PHYSICAL PROPERTIES OF SULFIDE MATERIALS

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Abstract

A review is given of basic physical properties of sulfides in order to clarify for mineralogists the interest solid-state physicists have in these materials. After a brief description of the localized and itinerant approaches to the behavior of electrons in solids, some examples of the magnetic and electric properties are detailed, particularly those studied by means of neutron scattering. Particular topics include the magnetic structures (and their relation to exchange interactions) in the polymorphic forms of MnS, chalcopyrite, the Eu chalcogenides and Li-substituted MnSe; and the semiconducting, photoconductive and ferroelectric behavior of the IV–VI compounds, especially the Pb salts. In all these cases an attempt is made to show how these compounds are interesting in their own right, in providing clear examples of fundamental phenomena, and how they show promise of future technological applications.

The title of this review promises a great deal more than it can deliver. To describe adequately all of the physical properties of sulfide materials would be impossible in a volume, let alone an article of this length. Therefore it is first necessary to establish clearly the purposes I have in mind and, guided by these, to set out the limitations to the topic.

Scope and Purpose of the Article

Sulfides in the last decade or so have been the subject of quite intensive research in solid-state physics, primarily because they exhibit very clearly many types of basic phenomena, and are thus generators of new theories and proving grounds for existing ones. Since most sulfides exist as or have prototypes in minerals, the needs for interdisciplinary communication between physicists and mineralogists are clear. Beyond the simple transferral of information, interesting as this may be, new motivation may channel research into mutually profitable directions, thus strengthening both fields.

Two broad areas have comprised most of the research on sulfides, magnetic properties and electrical properties, and I intend to cover these more thoroughly, with brief mention of other areas that are not yet fully exploited. To avoid being encyclopedic in such an effort, the approach will be to describe qualitatively such general concepts as will be necessary, and then to list several specific examples that illustrate the general phenomena in a particularly striking way.

Of course, subjective bias is impossible to avoid in the selection of such examples, and mine as an experimental physicist working on neutron scattering from magnetic materials will be apparent. Although many interesting subjects will thus be omitted, I hope to leave the reader with some feeling for the genesis of the interest physicists have in studying sulfides, and some appreciation of the wealth of physical phenomena that are found in this class of materials.

Basic Concepts in the Description of Electrons in Solids

A convenient basis on which to classify the phenomena under discussion is the description of electrons in solids—that is, the types of wave functions $\psi(X,t)$ whose squared amplitude is the probability density of finding the electron at position X at time t. There are two models for constructing the wave functions appropriate to atoms in the solid state, which can be described loosely as the localized model and the itinerant model.

These two approaches trace their ancestry directly back to the first many-body problem by solved quantum mechanics, the hydrogen molecule. When two H atoms are brought together, one must decide what forces constitute the basic situation and what forces are to be treated as a perturbation. The Heitler-London model takes the wave function of one electron moving about each nucleus as the starting point, and the molecular orbital model takes the two electrons moving about the common center of the two nuclei. It is important to realize these are two ways of looking at the same phenomena: they both give results in agreement for the hydrogen molecule problem and indeed, it can be shown there is a continuous transition between the two as the distance of atomic separation varies. The localized versus itinerant character can thus be thought of as a measure of "apartness" of the atoms relative to the particular interaction they exert on each other. Applied to solids, these two types of theories lead to descriptions of ionic and covalent bonded compounds on the one hand and to the energy band theory of solids on the other.

The energy-band theory of solids starts with a first approximation of nearly free electrons moving in the periodic potential of the atom cores. In order to review some of the basic concepts of this theory, let me discuss some of the language, of band structurists. As the individual atoms are moved together, it is found that the discrete atomic energy levels broaden into bands of allowed energy. The solution to the simplest problem, one electron per atom in a one-dimensional crystal, is shown in Figure 1. The dashed line shows the energy versus wavenumber $(k=2\pi/\lambda)$ of the free electron, the familiar parabolic energy-momentum dependence $(E=p^2/2M$, where $p=\hbar k)$; as a consequence of the periodicity of the potential, discontinuities are introduced at wavelengths half the spacing between the atoms, separating the energies of the electrons into allowed bands separated by forbidden gaps. This figure also illustrates the concept of the Brillouin zone;
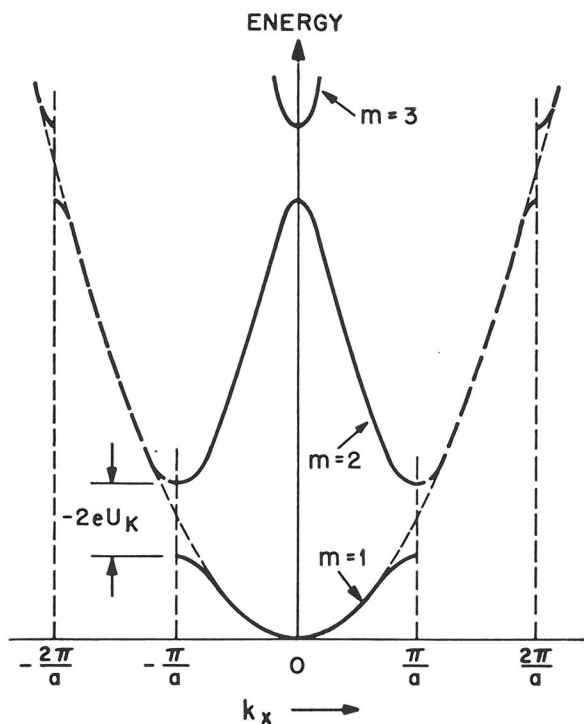
Fig. 1. Energy versus wave number for an electron in a one-dimensional periodic potential. U_K is the K'th Fourier component of the periodic potential. Light dashed line: free electrons; heavy dashed line: electrons in periodic potential; solid lines: removal of curve segments from higher zones to the reduced zone. (From Goodenough, 1963). (Reprinted by permission of the publisher.)

the reciprocal wave-number space illustrated here is a generalization of the reciprocal lattice familiar to crystallographers, and the Brillouin zone is the "unit cell" of the reciprocal lattice—a surface in wave-number space formed by planes erected halfway between each Bragg spot and its neighbor. Again because of the periodic nature of the crystal, all the information in the problem can be contained on one reduced zone, thus the folding back of the segments labelled by the band indices $m = 2$ and $m = 3$.

The final concept needed is the parameter relating to how the allowed energy states are populated by the available electrons. This is specified by the Fermi level, an energy value determined by filling the band states up to the maximum number of electrons available. In real crystals, far more complicated than the simple example illustrated here, the energies of the bands vary in three dimensions in k-space in a way reflecting the symmetry of forces acting between neighbors; and the Fermi level will not be a constant line, as it is here, but will form a complicated boundary. The shape of this boundary, called the Fermi surface, is an important quantity characterizing the behavior of the solid.

Concepts in the localized electron approach are somewhat simpler since the picture is essentially one of isolated atoms held together by ionic, covalent and repulsive forces,

whose densities overlap slightly but not enough to destroy the validity of the atomic energy levels calculated for the free atom. One of the basic concepts here is the idea of exchange interactions and covalent bonds. The central concept of the covalent bond is that a lower energy can be achieved by sharing electrons between neighboring atoms in directional, hybridized orbitals. The qualitative ideas of electron sharing have had a great influence on the physical understanding of magnetic exchange. In the following discussion, the reader is reminded that it is useful to try "keep track" of an individual electron although electrons are transferred between atoms.

The origin of the concept of exchange force again goes back to the hydrogen molecule problem. In the solution to that problem a contribution to the energy arises (paradoxically, in the present context) because of the indistinguishability of states in which the electrons exchanged places. This energy contribution combined with the Pauli exclusion principle (an axiom that states the total wave function must be antisymmetric in the exchange of space and spin coordinates) makes the singlet state, with the spins of the two electrons antiparallel, the ground state. It was realized by Heisenberg that this energy was identical in form to a scalar product of spin vectors, even though it is electrical in origin; and he hypothesized that such a mechanism could be responsible for ferromagnetism if the wave functions of the atom were such as to make the triplet state with parallel spins lie lowest. This single idea has been extremely fruitful in theories of magnetism, which attempt to derive the magnetically ordered state from microscopic forces between atoms.

Some of the models of exchange, other than ferromagnetic, that have evolved from this concept are illustrated in Figure 2. The first, superexchange, applies to cations with spins in d orbitals aligned by Hund's rule, separated by an intervening anion like oxygen with outer electrons in p orbitals (Anderson, 1963). In the first case, the spherically symmetric case of 5 d electrons, one of the pair of oxygen p electrons is promoted to the d shell of the overlapping cation wave function where it must be antiparallel by Hund's rule; the antiparallel coupling of the oxygen bonding orbitals makes the net spin of the cations antiparallel, and the excess magnetic energy gained by ordering these spins stabilizes the postulated excited state. By similar arguments, for a less than half-filled shell, superexchange predicts ferromagnetism. Indirect exchange does not involve promoting an oxygen electron, but rearranges the polarization of the oxygen electron density to keep electrons of parallel spin closer together—the same mechanism responsible for Hund's rule; the resulting coupling is always antiparallel or antiferromagnetic. Double exchange (Zener, 1951) is postulated for systems containing mixed valence states; a simultaneous transfer of electrons from cation to oxygen and oxygen to cation gains kinetic energy by contributing to the conductivity. This transfer occurs only if the ionic spins are parallel, so ferromagnetism always results. Finally, semicovalent exchange (Goodenough, 1963)
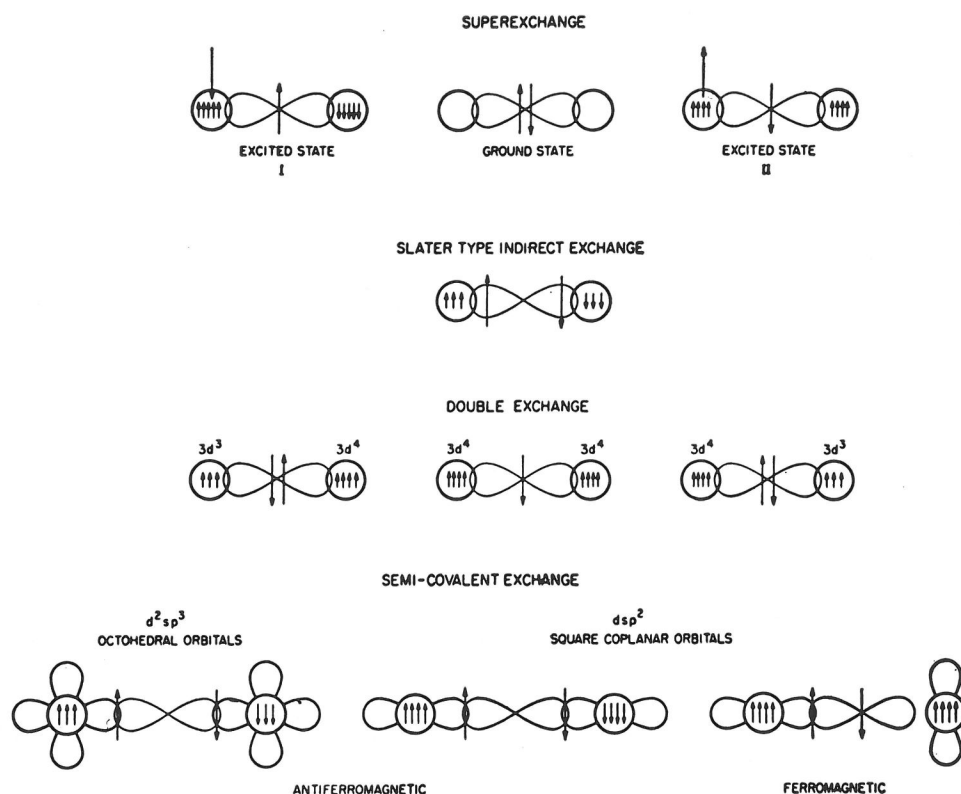
FIG. 2. Schematic representations of the different types of superexchange mechanisms. (From Shull and Wollan, 1956). (Reprinted by permission of the publisher.)

is a refinement of superexchange that takes account of covalence and orbital symmetry; it can result in either parallel or antiparallel coupling depending on the particular combination of the hybridized orbitals that are formed. The exchange mechanisms described here have had great success as phenomenological rules in accounting for many types of alignment that were actually observed (Kanamori, 1959; Wollan, 1960).

It is *convenient*, and I believe more intuitive, to discuss the magnetic properties of sulfides on the basis of localized concepts and the electrical properties on the basis of band or itinerant electron concepts. This is not to imply that each description cannot be used to predict both sets of properties—indeed they have been used that way. But, as remarked earlier, each type of theory represents a different way of looking at, or a different mix of approximations for, the extremely difficult problem of the energy states and wave functions of the 10^{23} atoms in a unit volume of the solid.

The Magnetic Properties of Sulfides

The "workhorse" theory of magnetism, the one that can explain the properties of localized spins, is the molecular field theory. Starting from the proportionality of the scalar product of spins with the exchange force, the theory attempts to minimize the exchange energy of the whole magnetic crystal through the "effective field" approach of

Weiss. The proportionality constant of this field to the magnetization is given by an appropriate sum of exchange constants over neighbors—usually restricted to nearest and next-nearest to render the problem tractable. One of the first signal successes of this theory was to explain the diffraction effects from magnetic crystals when they were studied by the method of neutron scattering.

Since the magnetic phenomena described are weighted so heavily toward neutron diffraction, it is necessary to say a few words about the types of information obtainable by this technique. For the present purpose, the central feature is that, in addition to the neutron-nucleus interaction that gives rise to Bragg peaks analogous to X-ray diffraction, there exists a comparable magnetic interaction between the neutron spin and atomic moment. This interaction gives rise to a magnetic component of the scattering which is the Fourier transform of the *magnetic moment* density in the crystal. This magnetic component is diffuse if the spins are disoriented as in the paramagnetic phase, and its diffraction symmetry tells whether the ordering scheme of the spins, called the magnetic structure, is parallel (ferromagnetism), antiparallel (antiferromagnetism), partly uncompensated (ferrimagnetism), or has some more complicated, noncollinear arrangement. A subsidiary feature of the technique is that the energy, as well as the momentum (wavelength) of the average thermal neutron in a reactor matches the elementary excitations in the solid—lattice

ELASTIC (BRAGG) SCATTERING

INELASTIC SCATTERING

$$\Delta \vec{k} = \vec{k_f} - \vec{k_i} = 2\pi\vec{\tau} + \vec{q}$$

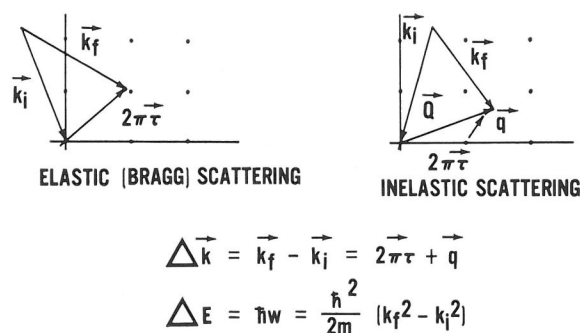$$\Delta E = \hbar w = \frac{\hbar^2}{2m} (k_f^2 - k_i^2)$$

FIG. 3. Reciprocal lattice representation of neutron scattering.

vibrations and their analogue, spin waves—hence their energy spectrum can be thus directly measured. The conditions for energy and momentum conservation in a simple cubic reciprocal lattice are sketched in Figure 3; the inelastic case may be considered as a generalization of "Ewald's sphere" construction for Bragg scattering where momentum is delivered to the individual atoms as well as the lattice, and the energy change is large enough to be detected, contrary to the case of X-rays.

The polymorphic forms of MnS and the magnetic symmetry of chalcopyrite. The three polymorphic forms of MnS all undergo magnetic ordering and the types of magnetic structures observed offer a striking example of the influence of bonding on the super-exchange interaction. The three structure types are rock salt, zincblende and wurtzite. Each Mn^{2+} cation has twelve nearest Mn^{2+}, neighbors in all three forms, but different numbers of S^{2-} anion neighbors

which provide the paths for superexchange. In the rock salt form the Mn^{2+} is bonded to next-nearest Mn^{2+} neighbors via 180° sulfur p-orbitals while in the other two forms the linkage is tetrahedral to nearest neighbors.

The magnetic correlations determined by neutron diffraction (Corliss, Elliott and Hastings, 1956) are summarized in Figure 4, which shows nearest and next-nearest cation configurations for the three cases. The important result is that the zincblende and wurtzite forms (with similar bonding but different cation arrangement) have the same magnetic structure, which differs from the rock salt spin structure, where the bonding is different. These results are consistent with the superexchange mechanism, since the antiparallel cation-anion-cation interaction couples next-nearest neighbors in the latter structure and nearest neighbors in the former.

The mineral chalcopyrite ($CuFeS_2$) is closely related to the zincblende form of MnS, the Cu and Fe systematically filling the Mn sites. The magnetic structure was also found (G. Donnay, Corliss, J. Donnay, Elliott and Hastings, 1958) to be closely related, in that the two iron atoms connected to a common sulfur atom are antiparallel. The solution of this structure is noteworthy in that it represents the first application of black-white symmetry to magnetic structure determinations. Figure 5 shows the relations of the iron moments to the symmetry elements of the space group $I\bar{4}2d$ determined from these studies.

The europium chalcogenides A system where variation in the exchange parameters is brought about solely by changes in cell dimensions, while the coordination polyhedra remain

NEAREST NEIGHBOR CONFIGURATION

STRUCTURE TYPE	ROCK SALT	ZINCBLENDE	WURTZITE
ANTI-PARALLEL	6	8	8
PARALLEL	6	4	4

NEXT NEAREST NEIGHBOR CONFIGURATION

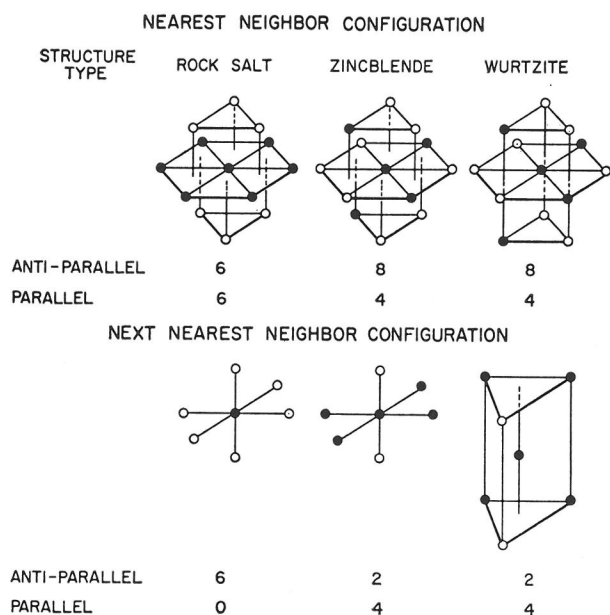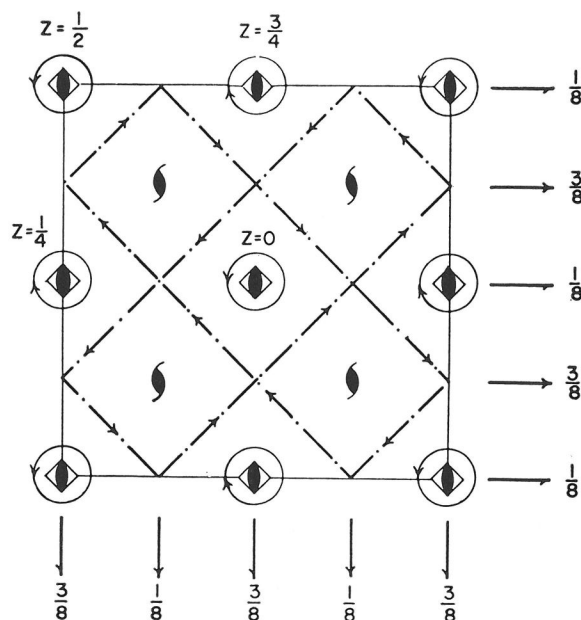|			
ANTI-PARALLEL	6	2	2
PARALLEL	0	4	4

FIG. 4. Nearest and next-nearest neighbor spin configurations in the three polymorphic forms of MnS. Metal atoms only are shown, and open and closed circles represent up and down spins respectively. (From Corliss, Elliott and Hastings, 1956). (Reprinted by permission of the publisher.)

FIG. 5. Magnetic space group symmetry elements in $CuFeS_2$. The spins are represented as current loops whose transformation properties are specified by the indicated symmetry elements. The z coordinates give the elevation and notation for symmetry elements are as in International Tables. (From Donnay *et al.*, 1958). (Reprinted by permission of the publisher.)

the same, is provided by the Eu chalcogenide salts EuO, EuS, EuSe and EuTe. These crystallize in the rock salt structure with the cell edge (and thus the next-nearest neighbor distance) varying from 5.1 to 6.6 Å. By means of magnetic susceptibility measurements, the first three were found to be ferromagnetic, the last antiferromagnetic. The nearest and next-nearest exchange interactions shown in Figure 6 were deduced (McGuire, Argyle, Shafer and Smart 1963) from the temperature dependence of the susceptibility, and a molecular field analysis.

If the assumption is made that J_1 is positive and J_2 negative, a coherent picture of the dependence of the exchange forces on distance follows, as shown by the dashed lines; the net resultant exchange force (solid line) then predicts a change form ferromagnetism to antiferromagnetism. Furthermore, this explantation predicts the EuTe will have the next-nearest neighbor (n.n.n.) correlation as found in rock salt MnS, and this was confirmed by neutron diffraction measurements (Will, Pickart, Nathans and Alperin, 1963). A precarious balance between parallel and antiparallel configuration was indicated by the fact that EuSe is a complicated antiferromagnetic in a zero external field but ferromagnetic when a field is applied (Pickart and Alperin, 1968).

Lithium-substituted MnSe. The rock salt phase MnSe is still another example of antiparallel n.n.n. correlation in its magnetically ordered phase. But when monovalent lithium

Fig. 6. Nearest neighbor (J_1) and next-nearest neighbor (J_2) exchange interactions derived from molecular field analysis of the Eu chalcogenides. (From McGuire *et al.*, 1963).

is substituted for divalent manganese, the resulting magnetic properties (Heikes, McGuire and Happel, 1961) provide a striking instance of the "touchiness" of exchange forces with respect to the various mechanisms discussed earlier. The substitution creates Mn^{3+} and Mn^{2+} pairs so that one might expect the double exchange mechanism to be operative.

This is indeed found to be the case, although the resulting situation is more complicated than expected. A magnetic phase diagram for compositions up to the solubility limit of 11 atomic percent Li is reproduced in Figure 7. One finds clear-cut evidence for ferromagnetism in the 10 percent Li sample, but it disappears about 20° below the Curie transition. Neutron diffraction (Pickart, Nathans and Shirane, 1961) showed that this transition was to an antiferromagnetic state, and indeed, one that differed from the lower concentrations by having a more nearly parallel n.n.n. configuration. Thus, although the small concentration of double-exchange coupled cations was able to swing the whole system ferromagnetic, as the temperature decreased and the mobile electrons became trapped, antiferromagnetism took over. However, a vestige of the ferromagnetic coupling remained behind and altered the scheme of the antiferromagnetic structure.
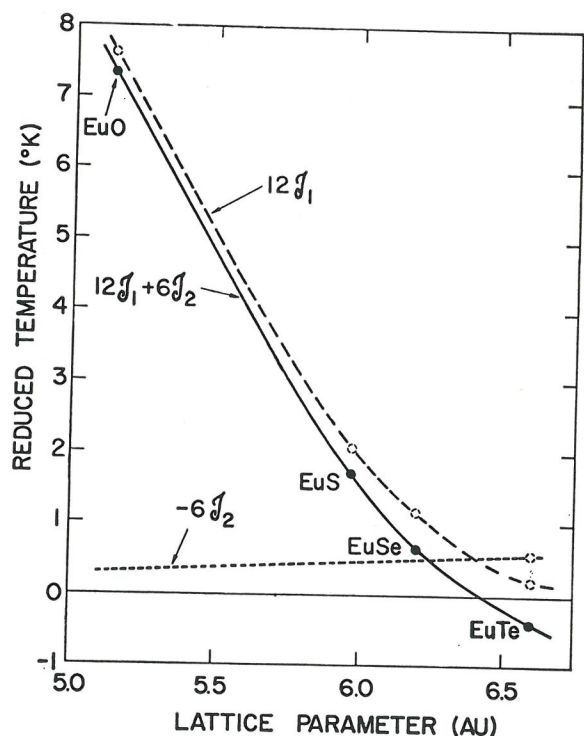
Spins as vectors: canted and spiral structures. The structures so far described have been collinear, *i.e.* the spins can be represented by plus and minus scalar quantities. What happens when an assembly of spins finds itself with comparable nearest-neighbor forces that dictate parallel alignment and n.n.n. forces that dictate antiparallelism? The answer, as already alluded to in the case of EuSe, is that noncollinear arrangements are adopted. The first such verified structure, in fact, was in the hexagonal NiAs phase of CrSe. The "spin" cell is enlarged to include three Cr spins in each basal plane and these adopt a "tepee" or umbrella arrangement that alternates in successive layers (Corliss, Elliott, Hastings and Sass, 1961).

Molecular field calculations, however, show that in general the lowest energy state of such a system is in fact a spiral arrangement (Lyons and Kaplan, 1960), of which the collinear and noncollinear structures are special cases. If the alternation direction is considered the propagation direction of a spiral helix, the ferromagnetic case corresponds to a 360° phase change or turn angle, the antiferromagnetic to a 180° phase change, and so on. It is not necessary in general for the repeat distance to correspond to the unit cell distance, although this generalization would seem at least superficially to hold conceptual difficulties for the theory of space group symmetry.

Several of such spiral structures have been discovered in sulfur compounds. Indeed, the iron series chalcogenide spinels exhibit simple Néel ferrimagnetism (unequal antiparallel spins) as in $FeCr_2S_4$ (Shirane, Cox and Pickart, 1964) simple ferromagnetism, as in $CrCu_2Se_4$ (Lotgering, 1965) and helical antiferromagnetism in $ZnCr_2Se_4$ (Plumier, 1966). A visual representation of such a spin arrangement in $MnSO_4$ is given in Figure 8. This wealth of spin arrange-
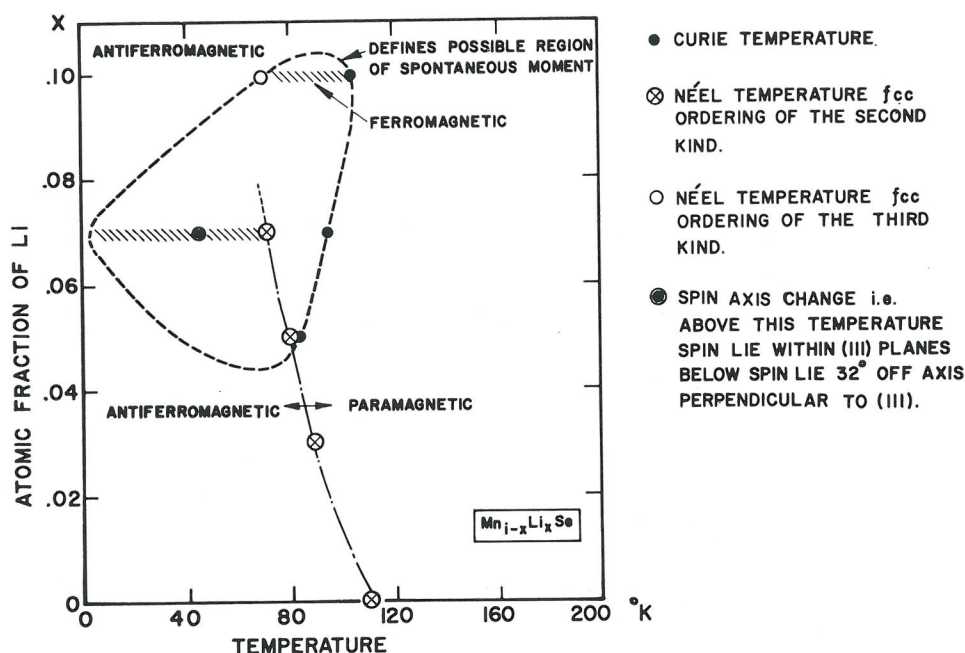
FIG. 7. The magnetic phase diagram of the Li_xMn_{1-x} system.

ments is philosophically satisfying in the sense that almost every conceivable type of ordering has now been observed.

Seeing the covalent bond. I spoke before of exchange interactions being propagated by the overlap of cation and anion electron densities. The question naturally rises, if such polarized spin density indeed exists in ligands, is there a sensitive enough method to observe it directly? The answer is yes, and the method is polarized neutron scattering, where the neutron spin-electron spin interaction is maximized by making it interfere constructively with the nuclear scattering. An example is provided by antiferromagnetic $CuSO_4$. The Cu^{2+} ions in this orthorhombic structure are sufficiently far apart that super exchange via *two* intervening anions is required, and evidence has been obtained that intervening SO_4^{2-} groups are very slightly spin-polarized.

After measuring as many of the weak magnetic scattering amplitudes as possible, a Fourier synthesis of the magnetization density projected onto the (100) plane, illustrated in Figure 9, was made (Menzinger, Cox, Frazer and Umbayashi, 1968). Note that while the majority of the
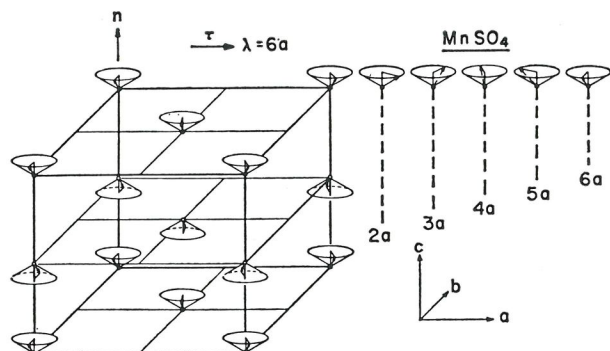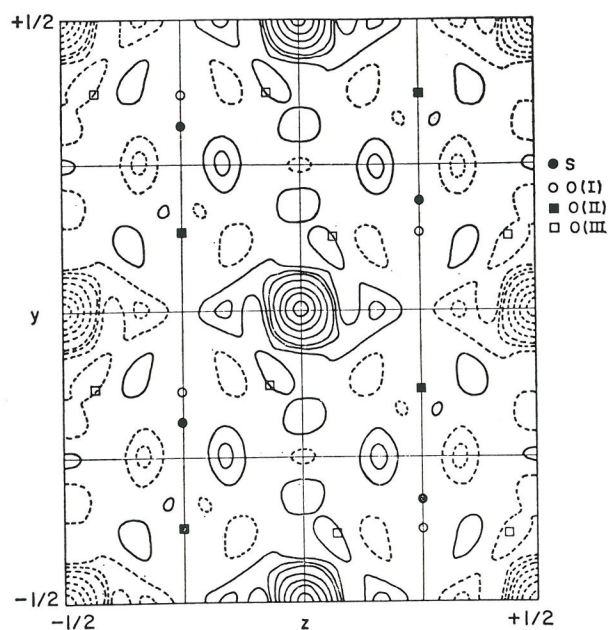

FIG. 8. A representation of the conical spiral in $MnSO_4$. The transverse (helical) component advances in phase 360° in six lattice spacings along the a direction. (From Will *et al.*, 1965). (Reprinted by permisson of the publisher.)

FIG. 9. A Fourier projection of the magnetization density in $CuSO_4$ on the (100) plane. Note the anisotropy of the density about the Cu positions at y(0,1/2)z(0,1/2) and the smaller pileup of density between them. Positive and negative densities are indicated by solid and broken lines respectively. (From Menzinger *et al.*, 1969). (Reprinted by permission of the publisher.)

magnetization density is localized on the Cu^{2+} ions (the solid and dashed lines refer to positive and negative equidensity contours), there are significant densities observed at a projected distance of 2.5 Å away, clearly too far to belong to the Cu^{2+} ionic density, however, anisotropic.

ELECTRICAL PROPERTIES OF SULFIDES

Turning to a discussion of electrical properties, we find three major areas where sulfide compounds have been at the center of activity: semiconductors, photoconductivity and ferroelectricity.

Semiconductors. To discuss semiconducting properties, we return to the band theory concepts described earlier. There we described the Fermi energy, the level in energy-momentum space up to which energy states were filled, which is well-defined at absolute zero. As the temperature is raised the Fermi surface becomes fuzzy; electrons are excited above this level by thermal energies of amount kT and as more and more of them receive enough energy to cross the forbidden gap from the valence band, where they are relatively tightly bound, to the conduction band, where they are nearly free, the conductivity increases. This situation holds in intrinsic semiconductors, which are very pure; in extrinsic semiconductors impurities create additional localized states whose energy lies within the band gap and serve as traps for electrons from the valence band, causing hole conduction (p-type), and sources for electrons for the conduction band, causing electron conduction (n-type).

The tools for the investigation of the band structure and the topology of the Fermi surface are many: transport phenomena such as resistivity and Hall effect, which measure the number, sign and mobility of charge carriers; optical phenomena, including reflectance and absorption which trace out the transitions near the band edges; cyclotron resonance and oscillations in the susceptibility and magnetoresistance which detail the trajectories of the electrons on the Fermi surface. These latter measurements have become more important as high magnetic fields and very pure samples have become available, because they depend on the electron being able to complete several precessional orbits in the field before being scattered by impurities. The frequency of these oscillations, which occur because the "free" electrons are quantized according to their orbital moment, is a measure of extremal orbits equivalent to cross-sections of the Fermi surface.

1. Fermiology of the lead salt semiconductors. The lead salts PbS, PbSe, PbSe and PbTe have long been a focal area of semiconductor research because of the wide variation in carrier concentration that can be obtained by controlling the composition and degree of stoichiometry. Transport and optical measurements (Scanlon, 1959; Allgaier, 1958) established the band gaps and energy surfaces of these materials; these measurements stimulated theoretical calculation of the energy band structure, which in turn have been tested out by more sophisticated measurements designed to caliper the Fermi surface.

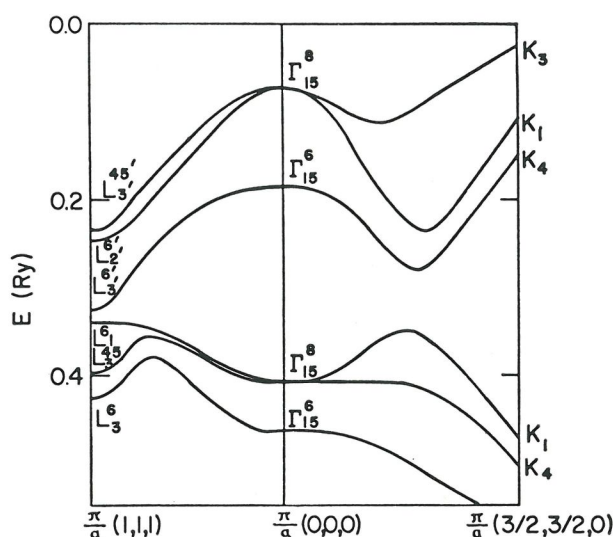The degree of detail achieved in current calculations is

FIG. 10. Details of the calculated band structure in PbTe illustrating the calculated band extrema and the forbidden gap in the [111] direction. Labels refer to the symmetry of the wave functions of the individual levels. (From Lin and Kleinman, 1966). (Reprinted by permission of the publisher.)

illustrated in Figure 10. This is indeed a far cry from the simple parabolic energy bands envisaged in the nearly-free electron theory; still, some resemblance to the features of Figure 1 is there. The good correlation established between these energy level diagrams and the optical, transport and oscillatory measurements (Burke, Houston and Savage, 1969) lend credence to the model now generally accepted for the lead salts, nearly parabolic extrema in [111] directions of momentum space as indicated in Figure 10.

2. Band crossing in lead-tin telluride. Some interesting experimental data have recently been obtained on the lead-tin telluride alloy system that suggests that the assignment of valence and conduction bands is reversed from one end of the system to the other. The evidence for this phenomenon appears in resistivity (Dixon and Bis, 1968), and laser emission studies (Dimmock, Melngailis, and Strauss, 1966). It holds out the promise of achieving very narrow energy gaps by controlling the composition, which could lead to extremely long wavelength optical detectors and lasers.

Photoconductivity in PbS. It has long been known that polycrystalline PbS films, when sensitized by baking in sulfur or oxygen, gave enhanced conductivity when illuminated by infrared light. The mechanisms for such effects were never clear because films were not always reproducible or uniform. Recent advances in the growth of expitaxial single crystal PbS films give promise of sorting out the several mechanisms that may be responsible for the photosensitivity.

One study (Riedl and Schoolar, 1968) involved scanning a microscopic light spot over the area of the films; photovoltaic effects were observed that could be correlated with rows of defects in the films. Furthermore, the specifics of
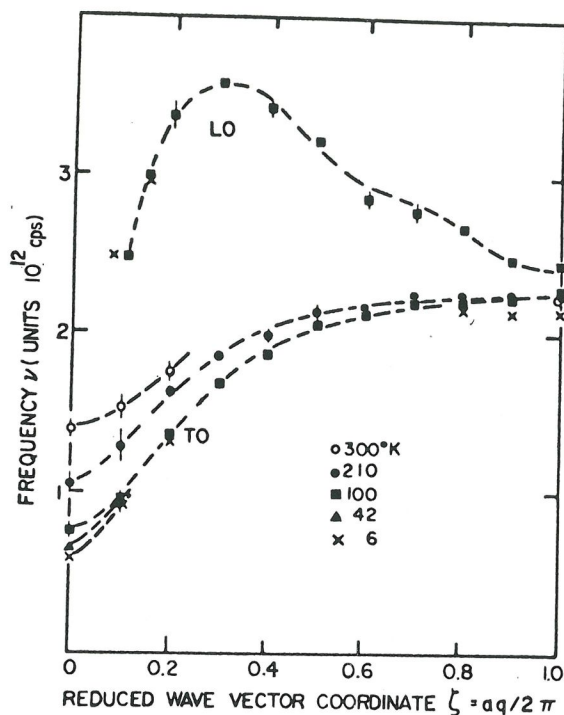
FIG. 11. Energy versus wave number relations for the transverse (TO) and longitudinal optic (LO) lattice vibrational modes in SnTe as determined from neutron scattering. Note the decrease in energy or "softening" of the TO made with decreasing temperature. (From Pawley *et al.*, 1966). (Reprinted by permission of the publisher.)

the behavior of the photosignal with biasing field indicated that an *n-p-n* junction localized at the defect was responsible. Other uniform epitaxial films were grown in which at least two basic mechanisms other than junctions were identified (Schoolar, 1970), characterized by differing lifetimes: one from oxygen-induced defect states that serve as electron traps from which photo-exitation occurs: the other attributed to the intrinsic photo-conductivity due to creation of electron-hole pairs that increase the carrier concentration. These thin film studies not only explain the variety of responses observed in polycrystalline films but give promise of leading to reliable, reproducible photosensitive detectors.

Diatomic ferroelectrics. Ferroelectricity is the electrical analogue of ferromagnetism in that a spontaneous polarization of charge occurs in a crystal at the ferroelectric transition. There is a large body of evidence (Cochran, 1959) that such transitions are occasioned by the simultaneous, static displacement of atoms participating in a transverse optical mode of the lattice vibrational spectrum, *i.e.*, one where atoms are vibrating 180° out of phase and transverse to the propagation direction of the wave. Such behavior can be studied by inelastic neutron scattering, for as the temperature decreases toward the transition, the energy of this particular mode decreases (spoken of as "softening" of the mode) until the crystal becomes un-

stable against the permanent displacement of the atoms (spoken of as a "frozen" mode).

In nature most of the known ferroelectrics are complicated ionic structures where the ferroelectric transition can be detected by an anomaly in the static dielectric constant. The alloys of (Sn–Ge)Te, which have high carrier concentrations that prevent measurement of the static dielectric constant, have recently been studied by neutron scattering (Pawley, Cochran, Cowley and Dolling, 1966); their results for SnTe are shown in Figure 11. The decrease in energy or "softening" of the TO mode with temperature is clearly seen. For this composition the energy never does reach zero, but on the basis of these results and the known displacive phase transition in the alloys related to this mode the conclusion was drawn that GeTe is the first example of a semiconducting, diatomic ferroelectric.

UNEXPLORED PATHS AND FUTURE DIRECTIONS

Some fields of investigation that are quite powerful but have not as yet been fully exploited in the realm of sulfide materials are listed below. Along with continuing development of earlier described fields, they show great promise for future progress.

Phase transitions. Recently a growing body of theory treating the thermodynamic behavior of phase transitions of many types has been accompanied by experimental studies, particularly by the critical scattering of neutrons associated with these transitions. Again, such critical scattering can be of magnetic or nuclear origin and can detail the frequency and wave number dependence of the modes involved in the transition, whether vibrational (spin waves and lattice vibrational) or diffusive. An obvious connection exists between this type of microscopic information and macroscopic phase equilibria determinations.

Atomic correlations in compound liquids and gases. Neutron scattering methods can also be used to obtain diffraction patterns from disordered systems, such as liquids or vapors, and the data can be Fourier-inverted to yield a radial distribution or correlation function for the atomic positions. Studies on liquid alloy systems and gases have been limited because of the inherent complexity, but the analytical difficulties will no doubt be solved in future. An interesting application is the study of the degree of atomic segregation on both sides of the melting point in disassociative versus associative phase transitions.

Magnetic semiconductors. A relatively new area of interest marries the two broad categories discussed earlier. As a matter of fact, most of the compounds that have been found to exhibit both magnetic and semiconductive behavior are sulfide-type materials—the rare earth chalcogenides and the transition metal chalcogenide spinels. A wealth of new effects are being found relating to the influence of spin polarization on the band energies that will no doubt result eventually in practical devices.

Lattice vibrational spectra and force constants. As in the

case of neutron scattering from liquids, this is an active field that has not yet been extensively applied to sulfides. The lattice vibrational spectrum contains all the information necessary to specify the interatomic force constants which can be correlated with the hardness, melting point, coefficient of thermal expansion and other physical properties.

SUMMARY

This cursory review of the wealth of physical properties exhibited by sulfide materials, mineral or synthetic, has, I hope, helped convey the impression that these materials have been intimately involved in the discovery and development of some of the most fundamental concepts in solid-state physics. The corollary aspect which I have covered but briefly, because it is outside my area of specialization, is that in many cases these materials have generated important practical applications or give immediate promise of doing so. I hope the reader in the field of mineralogy will realize the important contributions his field has made in the study and characterization of mineral phases, for ultimately the solid-state physicist can make no progress without prior advances in the synthesis of materials.

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