

# Novel Electronic Materials

## *the MX family*

*Alan R. Bishop and Basil I. Swanson*

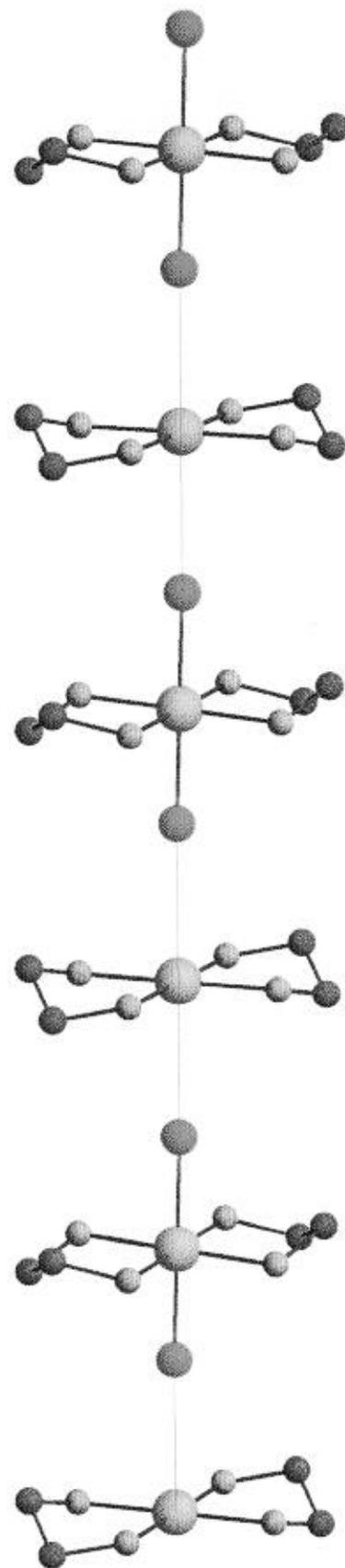
The Laboratory and the nation are increasingly faced with demands for novel electronic materials needed to advance special-purpose technologies. Those demands have already led to extraordinary discoveries and applications of novel materials. Recent examples include self-assembling multilayer thin films for use in sensors and nonlinear optical devices and electrically conducting organic polymers that produce blue light by electroluminescence (light in that spectral region is unavailable from conventional light-emitting diodes).

Standard, or "textbook," electronic materials (such as copper and silicon crystals) are ordered materials made up of simple unit cells (the repeating units of a crystal). The theories to describe those materials are relatively simple: the electrons are treated as nearly noninteracting and the theories are applied only in situations where the displacements of the atoms from their equilibrium positions in the crystal lattice are small. However, the last fifteen years or so have been marked by the synthesis, microscopic characterization, and increasingly predictive modeling of rich families of materials that are very different from traditional materials. Research on these families of materials has led to major awards (including several Nobel Prizes) and new technologies. The families include amorphous semiconductors, quan-

tum-Hall-effect materials, materials with artificial structures on mesoscopic scales (a few hundred or thousand atoms), ultrathin films, synthetic metals (such as conducting polymers), quasi-crystals, organic superconductors, high-temperature superconductors, and buckminsterfullerenes, to name a few.

These "novel electronic materials" generally display significant differences from the former textbook materials. In particular, many are anisotropic (composed of chain-like or plane-like configurations of atoms), artificially structured into stable or long-lived metastable forms, inhomogeneous, or composed of complex, low-density unit cells, and many have various combinations of those properties. Indeed, the subject of novel electronic materials lies between textbook chemistry, physics, and biology, and we speak of "soft condensed matter" or "condensed-phase chemistry" in an attempt to capture the spirit of the new interdisciplinary ground.

The essential and newly emerging research strategy for all of these fascinating materials is a very close team approach involving synthesis, characterization, and theoretical modeling. This approach has been adopted vigorously at the Laboratory, since it is well suited to the Laboratory's extreme breadth of capabilities and tradition of tackling complex issues from a multidisciplinary per-



*Side view of a PtCl chain in an MX solid. The Pt ions are bonded to ethylenediamine ligands.*

spective. Those strengths have proven very attractive to industrial collaborators as the Laboratory develops closer relations with industry. We describe here some notable successes of the application of our strategy to one newly emerging family of materials—metal-halogen (MX) linear-chain complexes. MX materials are discussed in detail below, but first we should explain the general challenges posed by the development of novel electronic materials.

It is now abundantly clear that the method of synthesis, the resulting microstructure (local atomic patterns), and the macroscopic (bulk) properties of novel electronic materials are inextricably linked. Desirable optical, magnetic, and other macroscopic properties are found to depend crucially on details of microstructure, which in turn are controlled by the details of the synthesis. Understanding those relationships is a goal of synthetic chemists and materials scientists as well as of experimentalists developing characterization techniques with ever-improving spatial and temporal resolution—such as ultrafast optical spectroscopy (which can resolve times approaching  $10^{14}$  second) and scanning tunneling microscopy.

Therefore, the ultimate aim of theoretical modeling must be to short-circuit trial and error in the synthesis-characterization-modeling-application program by predicting which modified or entirely new materials will have optimal properties and how those materials can be synthesized. However, that aim is extremely difficult to achieve using current theoretical techniques. The materials in which we are interested have strong electron-lattice and electron-electron interactions that compete on different length and time scales, produce

strongly nonlinear and nonequilibrium features, and make the properties of the material very sensitive to its microstructure. In fact, the existence of and competition between these complex properties are directly responsible for the very novelty of the materials and give rise to their potential for meeting the rigorous demands of device engineering. At the Laboratory we are trying to develop new techniques for modeling those materials by bringing together traditional techniques from quantum chemistry, the study of electronic band structure, and many-body physics. We are validating theory by direct experimental tests as part of our synthesis-characterization-theory-application team approach.

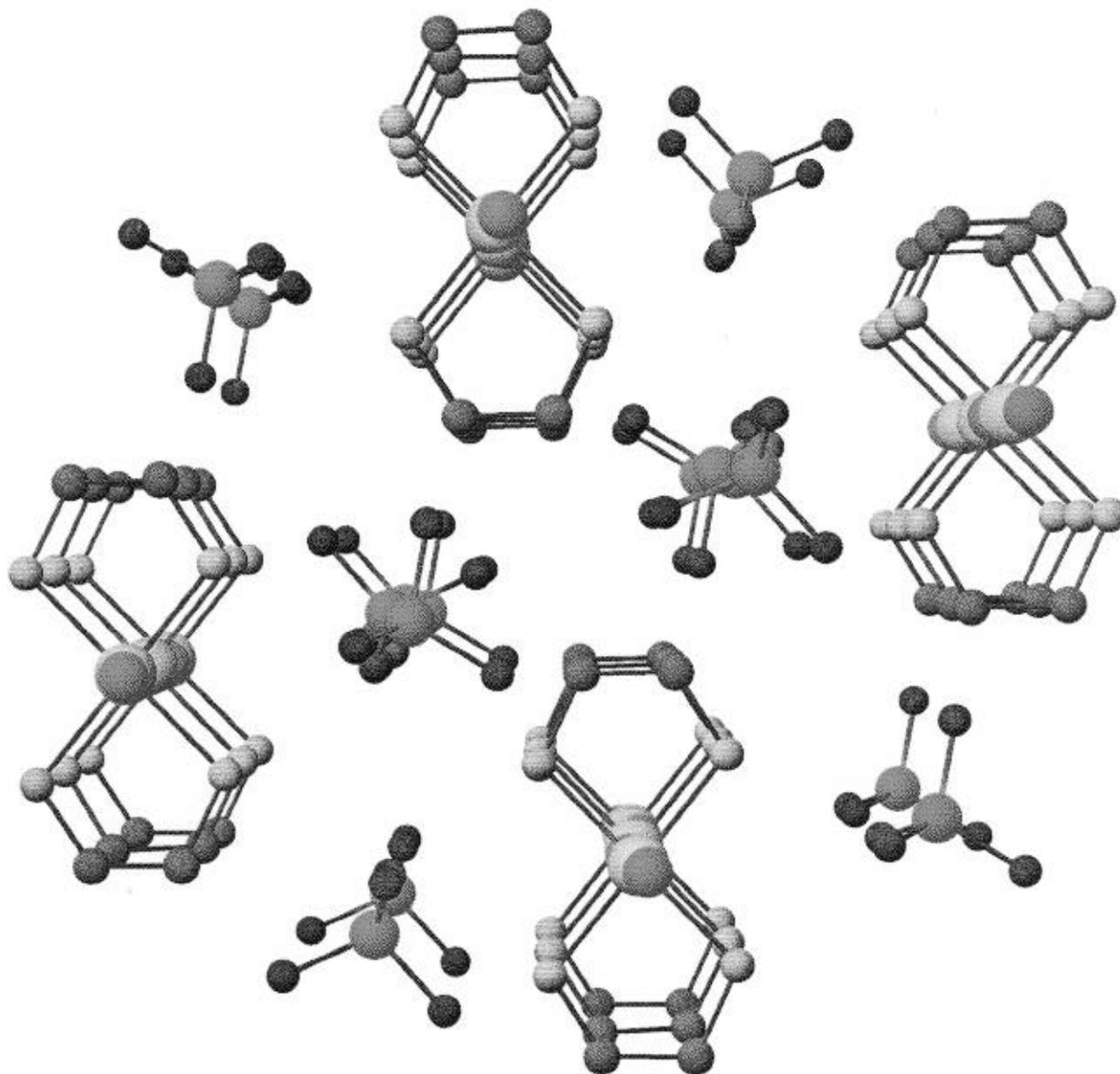
## MX Materials

The MX family of compounds is particularly rewarding to study for a number of reasons. They are fine subjects for working out an integrated development strategy. They are complex enough to exhibit much of the sensitivity discussed above but just simple enough to allow substantial microscopic characterization. The various compounds of the family exhibit a remarkable range of strengths of competing forces and consequent physical properties. They share fundamental features with other novel electronic materials, such as conducting polymers and organic and high-temperature-superconductors, and therefore test our ability to model an extremely wide range of physical properties. Finally, in learning how to synthesize, model, and fabricate them, we have discovered that they have substantial technological potential in their own right.

Although the MX family now represents one of the very best examples of international success in the synthesis-characterization-modeling-application strategy, it is important to emphasize that the research challenge is far from completely met—at the Laboratory or anywhere else. For the MX class, we have had success in controlling microstructure by varying the method of synthesis. We can make single crystals, thin films, and junctions between different members of the MX family. Likewise by applying many-body modeling techniques to known specific microstructures, we have made precise predictions of optical, electronic, and magnetic properties, which in turn we measured with precise microscopic characterization tools. Some of those successes are outlined below. Yet the “holy grail,” the ability to predict what synthesis method will lead to desired macroscopic properties, remains unachieved for the MX materials, as indeed for all such complex materials.

Figure 1 depicts the basic crystal structure of MX materials. Most importantly they contain parallel chains of metal ions (M), such as platinum, palladium or nickel, alternating with halide ions (X). The metal ions are attached to molecular complexes (ligands) that act to hold the chains in place in the three-dimensional crystal structure. However, electronic, optical, and magnetic properties of the MX solids are determined mostly by the electrons and ions along the metal-halide chains, so the electronic character of the solids is strongly *one-dimensional*.

Two properties of MX materials are crucial in producing their novel electronic and optical properties: first, they have broken-symmetry ground states whose crystal struc-



**Figure 1. The Structure of a Typical MX Material**

The crystal structure sketched here is that of  $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{ClO}_4)_4$ , where en stands for the molecule ethylenediamine,  $(\text{CH}_2\text{NH}_2)_2$ . The view is approximately down the Pt-Cl chains, the most important axis for electronic activity. Pt atoms are represented in blue and Cl in green. Each ethylenediamine ligand binds to a Pt ion on a chain. The spaces between the chains are filled with rows of  $\text{ClO}_4^-$  ions, called counterions because they provide the charges needed for overall electric neutrality.

tures are nearly perfect over large domains, and second, they have gap states, electronic states above the ground state that are created by defects, impurities, structural inhomogeneities, and photoexcitation.

### Broken-Symmetry Ground States

Figure 2 illustrates two examples of broken-symmetry ground states in MX materials. In both cases the metal-halide chains in their ground states are

less symmetrical than a regular alternation of metal and halide ions. Specifically, each unit cell of the chain contains two metal and two halide ions rather than just one of each.

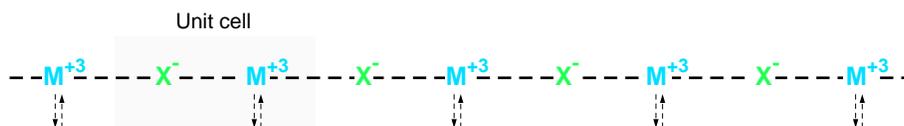
In the ground state of the PtCl compound the unit cell is doubled because the electrons and ions are shifted from their symmetric positions. The structural distortion creates a periodic variation in charge density called a "charge-density wave" (CDW). The distortion is a direct result of electron-electron and electron-ion interactions. Structural

distortions that double the unit cell were predicted to occur in low-dimensional electronic materials by Peierls in the 1950s and have since been found in many such materials, including most MX compounds. (Incidentally, Peierls was an important member of the Laboratory's Theoretical Division during the Manhattan Project.) The existence of the CDW ground state of the PtCl solid was successfully predicted by our theoretical modeling.

Figure 2 also illustrates a second type of broken-symmetry ground state

## (a) Hypothetical Symmetric Ground State

Metal-halogen distances are equal; charge and electron-spin configurations are symmetric. Spin of unpaired electron on metal ion has equal probability of pointing up or down.



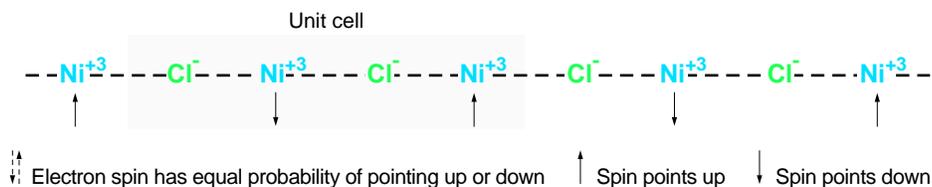
## (b) Charge-Density Wave in PtCl Chain

Electron-spin configuration is symmetric but charges on metal ions alternate between +4 and +2 and halogens move closer to Pt<sup>+4</sup> ions, breaking the charge and lattice symmetry in (a).



## (c) Spin-Density Wave in NiCl Chain

Metal-halogen distances are equal; charge configuration is symmetric but unpaired electrons on metal ions alternate in direction, breaking the spin symmetry in (a).

**Figure 2. Peierls Transitions to Broken-Symmetry Ground States**

The MX chains exhibit Peierls transitions to broken-symmetry states. A Peierls transition is a spontaneous transition of a one-dimensional chain from a symmetric configuration like that shown in (a) to a less symmetric but lower-energy configuration like those shown in (b) and (c). The symmetry breaking causes the unit cell to contain twice as many atoms and thus to double in size. Two types of broken-symmetry ground states are found in MX solids, depending on the metal (M) and halide (X). (b) The charge-density-wave (CDW) ground state in a PtCl chain. The charges on the metal ions (Pt) alternate between +2 and +4. The lattice is distorted from the symmetric configuration so that the halide ions (Cl<sup>o</sup>) are bound more closely to the more highly charged neighboring metal ion than to the other. (c) The spin-density-wave (SDW) ground state in a NiCl chain. The lattice is symmetric because all bond lengths are equal, but the spins of the unpaired electrons on the metal ions (Ni) alternate in direction. The symmetry breaking of the CDW and SDW ground states results in electronic configurations with an energy gap like the energy gaps characteristic of semiconductors (illustrated in Figure 3).

in which the spins of the unpaired electrons on the metal ions alternate in direction to form a “spin-density wave” (SDW). Spin-density waves occur in the ground states of only a few known MX materials, such as the NiBr and NiCl compounds. They are similar to the insulating states of high-temperature superconductors.

In both CDWs and SDWs, the doubling of the unit cell creates a gap in the band of allowed electronic energy levels. The gap forms between the occupied and unoccupied levels of the ground state and thus plays a role similar to that of the band gap in

semiconductors (see Figure 3), even though the mechanisms producing the gaps are quite different. Further, by “tuning” MX materials (that is, by varying the metal, halogen, ligand, pressure, and so forth) we can vary the size of the gap to values between approximately 1 and 3.5 electron volts, an unusually wide and technologically important range.

**Gap States**

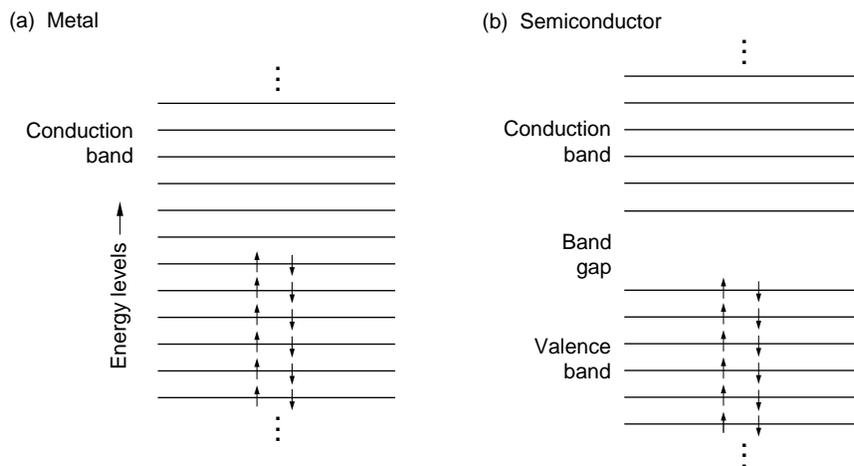
In both MX materials and semiconductors, local lattice distortions

caused by inhomogeneities or local defects (including impurities) can produce spatially localized electronic wave functions and cause the electronic energy levels near the band gap to move into the gap. The resulting gap states may involve zero, one, or two electrons (or holes, which are missing electrons), depending on the charge of the inhomogeneity. As shown in Figure 4, MX materials, like semiconductors, can be deliberately doped with a low density of impurity atoms that, by donating electrons to or accepting electrons from the host material, create charged gap states

such as polarons and bipolarons. Those excitations are local lattice distortions containing extra electrons or holes. Also illustrated in Figure 4 is the use of “photodoping” to create neutral gap states such as excitons. (Structural imperfections also cause electronic energy levels to move into the gap. Like photodoping, structural defects do not change the overall electronic charge in the material, so the resulting gap states are neutral.)

Much semiconductor device physics is based on modifying material properties to control the energies and occupation densities of the gap states. For example, if excitons are created, their decay can result in electroluminescence, a phenomenon exploited in light-emitting diodes. The presence of gap states also allows the absorption of light at energies (and therefore colors) different from the energy across the band gap (see Figure 5). Finally, conductivity, for either direct current or alternating current, is strongly influenced by the occupation density and nature of the gap states, especially charge-carrying states such as polarons or bipolarons. The gap states may diffuse along chains or quantum-mechanically hop along or between chains, as they are believed to do in conducting organic polymers.

Semiconductor research and development is therefore largely devoted to “engineering” the size of the band gaps and the nature and occupation density of the gap states. That type of engineering is similarly important in the MX family, but easier for two reasons. First, because MX materials are low-dimensional and have strong electron-ion interactions, their lattice distortions are large, leading to gap states whose energies are relatively far from the valence- and conduction-band edges.



**Figure 3. Electronic Energy Levels of a Metal and a Semiconductor**

In solids, the electronic energy levels are so closely spaced in energy that they form bands. For clarity only a few of the levels are shown here. Each level can be occupied by an up-spin electron (↑) and a down-spin electron (↓). Additional occupation is forbidden by the Pauli principle. (a) In a metal, the band of energy levels is partially filled. Transitions to the higher, unoccupied levels are easily induced, for example by applying an electric field. Once such transitions have occurred, electric charge can flow. (b) A semiconductor contrasts with a metal in having an energy gap between the top occupied level—the top of the valence band—and the lowest unoccupied level—the bottom of the conduction band. Therefore free flow of charge is inhibited unless a sufficiently strong electric field or light of sufficient energy transfers an electron across the gap.

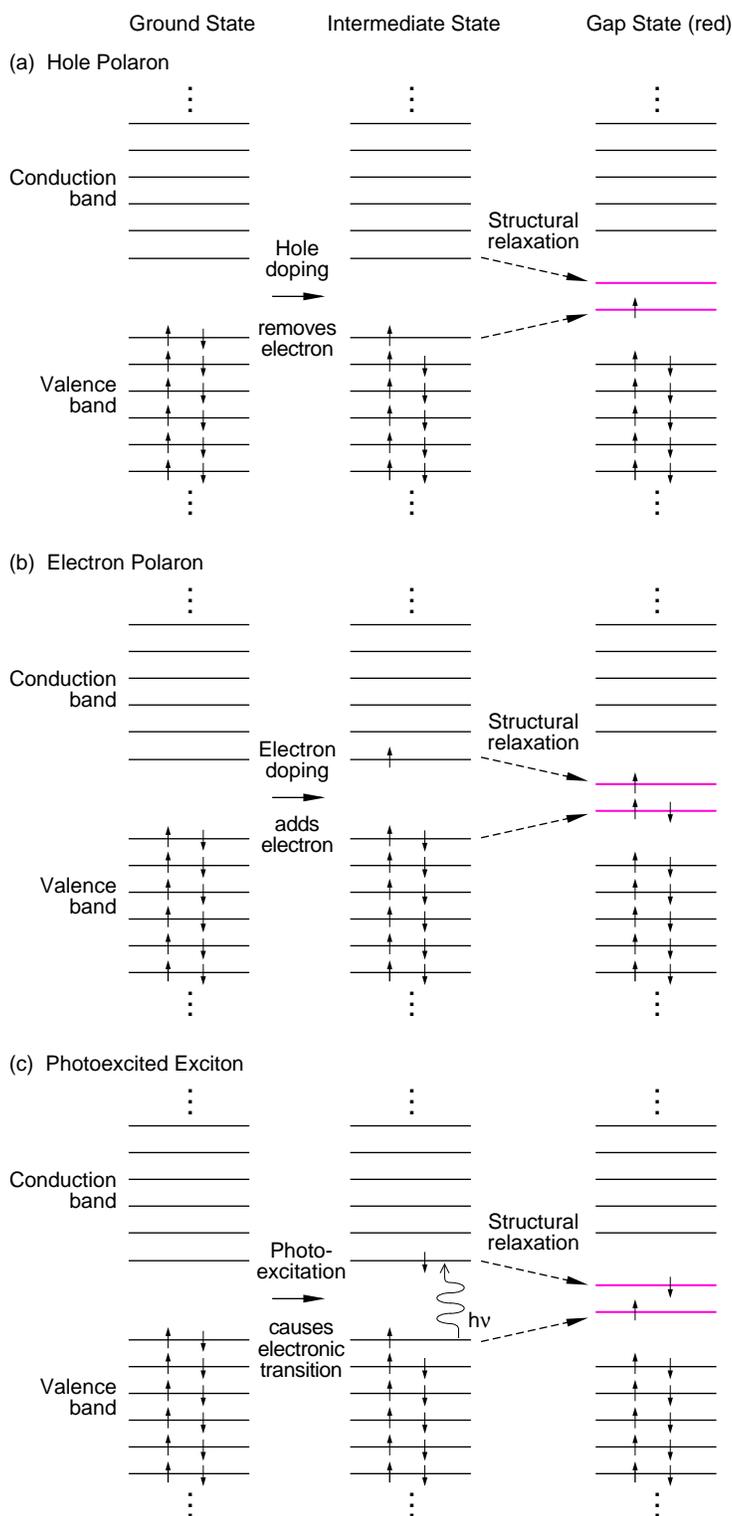
(In traditional semiconductors, the lattice distortions are much smaller and gap states remain near the edges.) Second, because of the *tunability* of the MX family, the size of the energy gaps can be varied over a strikingly large range to produce a range in the size of local lattice distortions from one or two unit cells (in PtCl) to more than thirty unit cells (in PtI), a potentially useful property for photonic and other technologies.

Gap states may also be created in MX materials by controlled inhomogeneities such as interfaces between different compounds in the family. The variety of available gap states allows for stringent tests of theory and modeling and opens up a wide range of technological possibilities.

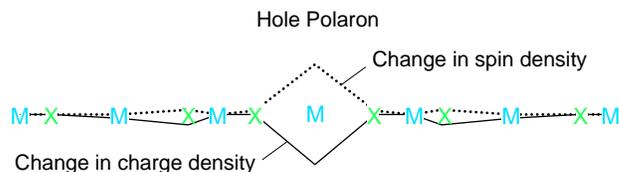
## Pure MX Solids

The optical and electronic properties of MX materials are most easily studied in pure MX compounds like that shown in Figure 1. At the beginning of our research, we discovered that all the earlier studies of the PtBr solid had actually employed samples in which as many as 12 percent of the halide ions were chloride rather than bromide. The assumption that those samples were pure had made it impossible to properly interpret experimental results, and the resulting misinformation further hampered the development of theoretical models. This episode illustrates the essential role of synthesis coupled with detailed characterization in materials research.

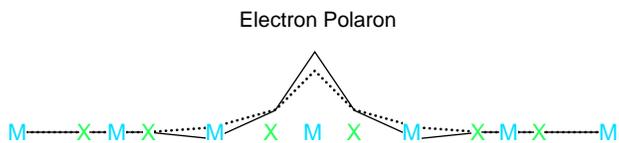
**Creation of Gap-State Energy Levels**



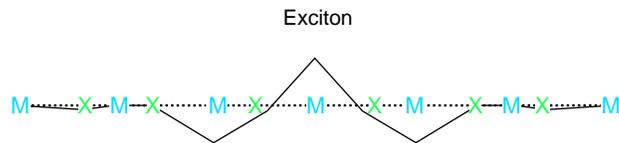
**Spatial Configurations of Gap State in PtCl Chain**



A hole polaron centered on a metal ion ( $M^{+2}$ ) increases the spin density and decreases the electron density, giving the metal ion a more positive charge. The increase in positive charge pulls the neighboring halide ions closer to create a local lattice distortion.



An electron polaron centered on a metal ion ( $M^{+4}$ ) increases both the spin density and the electron density, giving the metal ion a less positive charge. The decrease in positive charge allows the neighboring halide ions to move farther away to produce a local lattice distortion.



A singlet exciton centered on a metal ion  $M^{+2}$  produces changes in the electron density that even out the charge differences between the  $M^{+2}$  ion and its  $M^{+4}$  neighbors and consequently also even out the nearby bond lengths. Since the exciton is a singlet it does not affect the spin-density distribution.

Once we had pure MX materials, we determined their crystal structures more precisely than had previously been done (particularly by finding structural phase transitions involving slight shifts of atomic positions with-

in a CDW configuration). We then took advantage of the MX family's variable chemical make-up by studying the dependence of ground states on composition. It has long been known that the choices of both metal

and halogen affect the properties of an MX material. For instance, using chlorine as the halogen yields a strong CDW ground state; that is, the ions shift considerably from their symmetric positions, so the periodic

### Figure 4. Gap States

Three types of gap states—a hole polaron, an electron polaron, and a singlet exciton—are illustrated as they would appear in a PtCl chain. Also shown are the mechanisms that typically create them. (a) An acceptor dopant (an ion that readily binds to an electron) is close to a PtCl chain. The acceptor dopant withdraws an electron from the chain, becoming negatively charged and leaving behind a vacancy or hole in the highest level of the valence band. The hole behaves as if it had a positive charge. Once the hole has been created, a lattice distortion takes place that causes the highest energy level of the valence band and the lowest energy level of the conduction band to move into the gap. The resulting gap levels are occupied by any electrons that occupied those levels before the lattice distortion. The combination of the missing electron and the lattice distortion is called a hole polaron. As shown at right, the lattice distortion traps both the charge density and the spin density associated with the hole. The lattice distortion shown is in the strong CDW of a PtCl chain and therefore is highly localized, extending over only two unit cells. Polarons in chains with weaker CDWs, such as PtBr and PtI, are less localized. (b) A donor dopant (an ion that readily loses an electron) donates an electron to the lowest level of the conduction band. The resulting electron polaron is very similar to a hole polaron except that it contains an electron and therefore has a negative rather than a positive charge. (c) Here no extra charge has been added to the MX chain. Instead, light of an energy greater than the band gap has excited an electron from the top of the valence band to the bottom of the conduction band. As in (a) and (b), a lattice distortion follows, forming the gap levels illustrated. One level is occupied by a spin-up electron and the other by a spin-down electron to form a singlet exciton (one with zero total spin) that does not alter the spin density. The charge-density distribution of the exciton follows a “multipole” pattern. Other kinds of excitons are possible, including a triplet exciton in which the electrons occupying the two gap levels are pointing in the same direction.

variation in charge density caused by those shifts has a large amplitude. On the other hand, using iodine yields a weak CDW (the ions are close to their symmetric positions and the amplitude of the CDW is small). Materials with strong CDWs have large band gaps whereas those with weak CDWs have small band gaps.

Our group and those led by Yamashita (Japan) and Clark (Britain) have recently recognized that changing the ligands or counterions changes the spacing along the metal-halide chains and thereby provides an alternate method for tuning the material's electronic structure. We call that control the “template effect” because the ligands and counterions act as a template to which the chain geometry must adjust. The template effect allows us to vary electronic properties of MX solids over a wide range with high precision and to simplify both experimental characterization and theoretical modeling. We hope soon to use the template effect to create materials that have a metal-like phase.

### Excitations in Pure MX Solids

Our study of gap states in MX materials is an example of strong synergy between theory and experiment. We used several experimental techniques to produce and characterize a variety of gap states. We also developed models of the different possible gap states and solved them to predict what experimental results each type of gap state would lead to. We then used the experimental data to refine the models and theoretical interpretations, which, in turn, improved our understanding of the data.

Our basic model is a Schrödinger equation for electrons on a single chain. The Hamiltonian contains the Hubbard-model Hamiltonian, which describes interactions between spins of electrons on the same or nearby ions as well as quantum-mechanical “hopping” of an electron from one ion to an adjacent ion. Our Hamiltonian also contains “Peierls” terms, which describe the interaction between electrons and lattice distortions

(so that as the lattice distorts, both the local and hopping electronic energies change self-consistently) and terms for the elastic energy of lattice distortions.

Since different gap states are at different energy levels, they absorb light of different energies. A typical method for detecting and characterizing them is to measure their absorption spectra (see Figure 5). However, gap states in MX materials are rare. To enhance spectral signatures from them and to learn about the associated lattice distortions, we also used resonance Raman spectroscopy, which measures the energies of the characteristic lattice vibrations associated with the local distortions of the gap states.

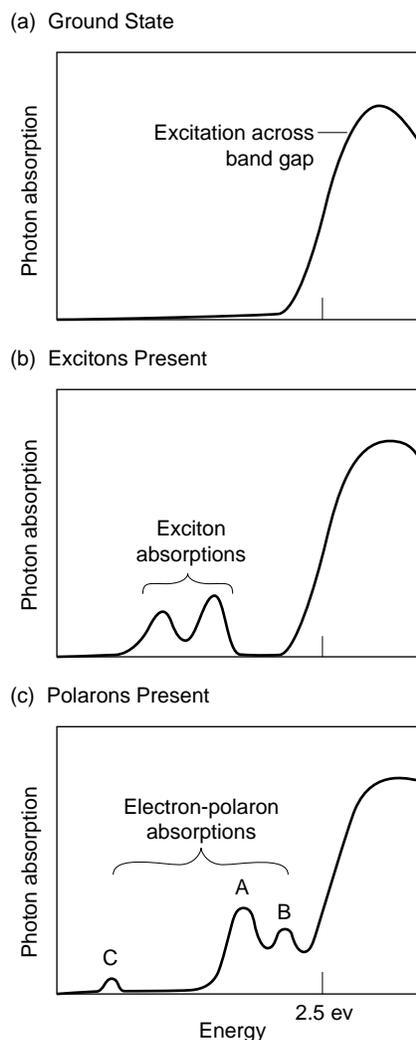
In resonance Raman spectroscopy, material is illuminated with light that is in resonance with a specific electronic transition. After interacting with that light, the material scatters light not only at the incident energy (Rayleigh scattering) but at higher and lower energies as well that differ by the energies of the

### Figure 5. Optical Absorption Spectra of Gap States

For light to be absorbed by an MX solid, the light must have enough energy to excite an electron from an occupied electronic level to a level that is not completely filled. (a) For an MX material in its ground state to absorb light, the energy of the light must be at least as great as the band gap. (b) If excitons have been created, for instance by photoexcitation, two energy levels move into the gap, so light can be absorbed at energies below the band gap indicated by peaks in the absorption spectrum. (c) Polarons can also absorb light at energies below the band gap. The energies are different from those absorbed by excitons as indicated by the absorption spectrum of electron polarons.

material's lattice-vibrational modes. The signals from vibrational modes that are coupled to the electronic transition are greatly enhanced, by as much as a factor of a million in some instances, compared with the signals that would be obtained by ordinary Raman spectroscopy. (In ordinary Raman scattering, as opposed to resonance Raman scattering, the incident light is not in resonance with any transition and so has a much smaller probability of interacting.)

To perform resonance Raman spectroscopy on the gap states in MX materials, we first cooled the material to below 10 kelvins and created gap states by photoexcitation. As illustrated in Figure 6, photoexcitation typically creates excitons which can decay to polarons. Gap states in MX materials are short-lived, but at temperatures below 10 kelvins a small fraction of them live long enough for the resonance Raman measurement to be made. We tuned the incident light to an absorption peak below the band gap that had been measured previous-



ly. From the frequencies of the emitted light we determined the vibrational energies of the local lattice distortions associated with the gap states. The measured energies of gap-state vibrations could then be used to estimate the number and lengths of bonds affected by the gap states' local lattice distortions because the energies of lattice vibrations are directly related to such structural features as the lengths and strengths of interatomic bonds.

We found that the resonance Raman and optical-absorption spectra

of the gap states in the PtCl solid matched our theoretical prediction for the vibrational spectra of polarons. Studies with electron paramagnetic resonance (EPR) spectroscopy, which measures electron spins and their interactions with the lattice, corroborated our identification of the gap states as polarons. Using the same technique we found that at low temperatures the excitations in the PtBr solid (which is a weaker CDW than the PtCl solid) are bipolarons. Bipolarons are similar to polarons but contain pairs of electrons or holes whose spins point in opposite directions. Above about 60 kelvins the bipolarons are observed to dissociate into polarons.

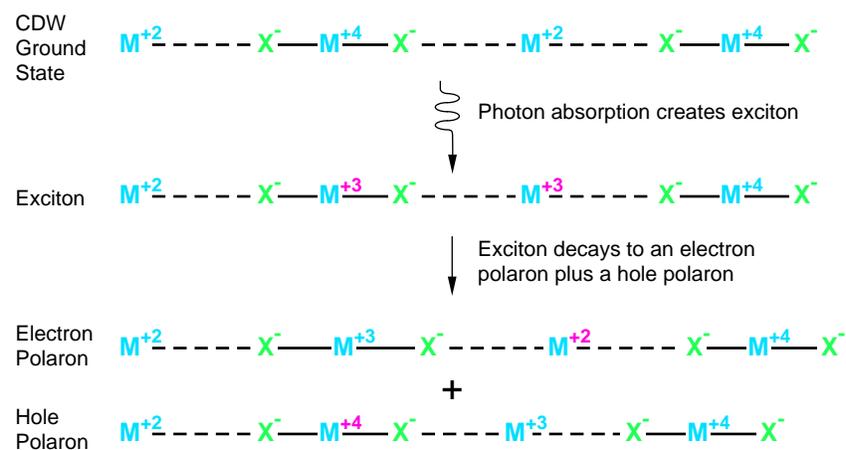
Since polarons and bipolarons have electric charge and can move along the chains (by diffusion or hopping), they play a critical role in the electrical conductivity of MX solids. Their mobility is low because the motion of polarons requires the motion of ions in the lattice, which are much heavier than electrons. Hence most MX materials are poor conductors. The mobility of the polarons increases, however, as the strength of the CDW decreases, because in a weak CDW the local lattice distortions of the polarons are less localized (as measured by EPR). We are hoping that if we can make an MX material in the transition regime between CDW and SDW ground states, its conductivity will be high.

Several groups had predicted that electron and hole polarons would have exactly the same absorption spectra. Thus, it was a surprise to find that, when we measured the absorption spectra using resonance Raman spectroscopy, the electron-polaron spectra were slightly different from the hole-polaron spectra. The difference is consistent with the in-

involvement of the halide-ion orbitals as well as the metal-ion orbitals in the polarons. When we incorporated the halide-ion orbitals into our theory, we were able to reproduce the spectra of both electron and hole polarons. The discovery of the unexpected role of the halides has been useful to Los Alamos theorists studying high-temperature superconductors. Those materials share many general features with MX solids; the oxide and copper ions they contain are analogous to the halide and metal ions in MX solids. There had been considerable debate about whether the oxide ions had any important effect on superconductivity in high-temperature superconductors. Guided by our experience with MX solids, Laboratory theorists are taking the oxide ions into account.

### Mixed-Halide MX Solids and Quantum Confinement

Platinum-halide solids made with significant quantities of two halogens can form high-quality single crystals. This result is another surprise because the metal-metal spacing of the PtI solid is quite different from those of the PtCl and PtBr solids, and normally solids of different structures form separate crystals. We attribute the unusual miscibility to the template effect. The chains in mixed crystals contain segments 1 to 10 nanometers long in which only one halide occurs, and the metal-metal spacing of the minority segments is forced to approach the spacing of the majority of the crystal. Thus mixed crystals contain metal-halide chains with metal-metal spacings, and consequently CDW strengths, quite different from those found in pure crystals made with the



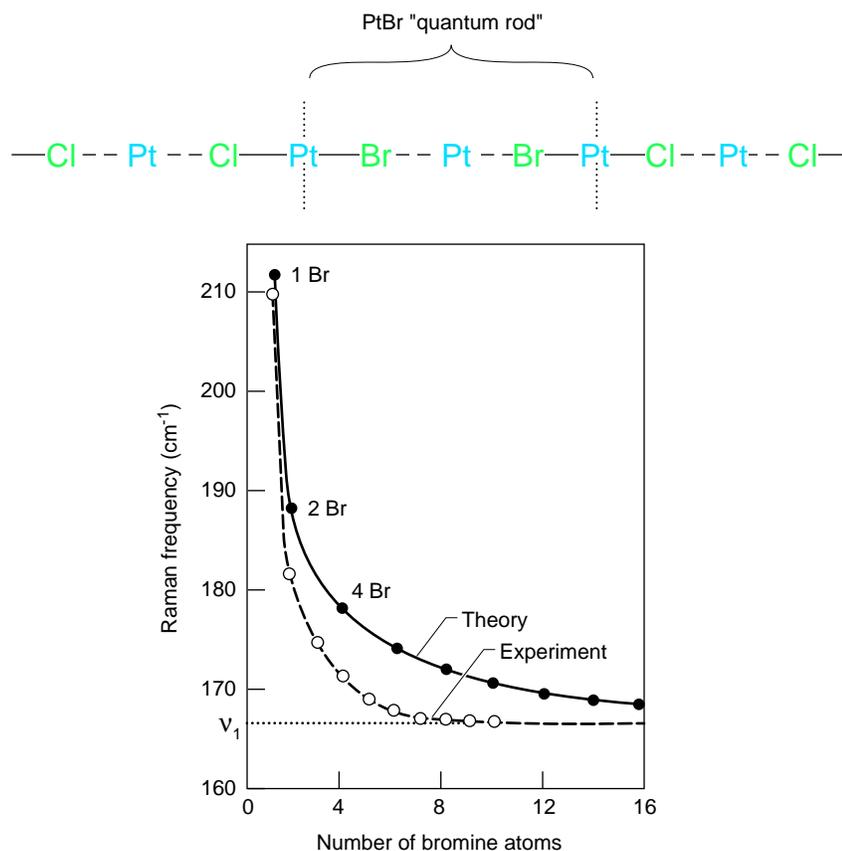
**Figure 6. Photoexcitation of Excitons and Polaron Pairs**

The figure illustrates the creation of an exciton through photoexcitation and its spontaneous decay to an electron polaron and a hole polaron. The first step is the same as that shown in Figure 4 c. In the second step the exciton, which is neutral, breaks up into a hole polaron (positive) and an electron polaron (negative). Here, instead of displaying the charge distributions of the excitons and polarons as in Figure 4, we schematically represent changes in the charge distributions by changes in the valences of the metal ions. The changes in valence are highlighted in red. Note that no charge is added in either step.

same halide. The most striking example is a mixed PtI/PtCl solid in which there is much more Cl than I. In that case the Pt-Pt spacings in both the PtI and PtCl segments are nearly as small as they are in a pure PtCl material. Consequently, in the PtI segments the iodide ions appear to be halfway between the Pt ions, as the halide ions are in an SDW, rather than closer to one Pt ion as they are in the CDW ground state of a pure PtI solid (see Figure 2). Evidently the PtI segments have been forced past the boundary of the CDW phase into some other phase, possibly an metallic phase or an SDW.

Experimental evidence suggests that in mixed-halide MX chains, electrons are confined to segments of one composition. The confinement is particularly clear-cut in PtCl/PtBr solids. As mentioned earlier, the lat-

tice and charge-density distortions of polarons in the strong CDW of PtCl compounds are highly localized. In other words, there is very little electronic communication along PtCl chains. When PtBr segments are embedded in a PtCl chain, the chloride ions at either end of a PtBr segment act as hard “electronic rocks” that isolate the electrons in the PtBr segment. The “quantum confined” behavior of electrons in such sharply bounded segments, or quantum rods, is amenable to theoretical modeling. For instance, electron configurations affect vibrational frequencies in such a way that short confined segments have higher vibrational frequencies than longer segments. We used resonance Raman spectroscopy to measure this effect in PtBr segments. We tuned the incident light to the band gaps in the PtBr segments, which are



**Figure 7. Segment-Length Dependence of Raman Frequency**

The molecule depicted is a PtCl chain containing a short PtBr segment. The theoretical curve (solid circles) gives the results of our calculations for the lowest vibrational (Raman) frequency of such a segment as a function of the number of Br ions in the segment. Frequencies measured by resonance Raman spectroscopy are also shown (open circles). The many measured frequencies close to the value  $\nu_1$  cannot be distinguished, so no data points are given beyond 10 bromine atoms. The frequencies have been assigned to numbers of Br ions based on the principle, thoroughly established experimentally and theoretically, that the vibrational frequency of a segment decreases with increasing segment size. The uncertainties in the measured frequencies are approximately the same size as the circles representing the data points.

lower than the band gap in the PtCl chain. Since the band gaps of the PtBr segments increase with decreasing segment length, we knew that if we gradually increased the energy of the incident light, starting from the band-gap energy of pure PtBr, we could excite PtBr segments in order of decreasing length. We measured the

resonance Raman spectra of the PtBr segments by that method. Figure 7 shows that the Raman (vibrational) frequencies are close to those predicted by our many-body model for PtBr segments of various lengths.

The properties we have discussed so far are of interest mostly from the standpoint of basic science. Poten-

tially more useful in devices are the properties of the junctions between segments. As shown in Figure 6, excitation of an MX solid with a photon whose energy is greater than or equal to the band gap can create an electron polaron and a hole polaron. Thus, exposing an MX solid to light creates equal numbers of electron and hole polarons throughout the material. Surprisingly, though, when a mixed PtCl/PtBr material is photoexcited, the majority of the electron polarons have resonance Raman spectra typical of polarons in PtBr whereas the majority of the hole polarons have spectra typical of polarons in PtCl. That result implies that, once created, the electron polarons tend to migrate to the bromide segments while the hole polarons tend to migrate to the chloride segments. Such separation of charge carriers also occurs in doped semiconductors and is the basis of many of their useful properties. We hope eventually to synthesize MX samples containing single junctions, in the same place in every chain, between regions of different composition. Such samples could be incorporated into photovoltaic devices. We expect that samples with single junctions could also efficiently generate coherent light at double the frequency of incident laser light (second-harmonic generation).

MX solids also appear promising for nanotechnology because they can be made in high-quality single crystals in which the electronic and optical properties vary on a scale of nanometers and because those properties can be controlled chemically through, for example, synthesis of mixed-halide crystals. If we could produce conducting phases, mixed MX solids could have junctions between conducting and semiconducting

segments; such junctions are needed to create nanoscale computers. A further requirement is the fabrication of superlattices: samples in which junctions are spaced at controlled intervals along chains and the junctions of different chains are lined up in parallel. Superlattices could also serve in solid-state lasers. We hope to prepare nanoscale superlattices using electrochemical growth methods that have already been used successfully with other materials. At present, superlattices and other nanoscale structures in materials for electronics can be created only through expensive vapor-deposition methods.

Another direction of our current work is the use of picosecond and femtosecond spectroscopy. At present, we can study only the longest-lived excitations: polarons and bipolarons at low temperatures. Using the laser apparatus that has been developed for ultrafast measurements, we hope to study short-lived excitations such as polarons at high temperatures and the still shorter-lived excitons (see Figure 6) as well. We will also look for such exotic states as “breathers” (stable, nonlinear, localized vibrational states) that have been predicted to occur in MX and related materials. Another goal that we and others are pursuing is making MX materials with different compositions. A particularly attractive possibility is replacing the metal ions with “binuclear” ions consisting of two metal ions (MM) bound together by ligands. Such ions are the subject of great excitement in the field of inorganic chemistry and the synthesis of MMX solids might enormously expand the potentials of MX materials. We hope that through continued collaborations involving synthesis, experiment, and theory, we will learn more



about the fascinating properties of MX solids and make available new materials that may be the basis of future advanced technology. ■

#### Acknowledgements

We are grateful to many colleagues with whom we have developed our understanding of MX solids, including Bob Albers, Meb Alouani, Tony Arrington, Dionys Baeriswyl, Alain Bulou, Robert Donahoe, Tinka Gammel, Joe Huang, Sara Hockett, Susumu Kurita, Steve Love, Richard Martin, Avadh Saxena, Brian Scott, and Laura Worl.

#### Further Reading

D. Baeriswyl and A. R. Bishop. 1987. Halogen-bridged metal complexes: Model compounds for high- $T_c$  superconductors? *Physica Scripta* T19: 239–245.

Sara C. Hockett, Robert J. Donahoe, Laura A. Worl, Alain D. F. Bulou, Carol J. Burns, Joseph R. Laia, David Carroll, and Basil I. Swanson. 1991. Mixed-halide MX chain solids: Effect of chloride doping on the crystal structure of resonance Raman spectra of  $[\text{Pt}(\text{en})_2\text{Br}_2][\text{Pt}(\text{en})_2](\text{ClO}_4)_4$ . *Chemistry of Materials* 3: 123–127.

J. Tinka Gammel, A. Saxena, I. Batistić, A. R. Bishop, and S. R. Phillpot. 1992. Two-band model for halogen-bridged mixed-valence transition-metal complexes. I. Ground state and excitation spectrum. *Physical Review B* 45: 6408–6434.

S. M. Weber-Milbrodt, J. Tinka Gammel, A. R. Bishop, and E. Y. Loh, Jr. 1992. Two-band model for halogen-bridged mixed-valence transition-metal complexes. II. Electron-electron correlations and quantum phonons. *Physical Review B* 45: 6435–6458.

S. P. Love, L. A. Worl, R. J. Donohoe, S. C. Hockett, and B. I. Swanson. Origin of the fine structure in the vibrational spectrum of  $[\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)_2][\text{Pt}(\text{C}_2\text{H}_8\text{N}_2)_2\text{Cl}_2](\text{ClO}_4)_4$ : Vibrational localization in a quasi-one-dimension system. *Physical Review B* 46: 813–816.

**Alan R. Bishop** (left) joined the Laboratory in 1979. He is currently leader of the Condensed Matter and Statistical Physics Group in the Laboratory's Theoretical Division. His interests include electronic and magnetic materials and nonlinear phenomena in er and materials science. He is actively involved in the Laboratory's Center for Materials Science and Center for Nonlinear Studies.

**Basil I. Swanson** (right) received a Ph.D. in physical-inorganic chemistry from Northwestern University in 1970. After a postdoctoral fellowship at the Los Alamos Scientific Laboratory and two university professorships, he returned to the Laboratory in 1980 as a staff member in the Inorganic Chemistry group. He served as the leader of that group from 1984 until 1988. Swanson is now in the Spectroscopy and Biochemistry group and was named a Laboratory Fellow in 1991. His areas of research include the structure and dynamics of solids, materials chemistry, and advanced electronic materials.