

Teaching general chemistry, solid-state chemistry and crystallography in one comprehensive undergraduate course: can the effect be synergistic?

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This contribution describes a 30-year experience of teaching a general course in solid-state chemistry for undergraduates, which introduces at the same time the main concepts of crystallography, gives an introduction to structure analysis techniques, and makes links to courses in inorganic chemistry, organic chemistry and biochemistry. Such a combination can be beneficial for bringing the fundamentals of crystallography (basics and techniques) closer to its 'users' – chemists, materials scientists, biologists – and can be considered as an attempt to create a course in 'applied crystallography'. The aim of the course is to teach chemists which chemical information can be retrieved from a crystal structure and how. This is complementary to more generally accepted courses, which teach how to obtain structural information and to describe crystal structures.

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1. Introduction: why did such a course appear?

In the 1970s, the Novosibirsk State University became the first university in the USSR to start teaching solid-state chemistry as a general course for all chemistry undergraduates. There was a need to train students in the fields of the reactivity of solids, materials science and mechanochemistry. The course in solid-state chemistry could be introduced only on the condition (the formal condition coming from the administration) that it included at the same time the elements of crystallography and the basics of structural analysis. It was necessary to fit many different topics into the same course, maintaining the coherence of the course and keeping it interesting not for professional crystallographers but for chemists, materials scientists and biochemists – the 'users' of crystallographic information. As we moved ahead with developing an approach to teaching the basics and techniques of crystallography adapted to chemists, it became clear that our experience of teaching 'applied crystallography' may be of interest for a broader audience. Nowadays, everywhere in the world more attention is paid to chemistry, biology and materials science than to 'classical crystallography', which is sometimes considered as boring and 'too scholastic' (this is not justified, but we have to work hard to overcome this attitude). We have already described the course at its early stage of development (Boldyreva, 1993a), but it has been greatly extended and modified since that time, as solid-state science and crystallographic tools have progressed. In the present contribution I shall try to give a few examples of how teaching crystallography can 'penetrate' into other chemistry courses and, in turn, how it can borrow concepts and approaches from other disciplines. Appendix A¹ contains the outline of the

course (54 academic hours of lectures and 54 academic hours of practicals), and in the main text of the paper I shall just briefly comment on the key points and give a few examples as illustrations. Selected examples of slides used in lecture presentations are deposited in Appendix B. Since our course is multi-disciplinary in its nature, it is not possible to use a few books only when preparing lectures and practicals. We use many original publications, permanently updating the examples. A full list of references that may help an interested reader (sorted according to topic, to facilitate navigation) is deposited as Appendix C.

2. Structures first, crystallographic concepts afterwards

Most textbooks on crystallography start with patterns, an introduction to symmetry elements, symmetry operations, symmetry groups, lattices, unit cells *etc.* Even though the patterns are beautiful, the symmetry concepts are really exciting and the group theory impresses with its power, chemistry students usually do not consider this material as relevant to their basic interests and are not motivated enough to study it if a course starts with this material. Therefore, rather than starting in a traditional way, we first let our students observe and enjoy the structures 'as given', widely using the modern visualization tools *Mercury* (Bruno *et al.*, 2002; Macrae *et al.*, 2006; http://www.ccdc.cam.ac.uk/free_services/mercury/), *Diamond* (<http://www.crystalimpact.com/diamond/>) and *PowderCell* (Kraus & Nolze, 2000), and the structural databases, namely the Cambridge Structural Database (Allen, 1998, 2002; Allen & Motherwell, 2002; <http://www.ccdc.cam.ac.uk/>), the Inorganic Crystal Structure Database (Allmann & Hinek, 2005; Belsky *et al.*, 2002; Bergerhoff & Berndt, 1996; Kaduk, 2002; <http://cds.dl.ac.uk/cds/help/icsd.html>), CrystMet (Le Page *et al.* 2002; White *et al.*, 2002; <http://www.tothcanada.com/databases.htm>) and the Protein Data Bank (Berman, 2008; <http://www.rcsb.org/pdb/home/>

¹ The appendices of this paper are available from the IUCr electronic archives (Reference: KK5073). Services for accessing this material are described at the back of the journal.

home.do). The main idea of this approach can be summarized as follows: let students first see the variety of structures in relation to the properties of chemical species forming these structures; teach them how to retrieve ‘chemical information’ from the data on a known structure stored in a standard format in a database using ‘user-friendly’ software; after that discuss how a structure with so many atoms can be ‘encoded’ in a very concise way and then ‘decoded’ when needed, thus introducing the basic concepts of crystallography. Subsequently, at a new level, we discuss the relation between crystal symmetry and physical properties, and the relation between crystal structures and solid-state transformations. At the final stage we give an introduction to the basics and practical applications of diffraction techniques: structure solution and refinement using single-crystal and powder samples, phase analysis, monitoring transformations in time and space, analysing stress, particle size and defects, and studying chemical bonds and excited states. We focus on chemical applications of diffraction techniques and on validation of results, since the course is taught to future users – only very few of them will perform the analysis themselves. Still, the users must be well trained to consider the results critically and to be able to see the signs of potential errors. This is why we discuss structure analysis at the final stage of the course, after the relations between physical properties and crystal structure have been considered – the knowledge of physical properties can help to avoid mistakes in structure solution. This sequence of topics (Table 1) has proved to keep chemistry students ‘alert’ during the classes and leads to them not considering crystallography as a subject that is far from their main field. A one–two-week ‘delay’ in teaching the crystal symmetry and basics of crystallography because of this preliminary ‘playing’ with the structures and considering them at an ‘intuitive level’, exploiting basic chemical knowledge, is more than compensated by students’ interest and motivation.

The first, introductory, block of lectures, ‘What can a structure teach us about chemical interactions?’, thus includes the following topics: (i) Structures of elements. Interrelation between the electronic structure of an element and the crystal structure. (ii) Structures of compounds. How often do we deal with ‘inorganic molecules’? (iii) Structures of organic crystals. Chemical bonds and noncovalent interactions. (iv) Chains, layers and three-dimensional networks in inorganic and organic structures. Framework structures.

2.1. Structures of elements

The first part of the module gives an overview of numerous very different structures in relation to the properties of elements on one side and to the properties of the solid as a whole (conductivity, colour, hardness *etc.*) on the other. We start with considering the periodic table of elements, and the students are asked which of the elements can form solids. It is at this very early point of the course that we discuss the role of temperature/pressure (T,P) conditions in defining the state of an element or a compound, and the effect of T,P on the crystal structures. Then we proceed by considering the crystal structures of elements in a systematic way, starting with the noble

Table 1

A comparison of the sequences of topics in a ‘traditional’ crystallography course and in our combined course of solid-state chemistry and crystallography.

‘Traditional’ crystallography course	Combined course (crystallography + solid-state chemistry)
Basics of symmetry.	Preliminary consideration of the variety of structures prior to gaining any crystallographic knowledge: exploiting general chemistry knowledge (‘intuitive structural chemistry’). Databases and computer visualization tools.
Structure solution techniques.	Basics of symmetry. Illustration of the basic concepts of crystallography using the examples considered in the previous module. Databases and computer visualization tools revisited. Structural chemistry revisited. Structure systematics.
Structural chemistry. Structure systematics.	Physical properties of solids in interrelation with crystal structures. Symmetry revisited. Solid-state reactivity in interrelation with crystal structures.
Physical properties of crystals.	Structure solution techniques. Validation of results. The knowledge of physical properties assisting to avoid mistakes.

gasses and ending with metals, that is, moving from the right side to the left in the periodic table. We consider the electronic structure of an element and try to ‘predict’ its crystal structure. We do not limit our consideration to ambient conditions. During the practicals, students are encouraged to retrieve crystal structures from the databases and work with them in the interactive mode, obtaining the distances between atoms and the angles between the bonds, expanding the structures, rotating them, watching in various orientations, and comparing several structures with each other. At this stage students can do this using the tools provided by the software, even if they do not understand the mathematics behind these tools. It is the structure itself that is the focus of attention. Each group of elements helps us to introduce some new concepts that are used in crystallography (Table 2 in Appendix D). It is very important that we consider the structures of the same element at multiple T,P conditions. For example, oxygen is considered in detail in the course of quantum chemistry preceding our course. However, the students are used to thinking of it as a molecule, not as a crystal. When we consider the recently solved high-pressure crystalline phases of oxygen, this gives us a chance to apply the molecular orbital approach, in order to analyse the nature of the bonds in the oxygen molecular clusters and polymeric chains in the ϵ and ζ phases, as well as of the intermolecular interactions in the same structures. The ‘oxygen example’ usually amazes the students, and ‘an amazement is the first step towards amusement’, towards an interest in a subject.

2.2. Structures of compounds: how often do we deal with ‘inorganic molecules’?

After the first topic on the structures of elements, the students are already prepared to consider a very important point: chemistry often deals not with individual molecules but with solids, and simple *brutto* formulae and chemical equations do not reflect the real complexity of the system. We approach this point in more detail in the following lectures. Our main purposes in this part of the course are as follows: (i)

to illustrate that there are no individual molecules in inorganic solids, only three-dimensional polymeric structures; (ii) to introduce the concepts of describing the structures as close packing of spheres of different sizes or, alternatively, in terms of coordination polyhedra sharing vertices, edges or faces; (iii) to consider families of structures as a 'theme' and 'variations'; (iv) to introduce the concept of atomic and ionic radii; (v) to revisit the concepts of polymorphism and polytypism; (vi) to discuss the factors determining a crystal structure: the ratio of atomic/ionic radii, the electronic structure of elements or both; (vii) to discuss the relations between crystal structures and solid-state reactivity and the possibility of exploiting crystal structures of precursors to obtain metastable forms of products. Some examples are given in Table 3 in Appendix E. Later in the course, when discussing physical properties, materials, defects, diffusion, phase transitions and solid-state reactions, we repeatedly come back to the same structures and structural types as were considered in the very first lectures, so that by the end of the course these structures are not only well recognizable but are also well related to the physical properties, synthesis and applications. We also revisit the interpretation of some effects and phenomena several times, each time at another level of understanding. For example, when discussing the transformations between iron oxides, in the first lectures we encourage students to compare the packing of O atoms in the three structures. We come back to the same examples once again later, when the students have more knowledge about the crystal symmetry, the defects and the mechanical properties of solids and can interpret the phenomena at a much deeper level. However, even when simply comparing the crystal structures students can make some guesses. What is even more important than a correct guess of an answer is that they start thinking in the right direction – they consider crystal structures when discussing solid-state reactivity.

2.3. Structures of organic crystals: chemical bonds and noncovalent interactions

The structures of organic crystals are usually well received by an audience of chemistry students, since they are, generally, interested in organic chemistry. We use these structures in the very first module of our course, in order to show how much knowledge an organic chemist can 'mine' from considering a crystal structure. The main aims in this part of the course are as follows: (i) to show that structural analysis nowadays has become a very important analytical technique in organic chemistry, and complements or, in many cases, even replaces spectroscopy and chemical analysis in finding the molecular structures of organic compounds; (ii) to let students work interactively with the crystal structures of their choice retrieved from a database, in order to obtain the values of bond lengths and angles in the common functional groups, selecting examples relevant for the courses of organic chemistry and for the course of biochemistry; (iii) to show that the noncovalent interactions in molecular crystals can modify the intramolecular geometry and electronic structure, and, as a consequence of this, that we can use the statistical analysis of

the molecular conformations, intramolecular bond lengths and bond angles in different crystal structures in order to study the intermolecular noncovalent interactions; (iv) to show that the packing of molecules in a crystal structure may give an insight into the intermolecular interactions that hold molecules together; (v) to introduce the concepts of a 'structure-forming unit', 'synthone' and 'hydrogen-bonded motif'; (vi) to show examples of multicomponent molecular crystals (salts and co-crystals), and to discuss which interactions hold these structures together, and why such a crystal is formed under some conditions, whereas under other conditions two separate phases would crystallize. Some examples of the problems we consider within this part of the course are given in Table 4 in Appendix F. The really important milestone in chemical education is when students start thinking beyond individual molecules when considering molecular crystals and get used to the three-dimensional polymeric structures not only of inorganic but also of organic crystals. This is very important in order to understand the physical properties of organic solids and their reactivity. The Cambridge Structural Database provides tools that make the analysis of the intra- and intermolecular geometry, as well as molecular packing and hydrogen-bond motifs, an interesting game for students. Before being able to analyse the symmetry of a structure (this comes in the second module of lectures only), students can very easily 'expand contacts' using the *Mercury* option (Bruno *et al.*, 2002; Macrae *et al.*, 2006), and in this way construct and visualize dimers, cycles, chains, layers and three-dimensional networks. The Cambridge Structural Database software is also very efficient for comparing the crystal structures in a series of selected compounds.

2.4. Chains, layers and three-dimensional networks in inorganic and organic structures: framework structures

This is the final topic in the first introductory module, which basically sums up some of the material that students should know from the first three lectures and from their own experience during the practical work with crystal structures. The main idea of the block is to give a general overview of the richness of crystal structures and of the similarities that exist between the 'inorganic' and 'organic' worlds. We compare the framework structures of inorganic minerals with the framework structures of organic and coordination compounds, and show that they can be described using the same language and, often, the same patterns (*e.g.* we show the similarities of quartz, cristobalite, diamond on one side, and metal–organic frameworks on the other). We discuss how, combining different coordination preferences of metals and the binding modes of ligands, one can obtain exciting structures with nanosize channels, which find applications in many modern materials (Gimeno & Vilar, 2006; Levine & Williams, 2009; Mas-Ballesté *et al.*, 2009; Noro *et al.*, 2009; Qiu & Zhu, 2009; Rao *et al.*, 2001; Shiju & Gulians, 2009; Suh *et al.*, 2008). At the same time, we show that the same coordination preferences of metals are observed in inorganic minerals and are important for geochemistry, as well as for 'classical' and modern inorganic materials: spinels, perovskites, sulfides *etc.*

The binding modes of ligands and their conformations, on the other hand, can be compared with what is observed in solutions of coordination compounds and in organic crystals.

3. Symmetry and basic crystallographic concepts as a tool to encode a structure in a concise way

After a general introduction to various crystal structures has been made during the first block of lectures, and students have gained experience of working interactively with structures, we start a very large second module devoted to the basic crystallographic concepts and formalism. The concepts of crystallography are very well represented in many textbooks and teaching pamphlets (e.g. Belov, 1951, 1986; Chuprunov *et al.*, 2006; Giacobozzo, 2002; Vainstein *et al.*, 1979; Zagalskaia & Litvinova, 1973, 1976; Zagalskaia *et al.*, 1983), as well as in *International Tables for Crystallography* (<http://it.iucr.org/>). We recommend these materials to students who want to go into deeper detail, but we also have our own concise manual adapted to our course (Boldyreva, 1993*b*). We widely use *International Tables for Crystallography*.

We start with considering the necessity to have some means of 'encoding' the crystal structures formed by very many species in a concise way. The approach used to describe molecular structures (giving lists of bond lengths, and valence and torsion angles) obviously cannot work in the case of crystals. Luckily, crystal structures have fragments, from which one can expand the whole structure using some operations, 'symmetry operations'. Two variants can be considered: (1) to expand a structure we use only the translation vectors (elementary translations); (2) to expand a structure we use all the symmetry operations (translations + inversion, simple and screw rotation, glide and mirror reflection). The selected fragments in the two cases will be, in general, different: either a basis or an asymmetric unit (which, in general, may be smaller than the basis). The coordinates of the selected fragments can be defined in a special coordinate system related to the translation vectors (crystallographic coordinates). The same structure can be encoded in different possible ways, depending on the selection of the elementary translations and the starting fragment. All the symmetry operations form a group, which is termed the space symmetry group. Each operation can be defined using a matrix for the transformation of the coordinates or as a symmetry element – a geometrical description of points remaining invariant in the operation. The consequent action of several operations on a point can be seen if the corresponding coordinate transformation matrices are multiplied. The presence of selected operations in a space symmetry group forms the basis of defining its point group, and of assigning the structure to a crystal system and a crystal family.

This very brief and schematic description of the general outline is aimed to show that the pragmatic users of crystallography (as chemistry students are) should see that they must learn a 'new language' because they really need it. We come back to the same entries in the databases that we used to visualize the crystal structures during the first introductory lectures, and now we show their syntax and teach the students

how to understand CIFs and how to create a CIF themselves (<http://journals.iucr.org/c/services/authorservices.html>; Allen *et al.*, 2004; Brown & McMahon, 2002; Westrip, 2010). We analyse the symmetry of the same structures as have been considered before, and train students in changing the crystallographic setting. We attract attention to the statistically unequal occurrence of different space symmetry groups, describing inorganic and organic crystal structures, and in this way we come once again, at a new level, to the interrelation between the interactions, the close packing, the symmetry and the crystal structures (Aslanov, 1989; Kitaigorodsky, 1955, 1971, 1983; Kitaigorodsky *et al.*, 1980; Zorky, 1984, 1986; Zorky & Afonina, 1979). The students work much with *International Tables for Crystallography*. The problems they have to solve range from deriving a space symmetry group from generators to drawing projections or fragments of crystal structures, if the space-group symmetry symbol, the cell parameters and the coordinates of the asymmetric unit are given. We also have a series of problems on the symmetry changes resulting from order–disorder phase transitions, or isomorphous substitution, and work quite a lot with group–subgroup relations (Aroyo *et al.*, 2006). We refer to these examples later in the course, when considering solid-state processes.

Although, because of time limitations, we cannot consider quasicrystals, incommensurate structures and noncrystalline solids in much detail in our course, the importance of these structures is so great that at least a brief introduction is necessary. We have found several ways to do this in a concise way. The formalism of Voronoi–Dirichlet polyhedra (Voronoi, 1952) is very helpful for describing the structures of crystalline and noncrystalline solids using the same language. We use it to introduce the concept of the coordination number, to discuss the evolution of a structure with increasing pressure, to compare several structural types and to describe quantitatively the structure of an amorphous solid (Blatov & Shevchenko, 2003; Blatov *et al.*, 2005; Fischer & Koch, 1979; Kascheeva *et al.*, 1999; Koch & Fischer, 1974; Medvedev, 2000; Sowa, 1988, 1990, 1991; Tanaka, 1986). We compare the description of a solid using the concepts of Bravais lattices and of Voronoi–Dirichlet polyhedra. In the second half of the course, when considering point defects and ionic conductivity, we again revisit this topic, to visualize the channels accessible for diffusion (Anurova & Blatov, 2009; Naumov & Boldyreva, 1999, Appendix C). The commensurately and incommensurately modulated structures are considered using the educational tools developed by Chapuis and his colleagues (Orlov *et al.*, 2006, 2008), as well as other educational materials (Christensen, 2010; van Smaalen, 1995, 2004, 2007; Sun *et al.*, 2007). We not only explain the basics of describing such structures but focus on the possible reasons why a structure can become modulated (in terms of the 'conflict' between the requirements imposed by the interactions between the closest and more distant neighbours in the structure, or as an 'intermediate state' between 'ordinary' periodic structures). In this respect, we discuss the studies of incommensurate structures as a probe to reveal atomic interactions in crystals (Arakcheeva *et al.*, 2005; Chapuis & Arakcheeva, 2004; Pan &

Chapuis, 2005). We consider modulations resulting from displacements, rotations, changes in the magnetic momentum and partial occupancy of positions. Examples are selected among the intermetallic compounds, minerals, two-dimensional layers of molecules adsorbed at a crystalline surface, high-pressure structures of elements discovered during the past decade, oxide materials and pharmaceuticals.

4. Symmetry as a tool to predict properties

Starting from the very first lectures, we encourage students to correlate crystal structures with properties. First, they can do this at a very intuitive level, relying mainly on the visual impression from the structure and some basic knowledge of chemical bonding. After the space-group and point-group symmetry has been introduced, we can take a step forward and consider various physical properties at another level: using tensors and relying on the basic Curie and Neumann principles (Nye, 1985; *International Tables for Crystallography*; Shaskolskaya, 1982; Sirotni & Shaskolskaya, 1979). We give a definition of a property following Nye's (1985) classic textbook, and consider then properties that can characterize molecules and crystals, and properties that can be introduced for crystals only but not for the individual molecules. We give a general introduction to the physical properties of solids, which characterize the structural response to variations in temperature, pressure, magnetic and electric fields, light *etc.* It is very important that students (many of whom will be involved in materials sciences after graduation) start understanding the restrictions imposed by the crystal symmetry and the property symmetry, *i.e.* understand which structures are not allowed to have a particular property. At the same time, we show numerous examples of when a slight structural distortion is enough to overcome the limitations imposed by the symmetry. In this relation, we consider in more detail the structure–properties relations in the perovskite family. We also consider examples provided by the authors of the Bilbao Crystallographic Server (Igartua *et al.*, 1999).

We show that symmetry restrictions do not necessarily leave no degrees of freedom. For example, although both the temperature and the pressure are scalars, and according to Neumann's principle the symmetry of the crystal structure response to changing temperature, or to hydrostatic compression, should depend solely on the symmetry of the crystal structure, this does not necessarily mean that the anisotropy of structural strain on cooling and on hydrostatic compression must be similar, since there are many different ways to compress a low-symmetry structure without violating the Neumann principle. For example, in a monoclinic structure, the only restriction imposed by the symmetry is that one of the principal axes of the strain ellipsoid must coincide with the direction of the twofold axis or be normal to the only mirror or glide plane (Nye, 1985). At the same time, the structure may be the most compressible or the most robust in this direction. There is even more 'freedom' in all the other directions: any orientations of the remaining two principal axes of the strain ellipsoid are allowed, provided they remain orthogonal to each other and to the first principal axis.

The anisotropy of strain of a crystal is one example of a structure-sensitive property. In the case of molecular crystals it is determined by the conformational flexibility of molecules and the interplay between the different types of multiple intermolecular interactions, some of which are specific and directional while the others are not. The study of the anisotropy of strain can, therefore, serve as a tool for understanding the intermolecular interactions and structure–properties relations in molecular crystals (Boldyreva, 2003, 2004, 2010). In the case of minerals, the anisotropy of strain is related to the rotation and distortion of the coordination polyhedra (Hazen & Finger, 1982; Thompson & Downs, 2004, 2008, 2010). We illustrate this in several examples, and consider also structures with bulk negative thermal expansion, as well as structures in which the bulk compression is negligible but at the cost of a considerable linear structure expansion in some directions and structure compression in the others.

One of the most important applications of symmetry concepts in describing the properties of a crystal is related to the electronic structure. Our students have a special course in molecular spectroscopy and are used to applying the point-group theory when discussing molecular structures and properties. They know the ligand field theory and the linear combination of atomic orbitals molecular orbital approach, and are used to working with irreducible representations of point groups. Therefore, to rely on their previous knowledge in our course when considering the electronic structure and properties of extended solids we follow the guidelines given by R. Hoffmann in his lecture notes, kindly donated to us as a gift, a book (Hoffmann, 1988) and recent papers (Glassey & Hoffmann, 2002; Grochala *et al.*, 2007; Lee & Hoffmann, 2002). The concept of symmetry-adapted crystal orbitals is very close to what our students learn in their quantum chemistry course, when considering molecular orbitals as the symmetry-adapted linear combinations of atomic orbitals. Even without sophisticated calculations students learn very easily to predict some of the important features in the electronic structure of a solid, provided its crystal structure and the electronic structure of atoms/molecules is known. We consider the anisotropic structures of molecular metals and discuss the possible effect of the compression or of the Peierls instability (Hoffmann, 1988) on the band structure. At this stage, we recall the structures of elements and simple compounds from the first lectures and try to revisit the effect of pressure on them at a qualitative level, guided by Hoffmann's approach. We introduce the concept of energy bands, and compare the occupation of the levels in the energy bands in metals and dielectrics. We consider solids in which the atomic orbitals of one element contribute to a large extent to one band and those of another element to another band. We consider also solids in which one should first form linear combinations of the atomic orbitals for a group of atoms (a molecule, a coordination polyhedron), and then use these combinations to obtain the crystal orbitals and energy bands. A nice example is provided by binary compounds, *AB*, for which one can follow the changes in the energy gap as a function of the difference between the electronegativity values

of A and B , as well as from the cell parameters. The concept of energy-gap tuning is introduced in relation to modern materials and applications, such as light-emitting diodes or solid-state lasers (Ellis *et al.*, 1993). Students who would like to study the electronic structure of solids at a more advanced level are directed to Altmann (1994).

5. X-ray diffraction: how do we obtain information on the crystal structure from experiment?

After having considered the rich variety of crystal structures in relation to their properties, students are motivated and prepared enough to learn the techniques of solving and refining crystal structures. In the autumn semester of 2009 it was especially easy to motivate the students, since the Nobel Prize for chemistry had been awarded for crystallographic work related to biology. In our course we follow the guidelines given in many excellent textbooks on the topic (Clegg *et al.*, 2009; Glusker & Trueblood, 1985; Glusker *et al.*, 1994; Guinier, 1994; Hammond, 2001; Massa, 2007; Müller *et al.*, 2006; Pecharsky & Zavalij, 2009; Porai-Koshits, 1960, 1989; Pushcharovsky, 2000) as well as our own concise manual (Pavlov & Boldyreva, 1999). We start with diffraction of light, since this is what the students already know from their physics course, and then discuss the basics and applications of X-ray diffraction. Since we teach chemists, who will use the results, not experts in crystallography, who will have to do the job themselves, we pay less attention to the details of the mathematics beyond the diffraction techniques, limiting our discussion to really basic concepts and formulae. At the same time, it is important that chemists understand the limitations of the technique; therefore we have many training examples related to the validation of results, to the potential sources of errors and to the indications of these errors (Cranswick, 2008). We teach how to recognize the signs of disorder, or of a wrong assignment of an element, as well as the indications of a poor absorption correction and of a twin. We discuss how to prepare a sample and how to select a technique and experimental conditions for a particular problem (the choice of radiation, the wavelength of X-rays, neutrons and electrons, the choice of the data collection and data processing strategy *etc.*). We give examples of when a crystallographer can correct a chemist in molecular formula, and when, *vice versa*, a chemist could readily see the error of a not very attentive crystallographer. Such examples are collected by *e.g.* Massa (2007), and we also pick them up from scientific journals. One of my favourite examples, borrowed from Massa (2007), is related to $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ - $[\text{SiF}_6]^{2-}$ erroneously taken for $[\text{ClF}_6]^+[\text{CuF}_4]^-$, where the result was even reported in a journal with a high impact factor. We also use examples from our own practice, which can be new every year, and these are usually kept in the memory much better than some artificial problems. For example, when discussing absorption of X-rays, we consider not only the necessity to introduce corrections, to obtain more accurate intensities in single-crystal experiments. We calculate the diameter of a capillary that would be too large if we aimed to measure a powder diffraction pattern from an Mo complex in transmission mode, and discuss how this result depends on the

wavelength. We estimate the radiation absorption by the diamonds in a high-pressure cell, so that students can understand why a high-pressure experiment requires short wavelengths. We estimate the absorption of X-rays by different gasses (He, Ar, N_2) filling a high-temperature cell, to justify an optimum choice of an inert gas for an experiment. We also consider the possible erroneous conclusions on the kinetics of the solid + solid reactions, when a mixture of solids with different absorption capacity is treated: a layer of the strongly absorbing component at the surface of another component may shield the latter, so that its diffraction pattern is not observed, but this does not at all mean that the first component has disappeared or became amorphous. One more point, which is very important when teaching chemists, is that a diffraction pattern should be considered as a whole, and it is not correct to assign a single peak to a phase without having analysed the whole pattern. This is obvious for a crystallographer, but chemists often tend to consider diffraction patterns as if they were treating vibrational spectra (assigning a band to a molecular fragment). Therefore we pay attention to the phase identification using the PDF databases (<http://www.icdd.com/products/>; Kabekkodu *et al.*, 2002). Examples of the problems that are addressed are as follows: (1) what it may mean if the experimental intensity ratios of a powder diffraction pattern differ from the one calculated from the model based on single-crystal diffraction data; (2) which situation is better for a reliable phase identification: to have fewer or to have more reflections observed than predicted; (3) to what extent X-ray diffraction is a 'fingerprint technique', and under which conditions two compounds can be confused when looking at a diffraction pattern. We explain how diffraction data can be used to study chemical bonds and the electron density distribution in the ground and in the excited states, and how the kinetics of very fast processes can be followed in real time. In other words, we do not only teach the diffraction techniques as such, we teach them to chemists, and our main purpose is to show which chemical problems can be approached and solved, what errors can be made, and how they can be recognized. Those students who want to go further and are interested in technical aspects of the diffraction techniques are directed to the specialist books by Aslanov *et al.* (1998) and Lisoivan & Gromilov (1989).

6. Real crystals: different types of defects

The second half of the course deals with 'real solids', *i.e.* solids having surface and various internal imperfections – point defects (vacancies, interstitials, impurities), dislocations, disclinations, grain boundaries and bulky impurities. This topic has been well covered in textbooks and scientific monographs (*e.g.* Butyagin, 1991; Friedel, 1964; Hauffe, 1955; Kelly *et al.*, 2000; Kröger, 1964; Lidiard, 1957; Novikov & Rozin, 1990; Schmalzried, 1975, 1994; Tretyakov, 1978; Tretyakov & Putlyaev, 2006; Ubbelohde, 1965; Yaroslavtsev, 2009), and our approach in this part is rather traditional. Discussion of the point defects is traditionally based on considering quasi-chemical equations and treating the defects as if they were ions in diluted electrolyte solutions. Also in this part of the

course we refer to knowledge about the crystal structures whenever appropriate: when discussing the free energy of the formation of various defects and their mobility, the diffusion coefficients, the conductivity, and the anisotropy of diffusion and conductivity. We discuss the role of a crystal structure in determining which impurity can be introduced into a crystal and which site it can occupy. The defects in materials – in particular in the fast ionic conductors or in optical materials – are also discussed in close relation to crystal structures. We search for our examples in the scientific literature, modifying them quite often as we find something new and exciting, and at the same time we tend to discuss reactions in the systems for which structures have already been considered at the beginning of the course. For example, we discuss defects in perovskites and their role in the applications of perovskites as materials and in their solid-state reactivity (Antipov *et al.*, 2008; Merkle & Maier, 2008).

Discussion of dislocations, surface structures and properties, as well as of the structures and properties of the interfaces, is to a large extent based on considering the crystal structures. We pay much attention to the anisotropy of mechanical properties in relation to the anisotropy of crystal structures. The shear structures make us revisit the description of crystal structures in coordination polyhedra. When considering surfaces, we pay attention to the difference in the structures and properties of different faces, especially in organic materials built of molecules with hydrophobic and hydrophilic functional groups, so that some crystal faces may be hydrophobic and other hydrophilic. We discuss examples of when the crystal faces differ in their ability to react with gases or liquids. We also discuss why crystals are not round in shape, and why a real crystal habit often differs from the equilibrium one, how one can modify crystal habit and which properties can be affected as a result of such modification. We discuss the properties of solids that are determined by *meso* structures of the external surfaces and interfaces (optical properties, wettability, self-cleaning properties *etc.*), as well as the properties of bulky powders compared with those of single crystals.

While conductivity and spectroscopic measurements are important for studying point defects, and measurements of mechanical properties teach us much about dislocations, X-ray diffraction and electron microscopy are also very informative techniques. At this final stage of the course we revisit the analysis of diffraction patterns, in order to study the stress and strain in the sample, the nature of extended defects, and the size of the domains of coherent scattering in comparison with the particle size as estimated from microscopy data.

7. Processes involving solids (crystallization, dissolution, melting, sublimation, phase transitions, chemical reactions): thermodynamics and kinetics

Starting from the very first lecture, whenever appropriate, we give examples not of static structures only, but of the processes in solid samples in relation to the structures. At the end of the course, we devote several concluding lectures to a general summary, with the aim of examining examples previously

scattered through different lectures and practicals in the common context of the processes involving solids. The structure of a solid is no less important for its reactivity than the molecular structure of an individual molecule is for a gas-phase or a liquid-state reaction. The structure pre-determines the mutual juxtaposition of species with respect to each other, thus influencing the structures of intermediate complexes formed in the course of chemical reactions. We give examples of (i) when polymorphs of the same compound differ in their chemical properties, so that some polymorphs are inert and the others give different reaction products under the same conditions, (ii) when different polymorphs are transformed into the same chemical compound but at different reaction rates, and (iii) when different polymorphs under the same conditions give different polymorphs of the same chemical compound or (iv) give the same polymorph of the same compound, but in one case as a single crystal while in another as a fine powder. The concept of reaction cavity, the topotactic reactions, the topochemical principle, the precursor technique and many other concepts that play a central role in solid-state reactivity cannot be considered without a profound knowledge of crystal structures. The relaxation of mechanical stresses, which is enormously important for reactions in the solid state, is also determined by the crystal structure. The structure of the interface between two solids is important for 'solid + solid' reactions; the diffusion of components from one solid into another is also structure-sensitive. Reactions starting at the surfaces depend on the structures of selected faces and can be controlled by modifying the crystal habit, even if the chemical composition and the bulk crystal structures are preserved. During several final lectures, static and dynamic aspects of the influence of the structures on sublimation, melting, dissolution, crystallization, phase transitions and chemical reactions within solids and at their surfaces are considered. We base these lectures not only on many textbooks and monographs (Boldyrev, 1996, 1997; Boldyrev *et al.*, 1979; Boldyreva & Boldyrev, 1999; Butyagin, 1991, 2006; Desiraju, 1987; Garner, 1955; Hannay, 1967; Hedvall, 1966; Ubbelohde, 1965) but also on recent publications, in particular on those in which solid-state processes have been studied *in situ* using diffraction techniques. In this way we 'round-up' the course, which started with considering crystal structures and ends with considering crystal structures, but at another level of understanding.

8. Conclusion

It is not easy to describe in a paper how a large interactive course is delivered. I have tried to show the main trend and to illustrate it with a few examples. Our main principles of organizing the material can be summarized as follows:

(a) First try to amaze, show something unusual and exciting, and then teach how to approach the problem.

(b) Ask questions first, then show how to look for the answers.

(c) Revisit the same examples several times throughout the course, look at them from different points of view, discuss the problem from several aspects.

(d) Try to keep the parts of the course as coherent as possible, using the 'structure-properties relations' as a 'pivot'.

The effect of 'merging chemistry and crystallography' turns out to be synergistic: the knowledge of crystal structures and their symmetry gives new insights into the chemistry; keeping the chemical problems permanently in sight makes the audience motivated in mastering the new and often difficult language of crystallography. The aim of the course is to teach which information related to chemical and physical properties of solid compounds and materials can be retrieved from a knowledge of crystal structure, whereas more standard courses usually teach how to obtain structural information and how to describe a structure. The latter problem becomes our focus in a subsequent two-semester course, which is given for more senior students, when they have a chance to perform diffraction experiments and process data. This second course, as well as other more specialized courses for senior students (see Appendix G), are beyond the scope of this contribution.

Our educational materials (power-point presentations, collections of problems, examples and illustrations, lecture notes, and manuals) are all in Russian, since we teach our undergraduates in their native language. If our course proves to be of interest to a broader, international audience, we can prepare and make available selected educational pamphlets in English. Any criticism and advice are welcome. We are open to cooperation in the educational field and student exchange programmes; in the case of foreign students the classes can be given in English.

I would like to thank all my colleagues at the chair of solid-state chemistry of the Novosibirsk State University for their assistance in teaching solid-state chemistry over a period of several decades and many stimulating discussions on how to do our job better. I am grateful to several generations of students who acted as 'guinea pigs' in our 'educational experiments'. Without their sincere reaction we would never be able to see what is working and what is not. I am grateful also to many of my colleagues throughout the world, with whom I have had the chance and pleasure to discuss the problems of teaching solid-state chemistry and crystallography, and who have inspired me with many ideas and generously helped me with references and educational materials. Since 2000, our educational activity has been supported by a BRHE programme.

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