



A centennial: Evolution in the understanding of chemical ordering in metallic crystals



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ABSTRACT

Many important metallic alloys are characterised by the chemical ordering of their atomic component elements. Examples are beta brass (βCuZn – one of the components of common brass), many of the gold-base alloys used in dentistry, Nickel–Titanium shape memory alloys with superelastic properties (great stretchability, as used for orthodontic wires) and Nickel–Aluminium gamma-prime phase which strengthens superalloys for high-temperature turbines. The figure shown below (Fig. 1) represents such an ordered arrangement of two atomic species (could be copper and gold, or nickel and aluminium) on a face centred cubic lattice. The disordered lattice would have the yellow and blue atoms randomly distributed.

While such important materials, the realisation that these crystals are chemically ordered (in contrast to chemically-disordered alloys, such as alpha brass (αCuZn), steels, aluminium alloys, and most other metallic alloys) is a relatively new understanding, being just now one century old. It had been understood for a long time before that crystals contained spatially-ordered atoms, but not that there was chemical order hidden inside. It was only with the development of methods of diffraction of x-rays by crystals that it became possible to recognise and quantify such chemical order.

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1: 1912

Von Laue published his text on the diffraction of x-rays, to be regarded as waves, by crystals [1,2]. In his later Nobel prize address [3], he refers to the first public presentation to the Munich Academy in June 1912 of his work together with Friedrich and Knipping on the successful diffraction of x-rays. This presentation was made by the famous scientist Sommerfeld, his supervisor during his time as Privatdozent at the Ludwig Maximilian University of Munich.

X-rays had been discovered in 1896, but it was not thought that they could be regarded as waves since there was no evidence of refraction or diffraction (as understood from studies of light). Measurements of the energy of the x-rays suggested that they would have a small wavelength (if indeed they were waves) of the order of one Angstrom. But where could one find a lattice of such small dimensions?

Since about 1850, Bravais [4] had established the idea of crystals having regular atomic arrangements in three dimensions, as three dimensional lattices or space lattices. Such ideas had developed

from studies of the many symmetries of crystalline materials. Von Laue proposed using such a small lattice for experiments on diffraction. He obtained a fine, collimated x-ray beam by passing it through some lead sheets with a fine hole, and then passing it onto a well-oriented crystal with a sensitive film behind. A series of aligned spots was obtained, which was explained by the arrangement of diffracting planes in the crystal. Such a result confirmed that x-rays could indeed be considered as waves of very small wavelength and the diffraction observed depended on the position of atoms in the crystal, so it should be possible to analyse crystal structures.

It is interesting to note that Von Laue considered that complex crystals were made up of either atoms or molecules of the chemical sub-unit with these forming a three-dimensional grating, with each atom/molecule vibrating to emit secondary radiation, which then superposed to generate the resulting diffraction pattern. He was aware that crystals contained a regular arrangement of matter on lattice sites, but did not consider chemical ordering.

In November of the same year, the Braggs (father and son) presented their work on the diffraction of x-rays by crystalline planes at the Cambridge Philosophical Society. This work was not published until the following year.

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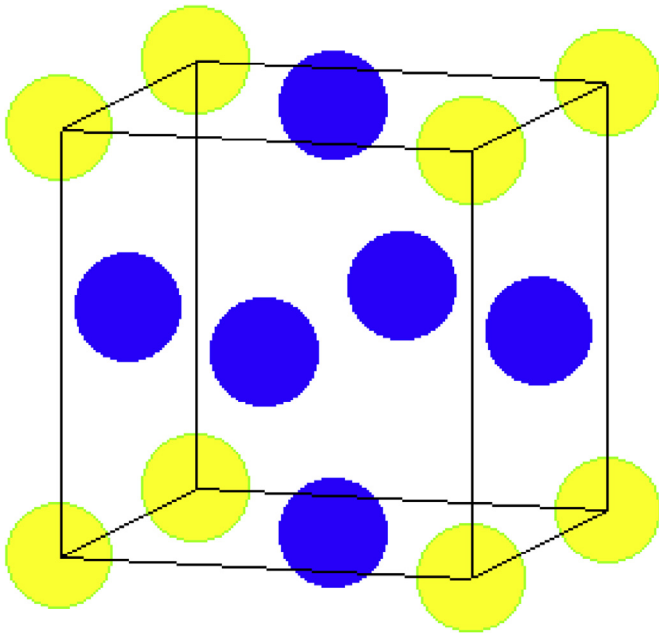


Fig. 1. Ordered arrangement of blue and yellow atoms on a face centred cubic lattice (as for copper and gold, or nickel and aluminium) to create the so-called $L1_2$ crystal structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2: 1913

The Braggs (William Lawrence – son, and William Henry – father) published their work which offered an easy method for understanding x-ray diffraction as reflections produced by crystal planes [5,6]. The basic theory of diffraction of x-rays by crystals had been developed by Von Laue, but required complex calculations to understand crystal structures. WL Bragg pointed out that diffraction could be pictured as reflection by parallel planes in the crystal leading to a simple relation between the diffraction angle, the wavelength of the x-ray waves, and the separation of the planes. This allowed very simple analysis of crystal structures, but also suggested a simple method based on reflection from the crystal planes for easy experimentation. Such an x-ray spectrometer was developed by WH Bragg which made diffraction analysis a very simple experimental technique.

Their first studies had examined alkaline halides, such as Potassium Bromide, with simple structure, and they found the reflections corresponding to the face centred cubic lattice. Further analysis by Bragg [5,6], including other salts such as Sodium Chloride, showed that the structure was composed of two interpenetrating face centred cubic lattices to produce an overall simple-cubic lattice. This confirmed that these crystals consisted of atomic lattices, not molecular lattices, as had been previously assumed. Even though the concept of order was not considered, this work indeed showed that the halide crystals were not molecular crystals but composed of two interpenetrating ionic lattices. This concept was not immediately applied to metallic alloys since it was thought that the strong ionic bonding inside these halides was the reason for the formation of the complex superlattice.

3: 1914

Max von Laue was awarded the Nobel prize for the discovery of the diffraction of x-rays by crystals [3]. Not only did his work confirm that x-rays could be treated as waves but also it confirmed

that crystals were regular arrangements of atoms.

In the same year, Cecil H Desch from the University of Glasgow published his long book on the examination, structure and properties of Intermetallic Compounds [7]. His book summarised the understanding of intermetallic compounds at that time, based on almost a century of work by chemists examining the alloying of different elements. There was now a lot of thermal analysis data that demonstrated that compounds could sometimes form between metals. Metallography could distinguish whether a phase mixture was present, and physical properties could be followed to study the evolution of intermetallic compounds with temperature or composition. The internal atomic structure was, however, poorly understood. The basic idea seemed to be that the crystal contained compounds, or molecules, of the intermetallic phase. The number or type of such molecules could change with composition or temperature, but there was little idea that such molecules were placed on crystalline lattices.

In the middle of the previous century, Rudberg [8] was possibly the first to define the term chemical alloy, or compound, based on studies of the variation of the temperature of fusion of various alloys with composition. Compounds between Silver and Copper [9] were deduced to be present from variations of their temperature of fusion, and similarly for some alloys of Zinc and Copper [10] based on colour changes on mixing these elements. Calvert and Johnson [11] saw changes of physical properties such as conductivity, hardness or density on alloying, while Matthiessen [12] used physical properties to develop understanding of the causes of property variations within phases or phase mixtures. By the first decades of the twentieth century hundreds of intermetallic compounds had been discovered. Metallography had become a major tool for distinguishing whether phase mixtures were present, with one of the important workers being Tammann at the Institute of Inorganic Chemistry at the University of Göttingen in Germany, from the beginnings of the century. At the same time, thermal analysis, that is studying freezing temperature changes, even sudden jumps in the initial or final melting temperatures, led to the development of equilibrium diagrams which defined composition regions where intermetallic compounds could be found. Such understanding was clearest with mixtures of non-ideal metals, for example compounds of Silver with Magnesium or Bismuth with Thallium, as seen by Tammann [13]. Things were more difficult when dealing with continuous solutions or where ideal metals were considered, as for example in the Copper–Zinc alloys where the Cu_2Zn_3 compound was clearly identified but the beta CuZn compound remained hidden to the experimenters. From such freezing temperature studies a sharp increase near a particular composition ratio was a clear signal of the presence of an intermetallic compound, understood as a compound molecule forming with that composition. Another important worker in this area was the Russian Kurnakov [14,15] who made significant contributions to the use of physical property measurements to analyse chemical compounds and determine the corresponding phase diagrams. He pointed out that singularities in physical property variations could be used to detect the appearance of intermetallic compounds. Metallography was useful for confirming the presence of such distinct phases, with phase mixtures seen for compositions outside that permitted by the single-phase compound. At the same time the chemical properties (ease of chemical attack), the mechanical properties (hardness, scratchability or brittleness), and the physical properties (conductivity, ferromagnetism) were often found to change abruptly near critical compositions, confirming the idea of specific compound compositions. It was difficult at this time to obtain pure, single-phase compounds in many systems, and considerable development of the processing methods for obtaining good samples was required before understanding of properties

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