when the atoms are closer than the radius of the 3d shell. In the studied alloy, the refinement of the site occupancy showed that the 4b (Ga site) contained as much as 22% Mn; that significantly alters the distances between the Mn atoms in the crystal and, as a result, also the exchange energy between some of the Mn atoms. Based on the analysis, the composition was determined to be $\text{Ni}_{1.91}\text{Mn}_{1.29}\text{Ga}_{0.8}$ [22].

In [23], Paulus et al. have used single-crystal neutron diffraction technique to understand the structural evolution of electrochemically oxidized $\text{La}_2\text{NiO}_{4+\delta}$ crystals as a function of temperature and the oxygen intercalation and to better understand the disorder of the apical and interstitial oxygen atoms. The structural evidence were found not to attribute a peroxide character between the apical and interstitial oxygen atoms situated in exactly $(1/4, 1/4, 1/4)$ of the $F4/mmm$ unit cell. They could also reinvestigate the structural phase transition of stoichiometric La_2NiO_4 crystals at 74 K. It was also observed that the symmetry changes from Bmab to Pccn and remains orthorhombic down to 5 K.

6. Conclusion

In summary, we have explained stoichiometry and nonstoichiometry in the compounds along with some of such examples and their applications. These interesting compounds are also explained from the structural point of view. The characterization of such compound in itself is interesting science. Employing neutron to probe such compound has proven to be an effective tool in identifying this phenomenon with more clarity. In order to understand the technique, the interaction with matter was discussed in brief. The importance of these neutron-based diffraction and scattering techniques has been explained with the help of some examples discussed above.

Author details

Som Datta Kaushik* and Anil Kumar Singh
UGC-DAE Consortium for Scientific Research Mumbai Centre, BARC, Mumbai,
India

*Address all correspondence to: sdkaushik@csr.res.in

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