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Of Special Interest

Report On "Integrating Materials Science into the Chemistry Curriculum"

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To understand solid-state chemistry, the same basic chemical concepts used in other areas of chemistry are applied.

Working on the premise that materials science is justifiably an appropriate place to begin teaching chemistry, George Lisensky and Dean Campbell demonstrated in their workshop a series of introductory chemistry laboratory experiments with solid-state chemistry as the focus. For the bulk of the workshop, participants broke up into various size groups,

"Integrating Materials Science into the Chemistry Curriculum" by George Lisensky and Dean Campbell was presented at the "Day 2 to 40" workshop symposium held May 10–11, 1997. The two-day event was held in the Willard H. Dow Chemical Sciences laboratory building on the central campus of The University of Michigan in Ann Arbor, Michigan. Each of the articles that comprise this issue was written by one of the group of reporters whom I asked to attend each session to take field notes and then follow up with the session leader and participants afterwards.

—Brian P. Coppola, Proceedings Editor

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simulating a chemistry laboratory session. A rational ordering of demonstrations in solid-state chemical paradigms to be covered in a typical laboratory section, from unit cells to band theory, was presented. At each stage, the materials used for the laboratory demonstrations were clearly defined, shown to be budget friendly, very safe, and robust enough for student use. All experiments impressed workshop participants that solid-state laboratories are feasible and accessible teaching tools with just as much ability to stimulate students as other fields of chemistry. All the while, a very effective methodology for teaching chemistry through solid-state concepts was demonstrated.

Chronology

1. George Lisensky takes quick survey of backgrounds of workshop participants; almost all are inorganic faculty at colleges or universities with some inorganic undergraduate students.

2. Lisensky describes the reasons for focusing on materials, and thus solid-state, chemistry in a first-year chemistry course: (1) a serious neglect of solid-state chemistry vis-à-vis its prominence in chemistry-related professions and (2) the adaptability of solid-state chemistry to current first-year chemistry curricula. Lisensky proposes that teaching chemistry from the solid state point of view appears poorly adaptable because few instructors have a strong background in this subfield, and the propagation of jargon in solid-state chemistry obscures the fundamental nature of many of its chemical paradigms. The point is made that one should be able to achieve all of the desired teaching goals in a first-year chemistry course using solid-state chemistry as the venue for presenting these chemical topics.

3. A brief guide is given to the audience of resource materials for integrating solid state chemistry into the chemistry classroom. Textbooks, CD ROM, and various guides to laboratory experiments are referenced.[1] Lisensky acknowledges the governmental and commercial agencies who sponsor the ongoing project in solid-state chemical pedagogy.

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[1] The books and CD-ROMs used in this workshop are available from The Institute for Chemical Education, Department of Chemistry, University of Wisconsin-Madison, 1101 University Ave.,Madison, WI 53706, phone: (608)262-3033 http://jchemed.chem.wisc.edu/ice.

4. Lisensky initiates a discussion on bonding theory in a style somewhat like a regular classroom lecture, posing questions and prodding for answers. The point is rapidly made that although covalent bonding is a standard focus of a first-year discussion in bonding theory, this is a distorted picture to give students. The various permutations of two or more elements from the periodic table only infrequently give rise to bonding interactions which are primarily covalent. The great variety of atomic bonding in solids allows a broader view of bonding to be presented early on.

5. Unit cells are presented as the fundamental model for teaching connectivity in (ordered) solid-state materials. A computer aided multimedia demonstration of cutting an orange is used to show how one spherical object can be permuted in pieces to form various unit cells. One participant suggests that actually bringing in a grapefruit and struggling with the cuts necessary for simple cells had been engaging for his students. The flexibility in determining unit cells is cited as an advantage to learning, as opposed to fact-based learning.

6. Model sets that are specifically designed to teach unit cells are passed out. (see footnote 1 for source) The workshop participants are now broken up into eight groups of two, and laboratory manuals are passed out for the model sets. Different groups are assigned to construct different unit cells and then compare their results with their neighbors. All groups eventually construct the same cells in time, and comparisons primarily give way to localized discussions on the nature and novelty of the model sets. Nearly all workshop participants have familiarity with the cells constructed.

7. A hammer, razor, and a finger-sized rock salt (NaCl) crystal are passed to out to each group. All the groups are instructed to chisel shards off the crystal, thus demonstrating cleavage planes. All groups have retained their model sets, and the assembled cells are used in conjunction with another computer-aided visual demonstration of cells being cleaved. Defects are also shown, and the arguments take the discussion from the level of bonding to structure–property relationships.

8. The model sets and salt crystals are recollected by Campbell, and pieces of tape are passed around with a layer of MoS on them. Clean pieces of adhesive tape are also passed around, and the audience is asked to use the clean tape to peel layers off

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from the MoS. The computer display is used to explain the effect and demonstrates these points: (1) not all solids are intractable refractory materials, (2) structure–property relationships can be easily understood at an atomic level for solids, (3) the seemingly limitless number of times peeling can occur clarifies the poorly understood nature of “atomic scale”.

9. The workshop moves into a new area when Lisensky begins discussion of diffraction and its importance as a tool for characterization of ordered solids. Lisensky produces a diffraction grating and a lecturer’s laser pointer and then turns off the lights. The striking patterning effect created captivates the audience while communicating the basic concepts of diffraction. Individuals are then given their own diffraction grating, through which the laser light reflecting from the wall can be ordered in any of the various patterns present on the grating. M. D. Curtis suggests developing new grating patterns to demonstrate less ordered solids.

10. Refrigerator magnets and normal magnets are passed out and the participants are asked to examine the effect of passing one magnet over the other. The alternating field polarities of the standard refrigerator magnet cause periodic repulsions and attractions when a normal magnet is passed over them. This is then related to the manner in which a scanning tunneling microcope (STM) analyzes surfaces with atomic resolution. A computer video of a Lego model constructed to mimic the operation of a typical STM analysis interface is shown.

11. Lisensky gives a lecture on the correlation of the zincblende structure to known semiconducting solids and briefly surveys where such materials are located on the periodic table. Both pure elements and alloys are shown to have ionization potentials governed by periodic trends. A rough 1:1 correlation of band-gap energies to ionization potentials is thus shown, and the experiment, “Periodic Properties and Light-Emitting Diodes (LEDs)” is begun.

12. A laboratory experiment from Lisensky’s textbook [1] is passed out, and the workshop groups used in previous demonstrations are reconstituted. Lisensky informs the audience that undergraduate students would normally have been responsible for much of the assembly of the circuitry, however it is mostly provided in preassembled form for the workshop participants. All of the materials

are collected by each group and the experiments are conducted locally with little initial supervision by Lisensky and Campbell.

13. A series of diodes is tested using the general alloy gallium-arsenic-phosphorus. The degree of phosphorus incorporation is used to tune the band gap and thus the frequency of emitted light. The experiment demonstrates several new aspects of solid-state laboratories: relevance to state-of-the-art technologies, the bridge between fundamental and applied science, and, again, the very engaging and colorful nature of solid-state experiments when fully thought through. Structure function is again displayed by cooling the diodes and watching the color changes due to contractions of the crystal.

14. The workshop runs out of time, but not before Lisensky and Campbell demonstrate a newly available diode that emits in the blue, but when cooled with liquid nitrogen, emits in the ultraviolet.

Report

The team of George Lisensky and Dean Campbell operate in two apparently well-defined roles, laboratory instructor and laboratory assistant. Lisensky’s style of presentation emulates regular laboratory instruction, but with occasional digression to place concepts within the context of the audience. Comment from workshop participants was frequent, but when discussions became lengthy, it became clear that the flow of presentation was being disrupted and Lisensky steered the workshop back on to his schedule. Throughout the presentations and demonstrations, Dean Campbell played a mostly passive role organizing the supplies participants would need for each demonstration; he offered a few comments on discussions concerned with these materials.

Speaking as one would normally speak to a classroom of introductory chemistry students, Lisensky began with a discourse on the place of solid-state and materials chemistry within the realm of chemistry as a whole. He made the point that solids are just as tangible as liquids or gases in every-day life, and that if the purpose of introductory chemistry is to develop in students a broad understanding of all matter, then most approaches fail in their treatment of solids. Lisensky explained why solids quickly get relegated to second-class status.

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1. Previous neglect of solid-state chemistry in traditional chemistry curricula means most current educators are poorly equipped to teach solid-state chemistry.

2. Most professionals who do have adequate training in solid-state or materials science are nonchemists, and have created a vocabulary of jargon that is not recognizable to the chemistry community at large. Indirectly, he made the point that further down the road in the chemistry curriculum the focus is consistently on discreet molecules, and this is reflected in introductory chemistry courses.

Solid-state chemistry readily becomes marginalized as a result of these problems. The unique concepts of solid-state chemistry are essential to a full background in chemistry, and for those with an interest in chemistry or chemistry related professions, industry is heavily involved with solid-state chemistry. According to Lisensky, "[solid-state chemistry] already embodies all of the principles [of chemistry]. I want to teach anyway. I don't want to throw away any topics; I just want to change the examples you use to teach those topics." To understand solid-state chemistry, the same basic chemical concepts used in other areas of chemistry are applied. Incorporation of solid-state chemistry into first-year chemistry courses does not then change the learning goals, but only the method by which they are presented. Lisensky implied that of all the problems with using solid-state chemistry in introductory courses, the excuse of instructors that teaching goals will be disrupted made the least sense. All that is required are a few highly motivated and creative instructors to make the changes necessary. Lisensky and Campbell proceeded to demonstrate their formula for the workshop participants.

Understanding the structure of matter is typically a first goal in introductory chemistry. According to Lisensky, his approach varies only on what materials are being emphasized: "I could confine myself to the upper-right-hand corner of the periodic table and get discreet molecules; this is where most people focus in on, but otherwise we wind up with solids, a lot." The focus in teaching the basics of the structure of matter then focuses on solids right away. Development of bonding theory can no longer focus exclusively on covalent bonds, but must address the whole spectrum of bonding possibilities simultaneously. This is desirable because students get a much broader background in bonding theory, but it also serves to complicate learning by simply creating more things to learn. One needs to take a step back and find something to tie it all together.

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Most workshop participants had clearly not previously encountered model sets designed for unit cells. The sets distributed by Campbell bore some superficial resemblance to traditional ball-and-stick models, but the fundamental design was to emulate a three-dimensional lattice. The components were a wooden palette with numerous color-coded holes, a good supply of steel rods of various lengths to insert into these holes, and transparent plastic balls of various sizes and colors. The instruction manual explained how to arrange the rods and balls of correct size to produce a macroscopic three-dimensional rendition of some unit cell.[2] Lisensky emphasized that the open-ended way of determining unit cells is a refreshing break from the rigid, fact-based nature of most introductory chemistry. During a multimedia demonstration accompanying this laboratory experiment Banaszak-Holl commented that bringing a sliced grapefruit into lecture and struggling with ways to create unit cells from the pieces successfully engages the students from his classes in learning about unit cells.

Lisensky and Campbell assigned three different unit cells to the groups to construct, one at a time. The three different cells to be constructed were not revealed until after all participants had made attempts to construct them using the instruction manual. All of the participants were engaged in the experiment, and we were encouraged to cooperate with other groups, just as would occur in a real laboratory setting. Most participants were experienced enough in solid-state chemistry to recognize the structure types corresponding to each new unit cell, and they prompted Lisensky to remind the participants that such an experiment with beginning students would typically fill a three-hour period, much more than the twenty minutes we spent to complete it. All subsequent demonstrations in the workshop were similarly fast moving.

After developing ways to think about the atomic structure of ordered solids, two shorter experiments followed that explored their structure–function properties. Small blocks of rock crystal along with a razor and wood mallet were passed to each group of participants. The participants then busied themselves with chopping up the crystals in a clean fashion, along cleavage planes. The mess created was minimal; the crystals cleaved very easily and only infrequently shattered. This brief but entertaining exercise was soon followed by a computer illustration of defects and cleavage planes in solids.

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[2] The kits can be obtained from The Institute for Chemical Education. See footnote 1 for details.

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Lisensky used the experiment to demonstrate some specific materials properties of crystalline solids: brittleness, rigidity, and their relationship to crystal defects.

The exposure to the unit cell models, although highly instructive, leaves one with a distorted perspective on the size of atoms. A second quick experiment to address this issue was performed to bring in an atomic-scale perspective of solids and demonstrate some other novel physical properties. Pieces of adhesive tape, some with a layer of molybdenum sulfide and some without, were passed around to all of the groups. The workshop leaders asked participants to repeatedly peel layers of MoS from this tape, using the clean pieces of tape. Lisensky stated that one layer of MoS on a piece of tape would last for an entire class length of stripping. This exercise made it clear that atoms are very small, allowing students to develop a new perspective that is not confined to solids as mere “blocks” of something. The experiment also allowed Lisensky to build an easily understandable structure–function relationship using the computer illustrations. MoS has a layered structure where discreet layers of sulfur atoms are forced to interact closely. This creates repulsive interactions, giving rise to weak interlayer bonding and resulting in the macroscopic physical property of being a soft, greasy solid. Although brief and apparently very simple, this experiment introduced key points showing the diversity and structure–function of solids. Through the whole of the workshop, no other single experiment appeared to achieve so many instructive goals in such an economic fashion.

Diffraction of X-rays from ordered or partially ordered solids is the primary characterization technique for directly visualizing the spatial ordering of atoms in solid-state materials, a technique which most undergraduate chemistry majors do not get exposed to in any depth. Actually conducting a laboratory experiment with X-rays of useful intensity is dangerous and unworkable for undergraduates. Lisensky and Campbell announced their diffraction experiment by turning off almost all of the lights in the auditorium and directing the participants attention to a blank projection screen. Lisensky produced a laser pointer and what appeared to be single slide from a slide projection machine. The slide was in fact a visible-light diffraction grating with several subdomains on the lens to produce a variety of diffraction patterns.[3] Lisensky took a few minutes to demonstrate the effect, and then Campbell passed out gratings to all of the workshop participants. The light from the laser pointer can be diffracted

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[3] Diffraction gratings were also obtained from the Institute for Chemical Education. See footnote 1.

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anywhere along its path to the eye, giving control of the patterns observed to the individuals if the instructor so chooses. All workshop participants took sublime pleasure in exploring the visual playground created by viewing laser light through the multidomain diffraction gratings.

In terms of materials costs, the projection-slide-size diffraction gratings were certainly not cheap, but again are a reusable, a one-time investment. One laser is also required although the gratings are designed such that individuals are not restricted by the activities of the person operating the laser pointer. The source of the laser light may enforce a group to view specific patterns by filtering the light through a grating; such a style would be suitable to “control freaks,” as stated by Lisensky. Overall, the demonstration is very flexible and tailor-made to hold the students’ attention. The limitations of traditional X-ray diffraction experiments are addressed here in two key ways. First, the high cost and inherent safety concerns of standard X-ray equipment are no longer an excuse to keep diffraction out of the undergraduate laboratory. Second, the very visual nature of the display allows a more effective communication of the principles of diffraction, without having to rely too heavily on a tedious, math-based approach. The demonstration was designed only for fully ordered solids, but M. D. Curtis suggested variations in the diffraction gratings which allow simulation of partially ordered solid diffraction, such as used in powder diffraction.

Lisensky continued the discussion on methodologies for determining the structure of solids. The recently evolved techniques of atomic-force (AFM) and electron-tunneling microscopy are now standard practice for analyzing the structures of solid surfaces. Much like X-ray diffraction, these microscopies are very expensive to conduct, hazardous in some manifestations, and critical in the understanding of solids. The surrogate device that Lisensky and Campbell produced to simulate these techniques for students was the humble refrigerator magnet. Refrigerator magnets are normally manufactured with the field polarity regularly alternating throughout, like a bunch of horseshoe magnets all lined up. This makes the magnet “sticky” on only one side. Lisensky and Campbell passed out one refrigerator magnet and one normal (dipolar) magnet to all participants. Everybody was then asked to pass the dipolar magnet over the refrigerator magnet, creating a beating as the magnets alternately repel and attract each other as a function of translation.[4] This example was easily extended to the actual

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[4] Magnets were obtained at the NSF Materials Research Science and Engineering Center of the

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function of force microscopy, using supplementary multimedia illustrations. This included a brief video of a Lego device constructed to demonstrate the functioning parts of an AFM. Presumably, such a device would actually be brought into classrooms for closer visual inspection.

The remaining demonstrations dealt exclusively with periodic properties. This topic is usually well-developed in most introductory chemistry classes, as descriptive chemistry still tends to play a large role in instruction. Most introductory laboratory courses revolve around periodic properties in some way, but only infrequently are solids the focus of such laboratory experiments. Solid-state chemistry, as a subset of inorganic chemistry, shares its richness in examples of periodic relationships. Lisensky and Campbell easily tapped into this resource, and then some, with their final demonstration on light-emitting diodes.

Lisensky began with a survey of periodic trends in conductivity, and how there is an empirical relationship between semiconducting properties, and the zincblende structure type. Periodic property relationships were extended to the next level, as the fine tuning of conducting properties can be further described in terms of ionization potentials. Ionization potentials are a simple, unassuming, and effective basis for developing an understanding of light emitting diodes. By generalizing ionization potentials in terms of the electronics of a material, a nascent understanding of band-gap energies was developed using periodic trends. It becomes easier to pull an electron out of an atom as one goes down the periodic table, and by mixing atoms within the same group, as in a normal LED, one can further fine tune the net ionization potential of the composite solid, and thus fine tune the frequency of emitted light.

The groups were all given an instruction guide, which detailed the construction of a circuit for powering up and measuring the resistance of a light-emitting diode. A series of LEDs, synthesized from binary gallium-group XV solids, was studied, and the relationship of the emitted light to periodic trends elucidated.[5] Campbell explained that normally the students would be asked to solder together the entire apparatus themselves, but in the interest of saving time for the workshop members, preassembled circuitry was used instead. Lisensky and Campbell openly regretted the time

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University of Wisconsin, http://msrec.wis.edu.

[5] LED kits are available from Mouser Electronics, 2401 Highway 287 North, Mansfield, TX 76063-4827, Phone: (800)346-6873, http://www.mouser.com.

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constraints which forced them to make this choice, as both agreed that students enjoy assembling the circuits themselves. Four diodes were collected and each consisted of gallium with a varying ratio of phosphorus and arsenic to balance. The ratio of phosphorus to arsenic controls the band-gap size, and thus the frequency (color) of the emitted light. The brand of diode selected was colorless when unlighted, unlike most commercially available LEDs that have an organic dye to give away the color even when not on. Lisensky observed that his students rapidly lost interest if they were not challenged to discover the colors of their diodes.

The primary characterization method was a voltage measurement; however, Banaszak-Holl commented that when such an experiment was conducted in Brown University's undergraduate inorganic chemistry lab course, a UV-Vis was used to directly measure the wavelength of light. Both UV-Vis absorptions and electrical potentials are equally adequate to quantitate the periodic trends being investigated in this experiment. A linear relationship between the voltage and the degree of phosphorus incorporation was easily established: phosphorus increases the band gap; thus, it causes a blue shift in the frequency of emitted light with increasing phosphorus incorporation, resulting in an increase in the resistance to electrical current. This experiment was obviously very colorful, and like the previous experiment using the laser and diffraction gratings, workshop participants thoroughly enjoyed tinkering with their experimental props.

Liquid nitrogen was used in the second part of the experiment to demonstrate the effect of temperature on the frequency of emitted light, and thus explore how changes in lattice distances affect the band gap. Each of the lighted diodes was dipped into a cup of liquid nitrogen, and the color change was observed. Consistently, a blue shift in the light occurred, indicating a decrease in the atomic bond lengths and an increase in the band gap; with stronger bonds, electrons are more difficult to ionize. The visual inspection was again reinforced with a numerical measurement using a voltmeter. One workshop participant noted that the diodes appeared to get brighter upon immersion in the liquid nitrogen. Lisensky explained that the cooling, which brings the atoms closer together, also reduces thermal vibrations of the lattice, thus increasing the efficiency of electrical transmission. This is a topic which Lisensky admits he avoids with his students, at least in the general discussions, but is also an unavoidable aspect of the experimental work. This small conflict was not further discussed.

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After all of the participants had finished the experiment, Lisensky and Campbell demonstrated a rather entertaining variation on the liquid-nitrogen experiment using a gallium nitride diode. This recently available and rather expensive diode would not be used in the written laboratory, but only demonstrated as an “encore” after everybody was finished. Gallium nitride emits in the blue at room temperature, but when dipped into liquid nitrogen, a farther blue shifts occurs, the visible light winks out, and it is replaced by the faint indigo shimmer of a low-end UV emitter (perhaps another good reason not to allow students to pursue this one on their own).

Reflections

Overall, the session was highly instructive, and workshop participants agree that the quality of presentation was likewise. As one workshop participant put it, “these guys are pros” at what they do, which is giving excellent demonstrations of their materials science experimental pedagogy. A major criticism from a few participants was the low level of interaction between workshop participants and leaders, beyond the simple “look what we’ve been doing for the past few years.” Although constructive mutual commentary did occur between the leaders and participants, this was not allowed to get very far, as the workshop leaders prioritized their presentation over true interactive discussion. Lisa Buttrey commented rightly that little possibility was left for the workshop to generate new approaches to teaching, outside of those being presented by the workshop leaders. Where possible though, workshop participants made various indications that such experiments as were presented might be integrated into their chemistry curricula. In no case did a workshop participant force the issue with leaders on the need to discuss aspects of the experiments. The majority opinion, which can only be inferred from the behavior of participants, indicated a desire to just let the leaders take charge of the show. Whether or not this session was defined as a workshop, enough of the participants knew what to expect from Lisensky and Campbell ahead of time to make this point moot.

Workshop Participants

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