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CRYSTALLOGRAPHIC CONTRIBUTIONS TO THE ENERGY PROBLEM

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CRYSTALLOGRAPHIC CONTRIBUTIONS TO THE ENERGY PROBLEM

The subject that I have been asked to address is one which is becoming a very important challenge for crystallographers. There is certainly no need for me to emphasize to this audience that there is a serious shortage of energy in the world, that it appears to be growing more serious with time, and that the problem is not going to be solved easily and quickly. The primary question of concern to us is, "What can we as crystallographers do about it?"

Many of you have already given a lot of thought to this subject and have even redirected your research accordingly. I doubt that I can add much to your ideas. However, many others of you have probably thought very little about the types of contributions that you can make, and I hope that my comments will help to stimulate some of you into becoming more involved.

Of course, the reason that crystallographers can make important contributions to the energy problem is because crystallographers obtain fundamental information on materials, and every advanced energy technology is materials limited. Therefore, our job, in principle, is quite straightforward. We need to use our experimental facilities and our skills in providing information that will lead to the development of new materials that are required.

A little over a year ago the United States Energy Research and Development Administration (which is now part of the Department of Energy) conducted a series of nine workshops in materials science. The purpose was to assess the needs for research on energy-related materials. The broad topics covered in these nine workshops are shown on my first slide. Each workshop was attended

SLIDE 1 - Nine ERDA Workshops on Materials Research

by leading scientists within the United States with special expertise in these topics and by scientists and engineers closely associated with the energy technologies. Of course, Number 3, the Workshop on X-ray, Neutron, and Electron Scattering, could very well have been called "the Workshop on Crystallography." This Workshop was held at the Oak Ridge National Laboratory, and many thoughts that I want to leave with you are a result of discussions held at that time.

One of the objectives of the workshops was to determine the types of materials research needed for various advanced energy technologies. My next slide gives you an idea of the wide variety of materials problems that exist.

SLIDE 2 - Materials Research Required by Energy Technologies

On the left are broad areas where materials with better properties could be beneficial to the energy technologies shown across the top. I do not wish to imply that this is a complete list; I merely want to point out that every energy technology requires research and development on many different types of materials. Furthermore, crystallography can play a very important role in the development of these materials. To indicate this fact, I am going to show you another chart with these same classes of materials research along with important properties that can be determined by crystallographic investigations. This is shown on my next slide.

SLIDE 3 - Materials Research Requiring Crystallographic Studies

It should certainly be apparent from this chart that there are many classes of energy-related materials where crystallographic information can be very important in materials development. These crystallographic investigations

are grouped according to properties of materials, which was the method used in the workshop. They involve every possible type of crystallography: structure investigations under a variety of external conditions, such as temperature, pressure, and atmosphere; elastic, inelastic and quasielastic neutron scattering; small-angle neutron and x-ray scattering; electron microscopy; and so forth.

It is doubtful that any other branch of science can compare with crystallography in providing such a wide variety of important information on energy-related materials. And, of course, the reason is one that we all recognize--in order to predict and develop new materials with special properties, it is necessary to understand those properties on an atomic scale in existing materials.

It is obviously not possible to go through this chart item by item and try to tell you about the types of research that are necessary. Instead, I shall merely try to guide your thoughts by pointing out some of the research investigations that have already been performed and others that are in progress. I have chosen four of these areas to discuss: radiation effects, catalysts, electrolytes, and superconductors. The particular examples that I shall mention were chosen not only because of their importance, but because they cover a wide variety of crystallographic techniques. Of course, many other examples would have been equally appropriate, and I want to apologize at the beginning to those of you who have done important work that I will not have time to discuss.

First of all, let's look at this area of radiation effects; this is extremely important, of course, in the construction of fission and fusion reactors, and it is also important in MHD devices. I shall limit my remarks

today to radiation effects in metals. Other techniques, such as electron spin resonance and optical spectroscopy, are very powerful tools for investigating radiation effects in insulators, but they cannot be used for such studies in metals. Most of the information, therefore, has to come from crystallographic investigations.

When metals are irradiated with energetic particles, atoms are displaced from lattice positions into interstitial positions, and the resulting Frenkel pair, interstitial and vacancy, is the basic defect produced by radiation damage. These defects, clusters of them in the form of dislocation loops, and voids pose serious materials problems in reactor design, because they are responsible for metal embrittlement, creep, swelling, and phase instabilities.

Although the production of self interstitials and vacancies in metals has been known for about 30 years, the configuration of the interstitial has been unknown. My next slide shows six possible self-interstitial configurations

SLIDE 4 - Six Self-Interstitial Configurations in a F.C.C. Lattice

for a face-centered cubic lattice. In the split interstitial configurations the displaced atom forms a dumbbell with another lattice atom so that the dumbbell is centered at a lattice position and is oriented along the directions indicated. These four configurations on the right were ruled out fairly easily by diffuse x-ray scattering measurements, actually Huang scattering, which I will discuss in more detail later. However, there was difficulty in determining whether the octahedral or [100]-split interstitial was the correct one. The proper configuration has been determined recently through very precise measurements of the diffuse x-ray scattering in the region between Bragg

reflections. With such measurements it is possible to obtain information on the atomic configuration and on lattice displacements very close to the defects. My next slide shows results obtained by Haubold and his associates at Jülich,

SLIDE 5 - Haubold's Results on Copper Interstitial

Germany for copper. The copper specimen was irradiated at 4°K to contain about 0.03% Frenkel pairs, and the measurements were performed at 4°K to prevent annealing effects from occurring. The figure at the left shows the measured intensity contours in a region of reciprocal space containing the (111) and (200) reciprocal lattice points. The other two figures give calculated contours for the [100]-split and octahedral configurations. Comparison with Haubold's data shows clearly that the [100]-split interstitial is the one that exists. These measurements are particularly notable because of the relatively large Compton scattering and temperature diffuse scattering that were present. The data were obtained using a 100 KW-rotating anode x-ray tube.

Unlike this type of diffuse scattering information, which is obtained from measurements between the Bragg peaks, by measuring the diffuse scattering near the Bragg peaks, usually referred to as Huang scattering, it is possible to obtain information on the long-ranging part of the strain fields due to the interstitials. This type of scattering is shown on the next slide. These are data for aluminum, and as you see in the figure on the left,

SLIDE 6 - Huang Scattering from Aluminum

this Huang scattering is relatively large compared to the temperature diffuse scattering. From this type of measurement around various Bragg peaks, information

on the symmetry of defects and defect clusters can be obtained. In fact, because Huang scattering measures the long-ranging strain fields, it is extremely sensitive to the formation of defect clusters. If there are several separate interstitials scattering incoherently, the intensity is proportional to the number of interstitials; however, if these interstitials cluster and scatter coherently, the intensity is proportional to the square of the number of interstitials. This effect was very important in studying the recovery of radiation damage by thermal annealing. Notice this figure on the right showing the thermal annealing of aluminum. The electrical resistivity decreases monotonically through this stage of annealing, which indicates a monotonic decrease in the number of Frenkel pairs. However, the Huang scattering first decreases and then increases dramatically. This effect, which was observed by Ehrhardt and his associates at Jülich, is due to the clustering of interstitials in the temperature range above 40°K. It clearly shows that the interstitials migrate freely at these temperatures and thereby resolved a controversy on interstitial migration which had existed for about 20 years. You notice from both the Huang scattering and resistivity data that essentially all interstitials have been annealed out of aluminum by about 300°K -- this has been accomplished by migration of the vacancies.

In general, for neutron damage in metals the only defects remaining above room temperature are clusters of interstitials and vacancies, which are in the form of small dislocation loops. From measurements of the Huang scattering very near to the Bragg peaks, it is possible to extract information on the concentration and size distribution of these loops. The next slide shows results

SLIDE 7 - Larson's Data on Dislocation Loops vs Electron Microscopy

that were obtained at Oak Ridge National Laboratory by Larson and his associates on the size distribution of interstitial and vacancy loops in neutron-irradiated copper at room temperature. For comparison, measurements by transmission electron microscopy are also shown. The comparison is quite reasonable, and it now appears that better quantitative data can be obtained, particularly for the smallest loops, by the x-ray technique. A more detailed analysis of this Huang scattering should be able to give separate size distributions for the vacancy loops and the interstitial loops that exist simultaneously in the crystals, but such an analysis was not attempted in the data shown here.

A very serious radiation damage problem that was encountered recently is the formation of voids in metals irradiated to a very high dose at elevated temperatures. This problem has been studied by both small angle x-ray and neutron scattering, and it will require much more research in the future. My next slide shows some small angle neutron scattering results. On the left are

SLIDE 8 - SANS of Voids in Irradiated Aluminum

intensity measurements obtained by Child and Spooner at Oak Ridge, taken on a single crystal of irradiated aluminum with the neutron beam parallel to the [100] direction. You notice the very anisotropic distribution of the scattering. On the right is a size distribution of voids that was measured in a similar sample of irradiated aluminum by Hendricks, Shelton and Schmatz in Jülich, Germany. This distribution, which shows most of the voids with a diameter about 400 Å, was obtained from data at very small angles where the scattered intensity was isotropic. They also studied the void morphology by examining the anisotropy of the scattering at larger angles and showed that the voids have a truncated octahedral shape. These types of investigations are continuing; it is necessary

to know the size distribution and morphology of the voids as a function of irradiation variables in order to determine the mechanisms for void formation and growth. Of course, electron microscopy plays a central role in these radiation damage studies, but diffuse scattering investigations are necessary in supplying complementary information.

I shall now turn to a second class of materials research -- electrolytes. There has been much interest recently in the use of high energy density batteries for load leveling utility systems, for electric vehicles, and for fuel cells. The possibility for major advances in battery systems can be seen by consideration of data on my next slide.

SLIDE 9 - Theoretical Specific Energy vs Equivalent Weight

Here, the theoretical specific energy, i.e., the energy that can be stored per unit weight, is plotted against equivalent weight for a number of possible electrochemical couples. The Pb-PbO_2 couple for the common lead-acid cell is near the bottom of the figure, and it is quite apparent that much more energy can be stored per unit weight with other systems. However, the best chemical combinations involve very reactive constituents so that an aqueous electrolyte would not be feasible. About 10 years ago, Kummer and Weber of the Ford Motor Company produced a radically different type of electrochemical cell, in which the electrolyte was a solid, called β -alumina. This solid was stable in the presence of both sodium and sulfur, which served as electrodes. Furthermore, even though it has a melting point over 2000°C , it is an ion-conducting electrolyte with the sodium ions moving almost as fast as if it were a liquid.

Crystallography has made major contributions to the development of solid electrolytes by structural investigations, which have helped to explain the

high conductivity and have provided a basis for predicting new electrolytes. Various systems have been studied, which include complex silver compounds, titanates, niobates, and a variety of intercalation layer-type compounds. The conductivity of some of them is shown on my next slide. Many of these materials

SLIDE 10 - $\log \sigma$ vs $1000/T$ (Ionic Conductivity)

have fairly complicated crystal structures, and all of them provide a mechanism whereby ions move easily between lattice sites. I am going to discuss β -alumina, because it is a very pretty illustration of the use of crystallography in providing an understanding of the transport properties of a material. Furthermore, it will undoubtedly be one of the first solid electrolytes used in commercial batteries.

The structure of β -alumina is indicated on my next slide. The idealized

SLIDE 11 - Spinel Block of β -alumina

composition is shown at the top, and there are many isomorphs. The sodium can be replaced by other monovalent ions, and the aluminum can be replaced by gallium or iron. The general features of this structure were solved by Bragg in 1937 and by Beevers and Ross in 1938. They showed that the compound crystallizes in a hexagonal unit cell, composed of spinel-like blocks of aluminum and oxygen that are separated by Na-O layers in mirror planes. In the space group for this structure there are three sites for the Na in a Na-O layer: the so-called Beevers-Ross site where they placed the Na, and the anti Beevers-Ross site and mid-oxygen position, which they considered vacant. As it turns out, the Na is not restricted only to this Beevers-Ross position, and that is the reason for the high conductivity. My next slide shows the distribution of

SLIDE 12 - Distribution of Na in γ -alumina at 20°C

Na in the Na-O layer at 20°C. These are fairly recent neutron diffraction data by Roth and Reidinger which were obtained at Brookhaven National Laboratory. In addition to Na at the Beevers-Ross site, it also exists at the mid-oxygen position, which are these three equivalent sites, and there is a little at the anti Beevers-Ross position in the center of the three mid-oxygen positions. Actually, this distribution between the three different types of sites varies with temperature, and it is different for other ions in some of the isomorphs. However, it is certainly apparent that such a disordered structure permits rapid diffusion of Na in this plane.

It has been possible to proceed much farther with crystallographic techniques and to determine the main factors that control the ionic conductivity. Many different groups have worked on the β -alumina system, but I would like to mention especially the large contributions by Roth and his associates in the United States and by Guinier, Comes and their associates in France.

First of all, the ideal composition shown here never exists -- there is always about 20% excess sodium, all of which is in these Na-O layers. Well, what about charge compensation for the excess sodium? Is it accomplished by Al vacancies or by excess oxygen? Roth and Reidinger have shown that charge compensation is produced by excess oxygen and that this excess oxygen causes a unique defect in the spinel block. This determination has recently been confirmed by the French workers. The excess oxygen is in the mid-oxygen position, and the next slide shows the defect that is produced. This Aluminum atom

SLIDE 13 - Frenkel Defect in Spinel Block

moves into an adjacent interstitial position directly above the mid-oxygen position, thereby creating a Frenkel defect, i.e., an aluminum vacancy-interstitial pair. By symmetry, this Frenkel defect is attached through the oxygen atom to its mirror image in the next spinel block. These defects help to stabilize the β -alumina structure by relaxing stresses caused by the small highly charged aluminum ions.

Of course, it is apparent that these defects affect the mobility of sodium ions in the conduction plane. In fact, manipulation of the defects by sample preparation or incorporating impurities should result in modified transport properties. Consequently, this is a situation in which crystallography not only explained the important physical property of a material but also showed how that property might be controlled. Actually, such a structural modification is exactly what occurs in another form of β -alumina, the so-called β'' -alumina. The two structures are very similar as shown on my next slide.

SLIDE 14 - Comparison of β -alumina and β'' -alumina

Whereas β -alumina is hexagonal and consists of two spinel blocks, β'' -alumina is rhombohedral and consists of three spinel blocks. Aside from that, the general features of the two structures are almost identical. However, the β'' structure does not have any Frenkel defects and it does not have the excess sodium and oxygen found in the Na-O layer of β -alumina. Furthermore, single crystals cannot be prepared without adding a third cation, eg, Mg^{+2} . The replacement of the small triply-charged Al^{+3} by a larger ion with smaller charge reduces the lattice strains. Since this structure does not have blocked paths in the conduction plane, you might expect a larger ionic conductivity.

That is exactly what is found; β'' -alumina has a conductivity several times higher than β -alumina and may turn out to be a more useful material as a solid electrolyte.

The third research area that I shall discuss concerns crystallographic investigations of another type of conductivity, namely superconductivity. Superconducting materials are needed to produce high field magnets in fusion reactors and magneto-hydrodynamic devices, they have potential in energy storage, and they are important in the conservation of electrical energy. There are two main objectives in present superconductivity research--to obtain superconductors with higher transition temperatures and to obtain superconductors which can transport higher currents. Crystallographic investigations are involved in both types of research.

One interesting crystallographic investigation on high temperature superconductors is the measurement of phonon dispersion curves by inelastic neutron scattering. My next slide is an illustrative example. These are

SLIDE 15 - Longitudinal Acoustic Modes in TaC and HfC

dispersion curves for the longitudinal acoustic modes in TaC and HfC that were obtained by Smith and Glaser at Oak Ridge in 1970. HfC does not become superconducting down to about 1°K, and the dispersion curves for HfC have a normal behavior. On the other hand, TaC is a relatively high temperature superconductor with a transition at about 10°K, and you notice these oscillations in the dispersion curves. These are isomorphous compounds in which the only apparent difference is the number of valence electrons. Therefore, it is believed that these oscillations are associated with the strong electron-phonon interaction required for superconductivity. The phonon dispersion

curves for other high temperature superconductors also show this behavior. Much theoretical work has been done, but there really is not a completely satisfactory explanation of these oscillations at the present time. However, it should be mentioned that theoreticians are making definite progress in this area; recent calculations of the phonon line-widths due to the electron-phonon interaction agree very well with experimental measurements.

Another area of crystallographic research associated with high transition temperatures concerns the effect of nuclear radiation on superconducting materials. My next slide shows the dramatic decrease in the superconducting

SLIDE 16 - Superconducting Transition vs ϕ

transition temperature of A-15 compounds as a function of irradiation with high energy neutrons; only Mo_3Os shows a relatively small effect. These are recent data of Cox, Sweedler, and Moehlecke of Brookhaven National Laboratory, who also showed that similar changes are found in some of the other superconducting parameters. They have made careful measurements of transition temperatures, long-range order parameters and lattice constants on many irradiated and unirradiated samples. From these detailed measurements, they have concluded that the principal reason for this change in T_c and in the other parameters is a disorder due to the two types of atoms changing sites. My next slide shows some of their data on the variation of the

SLIDE 17 - T_c vs S

transition temperature with the long-range order parameter S. You notice, of course, that T_c for Mo_3Os is relatively insensitive to site-exchange disorder. There are two sets of data for Mo_3Os ; in the samples of Flükiger, et al.,

disorder was introduced by quenching, whereas in the samples of Sweedler, Cox and Moehlecke, it was introduced by irradiation. These experiments also showed that annealing can restore the original T_c , lattice parameter, and long range order. Consequently, from a practical viewpoint, it may be possible to use these materials in a radiation environment, if provision can be made for periodic annealing.

The other important research in superconductivity involves obtaining higher currents in Type II superconductors, which are the important superconductors from a technological viewpoint. When these materials are placed in an external magnetic field and the field is increased above a specific value, the magnetic field is no longer repulsed from the superconductor but starts to penetrate it. The magnetic field within the superconductor exists as quantized flux lines called fluxoids, which are arranged in a two-dimensional lattice. Cribier, Jacrot and their associates at Saclay showed in 1964 that these fluxoids can be observed by neutron diffraction. My next slide shows

SLIDE 18 - Microscopic Field Distribution of Fluxoids in Nb

the microscopic field distribution that was determined by Weber, Schelten and Lippmann at Jülich for a sample of superconducting niobium. At the bottom is the cross-sectional view perpendicular to the two-dimensional fluxoid lattice, with contour lines representing the field distribution. The top view shows the intensity of the magnetic field in three dimensions. You notice that the two-dimensional lattice is triangular; this is the normal symmetry, but it can take other regular forms for various types of crystal symmetry if there is a strong interaction with the crystal lattice. The nearest

neighbor distance depends on the temperature and field, but it is always quite large--of the order of $2000 \text{ \AA}$ --so that the experiments must be performed at very small angles. One of the important results of the experiment shown in this slide was the determination of the distribution of magnetic field within a fluxoid; this distribution, of course, was determined by precise form factor measurements.

A practical goal is to understand the motion of these fluxoids, which occurs at high fields and currents. They start to move across the superconductor, dissipating energy and causing the material to become non-superconducting. If this motion can be pinned, higher currents can be obtained.

A large amount of the neutron scattering work on fluxoid lattices has been performed at Jülich by Schelten, Schmatz, Ullmaier, Lippmann and their associates. They have performed many types of experiments involving fluxoid morphology, magnetic field distribution and the effects of transport currents on the fluxoid lattice. Some very important results have come from their investigations. In one important investigation, they showed that when the fluxoid lattice moves at high currents, it moves as a periodic lattice. In another very difficult experiment, they measured the distribution of currents within a superconductor and showed that this distribution was consistent with the critical field model of superconductivity. They have also investigated the bending of flux lines due to Nb_2N precipitates.

More recently, investigations have been initiated at Oak Ridge by Christen, Tasset and Thorel using a very high resolution double-crystal technique to obtain very precise information on the fluxoid behavior. These measurements have revealed exactly how the fluxoid lattice is formed with increasing field and how it disappears with decreasing field. They have recently obtained a

very unexpected result which is shown on my next slide. These data show the

SLIDE 19 - Misalignment of Fluxoid Lattice

misalignment of the fluxoid lattice with respect to applied magnetic field, when the field was applied parallel to various crystal directions of Nb. Prior to these measurements it had always been assumed that the fluxoid lattice was exactly parallel to the applied field, but as you see here for Nb, there is usually some misalignment. Such a misalignment could be quite serious in the A-15 compounds where the interaction between the fluxoid lattice and crystal lattice is expected to be more anisotropic than in Nb.

The fourth area of crystallographic research on energy-related materials, which I have chosen, concerns catalytic materials. Of course, catalysts are important in a variety of technologies, but they are particularly important in the gasification and liquefaction of coal. For those of you totally unfamiliar with catalysts, let me say that there are many different types and my next slide shows some illustrative examples. This is by no means a complete

SLIDE 20 - List of Types of Catalysts

list; I merely want to point out the wide variety of both simple and complex materials that can be used as catalysts. Crystal structure investigations have provided a lot of important information, particularly on these complex systems, but I shall not discuss any structure studies. I shall limit my remarks to some crystallographic investigations that have been made on the simple metal catalysts.

In understanding catalytic activity, it is essential to know the details of the surfaces that are involved. As you know, the field of surface science

has really only become quantitative during the past 5 years or so. Solid surfaces can now be reproducibly prepared in high vacuum and studied by many techniques, such as LEED, Auger spectroscopy, energy loss spectroscopy, positive ion channeling spectroscopy, and so on. We now know that the stable surface can be characterized by one of several ordered surface structures which depend on the symmetry of the substrate. Furthermore, the various surface structures may have only slightly different free energies of formation, so that one surface structure may change into another more stable one as the temperature or chemical environment is changed. An illustration of this effect is shown on my next slide. These are data obtained at Oak Ridge

SLIDE 21 - Re-Ordering of Au Surface

by Jenkins, Zehner, and Noonan, which show how the structure of the (110) surface of gold varies with temperature. On the left is the simplest structure; it is one which is identical to the bulk, but it exists in gold only above 475°C. The more complicated structure on the right exists at room temperature. Positive ion channeling measurements by Appleton and his associates have shown that the first layer of this structure is relaxed inward toward the second layer by about 10%. This is a completely reversible process with temperature and obviously plays an important role in surface-related phenomena such as catalysis.

The physical geometry of the surface is also closely associated with catalytic activity as was shown recently by Somorjai and his students at the University of California at Berkeley. They carefully prepared surfaces of a platinum single crystal so that the surfaces were microscopically flat but contained atomic steps. Such a surface is shown schematically on my next slide. They found that a stepped surface showed considerable catalytic activity

SLIDE 22 - Schematic Representation of Stepped Surface

whereas an unstepped surface was essentially inactive. In fact, a stepped surface seemed to show selectivity to different hydrocarbon reactions, which was dependent on the step periodicity.

Information on the morphology of supported metal catalysts is also important in understanding catalytic activity. Although the particle size distribution can be obtained by electron microscopy, it is a tedious technique to obtain good statistical accuracy. Information on the area of catalysts exposed can be obtained from chemisorption measurements, but sometimes these results are unreliable. Therefore, x-ray scattering techniques have been applied to these problems. Small angle x-ray scattering measurements have been developed particularly by Renouprez, Imelik, Gallezot and their associates. These measurements show promise, but great care must be taken to make corrections for scattering from the pores of the support. One method is to eliminate this scattering by filling the pores with a fluid that possesses the same electronic density as the support.

In very recent work in the United States, Cohen and Sashital, working as part of a group including catalytic chemists, have studied platinum catalysts supported by silica. They have shown that a large amount of information can be obtained by very careful Fourier analyses of Bragg reflections. They were able to determine the existence of microstrains in the particles and to measure the crystallite sizes in a number of crystallographic directions. The next slide shows some of their data. Here you see data on

SLIDE 23 - Particles Sizes $\langle L \rangle_{hkl}$ in the $\langle hkl \rangle$ Directions
and Percentages Exposed

catalysts prepared in four different ways, with two specimens under each type of preparation. For the first method of preparation the platinum particles were comparable in size to the pores in the silica, and these particles showed microstrains. These other three preparations produced strain-free particles, and you notice that for each of them the platinum particle sizes in the various crystallographic directions are comparable. This means that the platinum particles are nearly spherical and not cubic as had been frequently assumed. The last two columns compare the percentages of particles exposed, as measured by x-ray scattering and by chemisorption; you notice that the agreement is good. Cohen, Sashital, and their associates also showed that the logarithm of the root-mean-square amplitude of vibration increased with the percentage of atoms exposed and that a correlation existed between the amplitudes of vibration and catalytic activity, which is shown on my next slide. The turnover number is defined as the molecules reacted per surface

SLIDE 24 - Correlation of Catalytic Activity

atom per second for three different hydrogenation processes--the hydrogenation of cyclopropane, methylcyclopropane, and propene. You notice the linear relationship between the catalytic activity and the root-mean-square vibrational amplitude obtained from the x-ray data. Such a correlation suggests that the catalytic activity is strongly influenced by the surface phonons of the catalyst. In other very recent investigations at the University of Kentucky, De Angelis and his associates have shown that careful analysis of the profile of a single x-ray peak can determine average particle size, microstrain, and the particle size distribution.

Before leaving the subject of catalysis, I would like to mention an exploratory experiment using synchrotron radiation by Lytle, Via, and Sinfelt at Stanford University, which appears to be a promising method for future investigations. My next slide shows some of their data on platinum catalysts

SLIDE 25 - EXAFS Data on Platinum

supported on silica. On the left of the slide are EXAFS data taken at 100°K. k is the photoelectron wave length, and $\chi(k)$ represents normalized fluctuations in the absorption coefficient measured between the L_3 and L_2 absorption edges. At the right are the corresponding Fourier transforms, which give the distances from a platinum atom to surrounding atoms. The top data are for a Pt standard, the center for a 10% platinum catalyst, and the bottom for a 1% platinum catalyst. From the peak intensities it was possible to determine that the surface atoms have a higher vibrational amplitude than the bulk atoms and that the surface atoms have an average coordination number of 7 compared to 12 for atoms in the bulk platinum.

This concludes the remarks that I planned to make about crystallographic investigations in four important areas of materials research related to energy technologies. Of course, there are many other areas that I could have chosen to discuss. There have been a number of important crystallographic investigations of high temperature materials, salt hydrates for use in energy storage, amorphous materials, polymers, and even coal itself. Moreover, the properties of metal hydrides have been studied at many reactor centers throughout the world. These hydrides could be very important in plans to use hydrogen as a primary fuel, because they offer great possibilities for the storage and transport of hydrogen cheaply and safely. Of course, neutron crystallography

offers an excellent method to determine information on bonding and diffusion mechanisms in these hydrides, which is necessary to develop optimum systems. Particularly important investigations on metal hydrides have been performed in Denmark by Andresen and his associates, in Germany by Springer, Alefeld, and Richter, and in the United States by Rowe and Rush of the National Bureau of Standards and by Flotow and Sköld of Argonne National Laboratory. It has obviously not been possible for me to discuss all of the important crystallographic investigations associated with materials for energy technologies, but I believe that the examples I have chosen are representative of the types of studies that can be performed.

In closing this lecture, I want to say just a few words about the future. If you as crystallographers want to make contributions that will help in the solution of the energy problem, what can you do? I wish that it were possible to list just a few crystallographic problems and tell you that their solutions would end our concerns about energy. Unfortunately, there is no such list! It is only possible to show again on the next slide the chart that I showed

SLIDE 26 - (Repeat of Slide 3)

earlier. These are the important types of crystallographic information that can be obtained in areas of research, which are needed to develop new materials required by the advanced energy technologies. It is obvious that crystallography is essential in the solution of these materials problems. Furthermore, as the existing problems are solved and new problems develop, crystallography will continue to play a dominant role in solving them.

There have been many recent developments in both equipment and techniques that can be applied to crystallographic problems. These new facilities and

techniques are opening many new research areas for crystallographers. My next slide lists some of the new research directions that could be very

SLIDE 27 - New Research Directions

significant in helping to understand various physical properties of materials.

Of course, neither the new techniques nor the new research areas can help to solve practical materials problems unless crystallographers know what the major problems are. We cannot do this by isolating our interests and our research. In order to make our best contributions, we must interact closely with other scientists.

In an excellent article in Physics Today about three years ago, Professor Guinier pointed out that the future of crystallography is bright--that there is much exciting work for crystallographers to do, but that it should be done in collaboration with chemists, biologists and especially with solid state physicists. He pointed out the need to study defects in the long range periodicity of the crystal, because these defects are frequently connected to the important physical properties of materials. I wish to emphasize his remarks! For those of you who wish to help solve materials problems related to advanced energy technologies, it is essential that you follow this advice. There are many areas in materials science where important new crystallographic information can be obtained, but it is necessary that you interact closely with materials scientists working in these areas. They need the results you can obtain from crystallographic investigations; you need their guidance in the choice of problems and their physical property measurements. You must use your expertise in trying to understand how structural characteristics--both long range periodicity and the lack of it--affect materials properties. This

Information is not only very important from a scientific viewpoint, but it is essential in the prediction and development of new materials with special properties.

DOE MATERIALS SCIENCES WORKSHOPS, 1977

WORKSHOP	LOCATION	DATE
1. ELECTRONIC, MAGNETIC, OPTICAL AND THERMAL PROPERTIES	ARGONNE NATIONAL LABORATORY	MARCH 9-11
2. SURFACE SCIENCE	LAWRENCE BERKELEY LABORATORY	MARCH 16-18
3. X-RAY, NEUTRON AND ELECTRON SCATTERING	OAK RIDGE NATIONAL LABORATORY	APRIL 13-15
4. LOW TEMPERATURE RESEARCH AND SUPERCONDUCTIVITY	BROOKHAVEN NATIONAL LABORATORY	APRIL 18-20
5. PHASE TRANSFORMATIONS, STABILITY, AND MATERIALS INTERACTIONS	LAWRENCE BERKELEY LABORATORY	APRIL 18-20
6. DEFECTS, DIFFUSION, AND RADIATION EFFECTS	OAK RIDGE NATIONAL LABORATORY	APRIL 27-29
7. ENGINEERING MATERIALS SCIENCE	OAK RIDGE NATIONAL LABORATORY	MAY 2-4
8. MECHANICAL PROPERTIES	ARGONNE NATIONAL LABORATORY	MAY 5-7
9. THERMODYNAMICS AND ELECTROCHEMISTRY	ARGONNE NATIONAL LABORATORY	MAY 18-20

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MATERIALS RESEARCH REQUIRED	ENERGY TECHNOLOGIES							ENVIRONMENT AND SAFETY
	FOSSIL	FISSION	FUSION	SOLAR	GEOTHERMAL	STORAGE	CONSERVATION	
HIGH STRENGTH	X	X	X		X			X
HIGH TEMPERATURES	X	X	X	X	X	X	X	
RADIATION EFFECTS	X	X	X					X
CORROSION, EROSION	X	X	X	X	X	X	X	X
CATALYSTS	X			X		X	X	X
POLYMERS				X			X	X
INSULATORS	X		X	X		X	X	X
ELECTROLYTES						X	X	
COATINGS, CLADDINGS	X	X	X	X	X		X	
SUPERCONDUCTORS	X		X			X	X	
METAL HYDRIDES			X			X		X
COMPOSITES	X	X		X			X	
AMORPHOUS			X	X		X	X	X
CEMENTS	X				X			X
SEMICONDUCTORS				X			X	X
FLUIDS	X	X	X	X	X	X		X
ALLOYS	X	X	X		X			X
CERAMICS	X	X	X	X		X	X	X

MATERIALS RESEARCH REQUIRED	CRYSTALLOGRAPHIC INVESTIGATIONS					
	CRYSTALLINE STRUCTURES	NONCRYSTALLINE STRUCTURES	SURFACE PROPERTIES	DYNAMICAL PROPERTIES	MAGNETIC PROPERTIES	DEFECTS AND INHOMOGENEITIES
HIGH STRENGTH	X	X		X		X
HIGH TEMPERATURES	X		X	X	X	X
RADIATION EFFECTS	X		X	X	X	X
CORROSION, EROSION	X	X	X			X
CATALYSTS	X	X	X	X	X	X
POLYMERS	X	X	X	X		X
INSULATORS	X			X	X	X
ELECTROLYTES	X	X		X		X
COATINGS, CLADDINGS	X	X	X			X
SUPERCONDUCTORS	X	X	X	X	X	X
METAL HYDRIDES	X		X	X	X	X
COMPOSITES	X				X	X
AMORPHOUS		X	X	X	X	X
CEMENTS	X	X				X
SEMICONDUCTORS	X	X	X	X	X	X
FLUIDS		X				X
ALLOYS	X	X	X	X	X	X
CERAMICS	X		X		X	X

OCTAHEDRAL

TETRAHEDRAL

CROWDION

$\langle 100 \rangle$ -SPLIT

$\langle 111 \rangle$ -SPLIT

$\langle 110 \rangle$ -SPLIT

Six Self-Interstitial Configurations in a F.C.C. Lattice.

ORNL-DWG 78-12814

X-RAY DIFFUSE SCATTERING FROM INTERSTITIALS IN
ELECTRON IRRADIATED COPPER AT 4°K

HUANG SCATTERING FROM INTERSTITIALS AND CLUSTERS IN
ELECTRON IRRADIATED ALUMINUM AT 4 °K

Dislocation Loops in Copper Neutron Irradiated at 316 °K.

S.A.N.S. AND SIZE DISTRIBUTION OF VOIDS IN ALUMINUM NEUTRON IRRADIATED AT 355°K

THEORETICAL SPECIFIC ENERGY OF ELECTROCHEMICAL COUPLES.

IONIC CONDUCTIVITY OF VARIOUS SUPERIONIC CONDUCTORS

SPINEL BLOCK IN β -ALUMINA

ORNL-DWG 78-12606

SODIUM DISTRIBUTION IN CONDUCTION PLANE
OF Na β -ALUMINA AT 20°C

ORNL-DWG 78-12607

FRENKEL DEFECT IN SPINEL
BLOCK OF β -ALUMINA

ORNL-DWG 78-12608

β -ALUMINA

β'' -ALUMINA

STRUCTURES OF
 β -ALUMINA AND β'' -ALUMINA
(idealized)

Longitudinal Acoustic Modes in Tantalum and Hafnium Carbide.

VARIATION OF T_c IN A-15 COMPOUNDS WITH NEUTRON FLUENCE ($E > 1$ MeV)

VARIATION OF T_C WITH LONG RANGE ORDER

ORNL-DWG 78-12612

MAGNETIC FIELD DISTRIBUTION IN
SUPERCONDUCTING NIOBIUM

Misalignment Angle $\Delta\psi$ vs α in $(1\bar{1}0)$ Plane

TYPES OF CATALYSTS

CLASS OF MATERIALS	EXAMPLES
METALS	Pt, Pd, Ni
ALLOYS	NiCu, PtAu, NiW, RuCu, ZrPt ₃
BORIDES	Ni ₃ B, Mo ₂ BC, Co ₂₁ Hf ₂ B ₃
OXIDES	CrAl ₂ O ₄ , MgAl ₂ O ₄ , Mg ₂ Mo ₃ O ₈ BaRuO ₃ , TiO ₂ · SiO ₂
SULFIDES	VS, V ₅ S ₈ , CoV ₂ S ₄ , La ₄ NiS ₇ , Al _x Mo ₂ S ₄
ZEOLITES	Ba(Al ₂ Si ₃ O ₁₀) · 4H ₂ O (K, Na) ₅ Si ₁₁ Al ₅ O ₃₂ · 10H ₂ O Ca(Al ₂ Si ₄)O ₁₂ · 6H ₂ O
ORGANOMETALLIC COMPLEXES	Pt ₃ [CN(C ₄ H ₉)] ₆ , Rh ₁₃ (CO) ₂₄ H ₃ , Au ₁₁ [P(C ₆ H ₅) ₃] ₇ I ₃
HOMOGENEOUS	Co ₂ (CO) ₈ C ₉₀ H ₁₄₈ O ₇₂ · 25H ₂ O

Au (110) SURFACE

○ FIRST LAYER ○ SECOND LAYER ● THIRD LAYER

SCHEMATIC REPRESENTATION OF A STEPPED SURFACE.

Particle Sizes $\langle L \rangle_{hkl}$ in the $\langle hkl \rangle$ Directions and Percentage Exposed

Catalyst	$\langle L \rangle_{111}$ (Å)	$\langle L \rangle_{100}$ (Å)	$\langle L \rangle_{110}$ (Å)	$\langle L \rangle_{311}$ (Å)	D_x (%)	D_h (%)
7.1-SiO ₂ -PtCl-S						
(1)	131	82	108	81	10	7.1
(2)	111	75	—	—	12	7.1
21.5-SiO ₂ -IonX-L						
(1)	49	43	45	47	25	21.5
(2)	48	43	45	47	25	—
27-SiO ₂ -IonX-S						
(1)	43	39	42	31	27	27.3
(2)	40	39	39	39	29	—
40-SiO ₂ -PtCl-S						
(1)	30	26	22	20	44	39.8
(2)	25	23	—	—	47

CORRELATION OF CATALYTIC ACTIVITY WITH
MEAN-SQUARE VIBRATIONAL AMPLITUDE

NORMALIZED EXAFS DATA FOR Pt

NEW DIRECTIONS FOR CRYSTALLOGRAPHIC RESEARCH

1. CONTROLLED ENVIRONMENTAL EFFECTS
2. TIME-DEPENDENT PHENOMENA
3. EFFECTS OF EXTERNAL TRANSIENT PHENOMENA
4. GRAIN BOUNDARY PROPERTIES
5. HIGH RESOLUTION ANALYTICAL MICROSCOPY
6. EFFECTS OF GASES ON VOID FORMATION
7. REAL-TIME MEASUREMENTS OF DEFECT DYNAMICS
8. STRUCTURE AND DYNAMICS OF SURFACES
AND OVERLAYERS
9. INTERACTIONS BETWEEN SUPPORTED CATALYSTS
AND SUBSTRATES
10. HIGH RESOLUTION INELASTIC X-RAY SCATTERING
11. MACROMOLECULAR CRYSTALLOGRAPHY
12. INHOMOGENEITIES IN GLASSES