Phase Transitions and the Chemistry of Solids[†]

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A variety of solids exhibit transformations from one crystal structure to another (polymorphism) as the temperature or pressure is varied. Besides such phase transitions involving changes in atomic configuration, solids also undergo transformations where the electronic or the spin configuration changes. The subject of phase transitions has grown enormously in recent years, with new types of transitions as well as new approaches to explain the phenomena having been reported extensively in the literature.[1,2] Traditionally, metallurgists and physicists have evidenced keen interest in this subject, but it is equally of importance in solid-state chemistry. In this article, I shall discuss some interesting types of phase transitions of relevance to solid-state chemistry investigated by my co-workers and myself in order to illustrate the scope and vitality of the subject.

General Features of Phase Transitions

During a phase transition, the free energy of the solid remains continuous, but thermodynamic quantities such as entropy, volume, and heat capacity exhibit discontinuous changes. Depending on which derivative of the Gibbs free energy, G, shows a discontinuous change at the transiton, phase transitions are generally classified as first order or second order. In a first-order transition where the $G(P,T)$ surfaces of the parent and product phases intersect sharply, the entropy and the volume show singular behavior. In second-order transitions, on the other hand, the heat capacity, compressibility, or thermal expansivity shows singular behavior.

We all know that when a liquid transforms to a crystal, there is a change in order; the crystal has greater order than the liquid. The symmetry also changes in such a transition; the liquid has more symmetry than a crystal since the liquid remains invariant under all rotations and translations. Landau introduced the concept of an order parameter, ξ, which is a measure of the order resulting from a phase transition. In a first-order transition (e.g., liquid–crystal), the change in ξ is discontinuous, but in a second-order transition where the change of state is continuous, the change in ξ is also continuous. Landau proposed that G in a second-order (or structural) phase transition is not only a function of P and T but also of ξ and expanded G as

a series in powers of ξ around the transition point. The order parameter vanishes at the critical temperature, T_c, in such transitions. Landau also considered the symmetry changes across phase transitions. Thus, a transition from a phase of high symmetry to one of low symmetry is accompanied by an order parameter. In a second-order transition, certain elements of symmetry appear or disappear across the transition; for example, when the tetragonal, ferroelectric $BaTiO_3$ in which the dipoles are all ordered, transforms to the cubic, paraelectric phase where the dipoles are randomly oriented, there is an increase in symmetry (appearence of certain syymetry elements) but decrease in order. In a ferroelectric–paraelectric transition, electric polarization is the order parameter; in ferromagnetic–paramagnetic transition, magnetization is the order parameter.

Many physical properties diverge near T_c, i.e., show anomalously large values as T_c is approached from either side. The divergences in different phase transitions are, however, strikingly similar. These divergences can be quantified in terms of critical exponents, λ:

$$\lambda = \lim_{\epsilon \to 0} \left| \frac{\ln f(\epsilon)}{\ln |\epsilon|} \right|$$

where $\epsilon = (T - T_c)/T_c$ and λ is called an exponent since $f(\epsilon)$ is proportional to ϵ^λ. The most important exponents are those associated with the specific heat (α), the order parameter (β), the susceptibility (γ), and the range over which individual constituents like atoms and atomic moments are correlated (ν). It so happens that the individual exponents for many different transitions are roughly similar (e.g., $\beta \approx 0.33$). More interesting is the fact that $\alpha + 2\beta + \gamma = 2$ in most transitions, independent of the detailed nature of the system. In other words, although individual values of exponents may vary from one transition to another, they all add up to 2. Such a universality in critical exponents is understood in the light of Kadanoff's concept[3] of scale invariance associated with the fluctuations near T_c. The exponents themselves can be calculated by employing the renormalization group method developed by Wilson.[4] Thanks to all these developments, we are now able to characterize all higher order phase transitions in terms of the physical dimensionality of the system, d, and the dimensionality of the order parameter, n. This is illustrated in the case of some observed phase transitions in Figure 1. It is noteworthy that there can be no phase transitions in one dimension if short-range forces alone operate.

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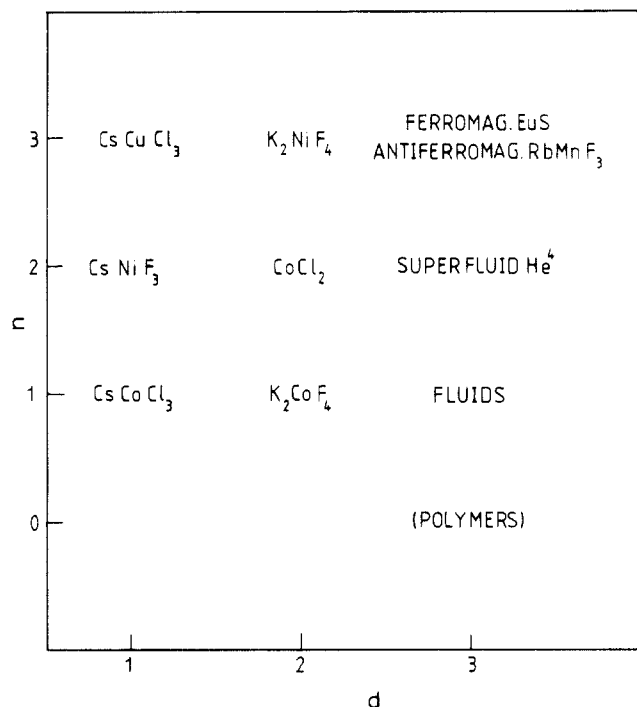(4) K. G. Wilson and J. Kogut, *Phys. Rep.*, 12C, 77 (1974).

Figure 1. Some observed phase transitions in the d–n plane.

Figure 2. Dialatation transformation from CsCl structure to NaCl structure of an AB-type compound. Symmetry about the the unique axis of dilatation $(3m)$ is preserved.

phase transitions of simple ionic solids. Thus, the Born model satisfactorily explains the relative stabilities of structures of simple ionic solids. On the basis of ionicity considerations, we can account for the structures of III–V, II–VI, and such binary compounds.[2] Some years ago, Buerger[6] classified phase transitions in solids on the basis of changes in the primary or higher coordination. Transformations involving primary coordination (e.g., CsCl structure–NaCl structure, aragonite–calcite) can be reconstructive or dilatational. Transformations involving second or higher coordination (e.g., α–β quartz, tetragonal-cubic transition of $BaTiO_3$) can be reconstructive or displacive. Buerger suggested that transformations involving changes in primary coordination such as in the CsCl–NaCl transition can occur more readily by a dilatational or deformational mechanism rather than by a drastic mechanism necessitating the breaking and making of bonds (Figure 2). It is interesting that the CsCl–NaCl transition is now considered to be martensitic with orientational relations between the two phases. It seems likely that phase transitions of many inorganic solids do not require diffusion and involve a deformational mechanism[2] wherein the parent and product phases have orientational relationships. Many such transitions may also exhibit soft mode behavior, an aspect that is worthy of investigation.

Polytypism

Solids such as SiC, ZnS, CdI_2, TaS_2, mica, and perovskite oxides exhibit polytypism wherein the unit cells of the different polytypic forms differ from one another only in the c dimension; the c dimension of polytypes of certain substances vary anywhere between a few angstroms and a few thousand angstroms. This phenomenon arises because of differences in the sequence in which the atomic layers are stacked in different polytypes along the c axis. Although several theories have been put forward to explain the varied characteristics of polytypic substances,[7] it is difficult to understand some of their features. These include the existence of different types of unidimensional order (since one-dimensional systems should not normally show long-range ordering), which is an apparent violation of Gibbs' phase rule (owing to the coexistence of several phases under identical conditions), syntactic coalescence (growth of different polytypic forms in different parts of the same specimen), and the existence of varying extents of disorder.

Another important aspect of phase transitions in solids is the presence of soft modes. Operationally, a soft mode is a collective excitation whose frequency decreases anomalously as the transition point is reached. In second-order transitions, the soft mode frequency goes to zero at T_c, but in first-order transitions, the phase change occurs before the mode frequency goes to zero. Soft modes have been found to accompany a variety of solid-state transitions, including those of superconductors and organic solids.[2,5] Occurrence of soft modes in phase transitions can be inferred from Landau's treatment wherein atomic displacements may themselves be considered to represent an order parameter.

It has been found convenient to classify phase transitions in solids on the basis of the mechanism.[2] Three important kinds of transitions of common occurrence are as follows: (i) nucleation and growth transitions, a typical example being the anatase-rutile transformation of TiO_2, (ii) positional and orientational order–disorder transitions, and (iii) martensitic transitions. A typical example of a positional order–disorder transition is that of AgI; orientational order–disorder transitions are exhibited by many solids such as ammonium halides, plastic (orientationally disordered) crystals, and salts of di- or polyatomic anions. A martensitic transition is a structural change caused by atomic displacements (and not by diffusion) corresponding to a homogeneous deformation wherein the parent and product phases are related by a substitutional lattice correspondence, an irrational habit plane and a pracise orientationl relationship. These transitions that occur with high velocities of the order of sound velocity were originally discovered in steel but are now known to occur in several inorganic solids such as $KTa_{0.65}Nb_{0.35}O_3$ and ZrO_2.

On the basis of our knowledge of crystal chemistry, we can predict the nature of structural changes in the

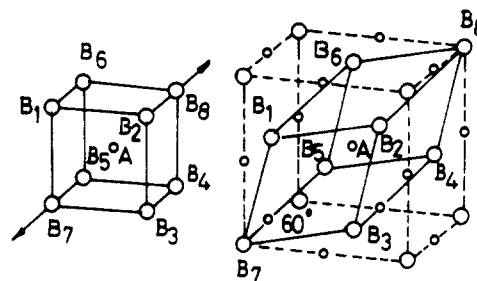(5) J. F. Scott, *Rev. Mod. Phys.*, **46**, 83 (1974).

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A B A B C A C A B C B . B A C A C B A B A C B C B A C A C B A B A C B C B A C A C B A . C A C A B C
B C A B A B C A . B A B A C B C B A C A C B A B A C B C B A C A C . C B A C A C B A B A C B C B A C
A C B A B A C B C B A C A C B A . C A C A B C B C A B A B C A C A B C B C A B A . A C B C B A C A C
B A B A C B . A B A B C A C A B C B C A B A B C A . . . . . . . . . B A C B C B A C A C . . . . . .
C B C B A C A C B A B A C B C B A C A C . C B A C A C B A B A C B C B A C A C . C B C A A C B A B A
C B C B A C A C B A B A C B C B A C . B C B C A B A B C A C A B C B C A B A B C A C A B C B C A B A
B C A C A B C B C . C A B C B C A B A B C A . B A B A C B C B A C A C B A B A C B C B A . . . . . C
A B C B C A B A B C A C A B C B C A B A B . B C A B A B C A C A B C . . . . . . . . . . A C B A B A C
B . . . B A C B C B A C A C B A B . B C A C A B C B C A B A B C A C A B C B C A B A B C A C A B C B C
A B A B C A C A B C B C A B A B . B C A B A B C A C A B C B C A B A B C A C A B C B C A B A B C A C
A B C B C A B A B C A C A B C B C . C A B C B C A B A B C A . B A B A C B C B A C A C B A B A C B C
. A C A C B A B A C B . A B A B C A C A . A B C A C A B C B C . C A B C B C A B A B C A C A B C B C
. . . . C B A C A C B A . C A C A B C B C A B A B C A C A B C . A C A C B A B A C B C B A C A C B A
B A C B C B A C A C B A B A C B C B A C A C B A B A C B C B A C A C B A B A C B C B A C A C B A B A
C B C B A C . . . . . . . . . . C B A C A C B A . . . . . . C B A C A C B A B A C B C B A C A C B A B
A C B C B A C A C B A B A C B . A B A B C A C A B C B C A B A B . . C A C A B C B C A B . C B C B A
C A C B A B A C B C B A C . . C B A C A C B A B A C B . A C A B C B C A B A B C A C A B C B C . C A
B < B C A B A B C A C A B C B C A B A B C A C A B C B C A B A B . . C A C A B C B C A B A B C A C A
B C B C A B A B C A C A B C B C . C A B C B C A B A B . . . . . . . . B A B A C B C B A C A C . . . .
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Figure 3. Display of long-range order as in 12R polytype (ABACBCBACACB) obtained by computer simulation (taken from ref 8b).

Since polytypism is essentially a one-dimensional phenomenon and the atomic layers exist in either cubic or hexagonal configurations, we can, in principle, treat polytypes as different ordered states of a spin-half Ising chain.[8] Since such an Ising chain should have long-range order at nonzero temperatures, it is essential to have an infinite-range interaction. At the same time, in order to obtain different ordered states of the chain, it is necessary to have a short-range interaction competing with the infinite-range interaction. Spin-half Ising chains with competing short-range and infinite-range interactions have been investigated by Theumann and Høye.[9] The Theumann–Høye Ising chain involves the nearest- and the next-nearest-neighbor antiferromagnetic interaction and an infinite-range ferromagnetic interaction of the Kac type. This chain exhibits different spin orderings at $T = 0$ for different interaction strengths and shows phase transitions as the interaction strengths are varied. In view of the close resemblance between the behavior of this Ising chain and that of polytypes, we have carried out[8] a Monte Carlo simulation of polytypes based on the competing interactions model. The basic Hamiltonian employed was that of Theumann and Høye.

The two states of the spin in an Ising chain can be taken to represent the two lowest energy configurations of a layer in a polytype, viz., the cubic (ABC) and the hexagonal (AB) configurations. Other layer configurations like AAB or ABB are of high energy and are not observed. We should, therefore, expect correspondence between the thermodynamic properties of a polytype and those of an appropriate Ising chain. In order to have an ordered spin arrangement in an Ising chain, it is necessary to introduce an infinite-range interaction among spins, the equivalent-neighbor type being most suitable for Monte Carlo simulations. The contribution to internal energy from this form of infinite-range interaction is given by $-J_{ir}M^2$. An analogous squared term

has been suggested for the major part of the contribution to the elastic energy between atoms of different sizes.[10] It is, however, necessary to add a competing short-range interaction term to the equivalent neighbor interaction term in order that the spin orderings in the Ising chain describe polytypism.

We have found that a general double-layer mechanism (e.g., ABCACB → ABCBCB or ABABCB) connects different states of the polytype chain with about the same probability as the spin–flip mechanism in magnetic Ising chains.[8a] It has been possible to simulate various polytypes with periodicities extending up to 12 layers in this manner (see Figure 3). During the growth of a polytype (whether it be from melt or vapor), it is reasonable to assume that the atoms in the layers are jostling about, leading to fluctuations in interlayer interaction strength. A proper simulation of polytypes should take into account such fluctuations.[8b] We have therefore treated the interaction parameters in the simulation as random variables (varying with time) during any given simulation and carried out a computer simulation of polytype growth from vapor, employing both constant and fluctuating short-range interaction parameters. We have obtained short stretches of fairly long ordered polytypes such as 14H and 33R in such simulations. It is my feeling that the simulations discussed hitherto may be useful in understanding the occurrence of long period structures which include coherent intergrowth phases in systems such as hexagonal barium ferrites and intergrowth bronzes. It appears that long periodicities could originate from more than one cause, but it is likely to be thermodynamic in some systems. This indeed appears to be the case in alloys such as CuAu. Sato and co-workers[11] have shown that the operative factor in such a system is the lowering of the total electronic energy by decreasing the size of the Brillouin zone; the requisite periodicity for creation of

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energy gaps varies in some systems with the electron/atom ratio.

Spin-State Transitions

Transitions of solids from magnetically ordered states to paramagnetic states are well-known. We have been interested in transitions between spin states of solids containing transition metal ions in the d^4–d^8 configuration. These transition metal ions can exist either in the low-spin or the high-spin ground state, depending upon the crystal field strength. In some of the transition-metal compounds, where the crystal field strength is close to the crossover point, interesting magnetic and structural behavior is observed. Spin-state transitions are known to occur in molecular systems of transition-metal complexes as well as in transition-metal oxides and other solids. Typical complexes belonging to the first category are $Fe(phen)_2(NCS)_2$ and $Fe(phen)_2$-$(NCSe)_2$. The latter category consists of solid materials such as MnAs and rare-earth cobaltites, $LnCoO_3$ (Ln = La or rare earth). The low-spin (t_{2g}^6) to high-spin ($t_{2g}^4 e_g^2$) transition in $LaCoO_3$ manifests itself as a plateau in the inverse susceptibility–temperature curve, the low- and high-spin ion ordering themselves on unique sites above a particular temperature.[12,13] The other rare-earth cobaltites, on the other hand, only show a maximum in the inverse susceptibility–temperature curve.[14] Spin-state transitions have been studied by several experimental techniques including measurements of heat capacity and magnetic susceptibility and Mössbauer spectroscopy. We have recently examined them by X-ray photoelectron spectroscopy[15] and NMR spectroscopy.[16]

Spin-state transitions have been found to occur in two-dimensional oxides of K_2NiF_4 structure. Thus, La_4LiCoO_8 shows a peak in the inverse susceptibility–temperature curve not unlike $NdCoO_3$ and other rare-earth cobaltites.[14] Trivalent cobalt in this system appears to transform from the low-spin state to the intermediate ($t_{2g}^5 e_g^1$) as well as the high- ($t_{2g}^4 e_g^2$) spin states.[17,18] Other oxides of cobalt of K_2NiF_4 structure[18] that seem to undergo low intermediate spin transitions are Sr_4TaCoO_8 and Sr_4NbCoO_8. in $LaMNiO_4$ where M is Sr or Ba, Ni^{3+} is supposed to be in the low-spin state[19] when M is Sr and in the high-spin state[20] when M is Ba. We have examined the $LaSr_{1-x}Ba_xNiO_4$ system[18] and found that, with increase in x, the width of the $\sigma^*_{x^2-y^2}$ band (already present when $x = 0$) decreases, accompanying an increase in the unit cell volume; high-spin Ni^{3+} ions are formed to a small extent with increasing x, but there appears to be no spin-state transition.

A successful model of spin-state transitions should be capable of explaining the following observations: (i) smooth as well as abrupt changes in the spin-state population ratio with temperature, (ii) occurrence of thermodynamically second-order transitions and first-order transitions in certain instances and a spin-state population ratio around unity near the transition, (iii) nonzero population of the high-spin state at low temperatures found in some systems, and (iv) a plateau or a peak in the plots of inverse magnetic susceptibility against temperature.

We have examined several models for spin-state transitions.[21] An earlier model described by Bari and Sivardiere[22] is static and can be solved exactly even when the dynamics of the lattice are included; the dynamic model does not, however, show any phase transition. We have investigated a dynamic model of spin-state transitions in which the high-spin and the low-spin states are mixed by a coupling to the lattice. The mode that can bring about such mixing is an ion-cage mode wherein the transition-metal ion moves off-center with respect to the octahedral cage in which it is placed. During such a vibration, the symmetry of the crystal field does not remain octahedral and hence the two spin states mix. This model predicts nonzero population of the high-spin state at low temperature but no spin-state transition. Susceptibility behavior of some Fe^{2+} complexes can be explained by this model.

We have also examined a two-sublattice model, where the displacement on one sublattice is opposite to that on the other, but this model shows only second-order spin-state transitions. In order to explain the occurrence of both first- and second-order spin-state transitions, we have explored a two-sublattice model where the spin states are coupled to the cube of the breathing mode displacement. This model predicts first- or second-order transitions but only zero high-spin-state population at low temperatures. The most general model that predicts nonzero high-spin-state population at low temperatures, a first- or a second-order transition, and other features appears to be one where the coupling of the spin states to a breathing mode is linear and that to an ion-cage mode is quadratic. Nonetheless, spin-state transitions in extended solids need to be further explored to enable us to fully understand the mechanism of these transitions.

Electronic Transitions

Among the phase transitions where electronic factors play a major role, the most well-known are the metal–insulator transitions exhibited by transition-metal oxides, sulfides, and so on. This subject has been discussed at length.[2,23,24] A recent observation[25] of some interest is that the metal–nonmetal transition occurs at a critical electron concentration as given by the particular form of the Mott criterion, $n_c^{1/3} a_H = 0.26 \pm 0.05$. The Verwey transition in Fe_3O_4 is associated with a marked jump in conductivity, but the material remains a semiconductor both above and below the transition temperature (123 K); below 123 K, there is

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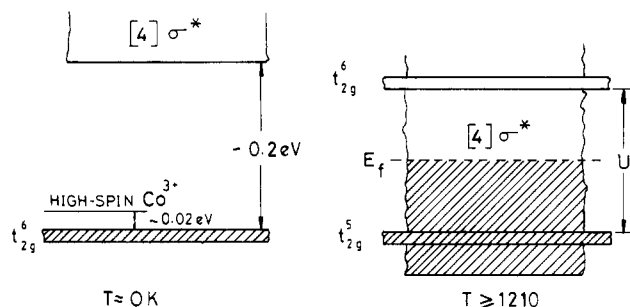
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Figure 4. Energy band scheme for $LaCoO_3$ at 0 K and above the first-order electronic transition at 1200 K (taken from ref 13). At 0 K, all the 3d electrons are in the t_{2g} level (low-spin state), and the high-spin Co^{3+} level is empty. Above 1200 K, the e_g electrons form a partially filled σ^* band and the t_{2g} electrons remain localized.

charge ordering of Fe^{2+} and Fe^{3+} ions. The Verwey transition has been a subject of intensive discussion,[24] but there is still some doubt with regard to the mechanism of the transition. In this section, I shall briefly present the features of a few other interesting electronic transitions investigated in this laboratory.

$LaCoO_3$ and other rare-earth cobaltites show first-order phase transitions around 1200 K, which seem to be essentially governed by the change in electronic entropy.[12,13,26] Temperature evolution of the electronic and spin configurations of cobalt in these cobaltites is interesting, and we have investigated this by employing Mössbauer spectroscopy[13,26] and X-ray photoelectron spectroscopy.[27] At low temperatures, cobalt ions are in the diamagnetic low-spin state (t_{2g}^6) and transform to the high-spin state ($t_{2g}^4 e_g^2$) with increase in temperature, the two spin states being clearly distinguished in Mössbauer spectra. Electron hopping between the two spin states gives rise to charge-transfer states (Co^{2+} + Co^{4+}) and associated increase in electrical conductivity. The magnitude of charge transfer depends on the acidity of the rare-earth ion. As the temperature is increased further, the e_g electrons tend to form a σ^* band; accordingly, the center shift in the Mössbauer spectra shows a decrease in this temperature region ($\sim$700–1000 K) due to progressive increase in the cation–anion orbital overlap. Mössbauer spectra show a single resonance with a chemical shift close to zero (corresponding to the band state of e_g electrons), as we approach the first-order transition temperature ($\sim$1200 K). Above 1200 K, the cobaltites become metallic due to the change in the nature of d electrons from localized to itinerant behavior (Figure 4). Since no change in crystal symmetry was noticed at the transition, it was considered that the entire entropy change was electronic in origin. However, it seems likely that there is an increase in the symmetry of $LaCoO_3$ (change from rhombohedral to cubic structure) after the transition.[12,13] Even so, the large ΔS of the transition (over 4 J K^{-1} mol^{-1}) can only arise because of a significant electronic contribution. The Lamb–Mössbauer factor (area under the resonance) decreases markedly before this transition, indicative of large ionic vibrations, and increases sharply above the transition, suggesting the

establishment of long-range order.

Another interesting electronic transition that we have been interested in is that of La_2NiO_4, which crystallizes in the two-dimensional K_2NiF_4 structure. Unlike K_2NiF_4, La_2NiO_4 is not known to show any long-range antiferromagnetic order but only shows deviations from Curie–Weiss law due to short-range interactions.[28] What is more interesting is that La_2NiO_4 undergoes a gradual semiconductor–metal transition[29] around 550 K; no structural change accompanying the transition has been reported. The Ni–O–Ni distance in La_2NiO_4 (3.86 Å) is shorter than in NiO (4.18 Å). The transfer integral, b, in NiO is close to the critical transfer integral, b_c, at which the description for localized electron states breaks down. In La_2NiO_4, b should be nearly equal to b_c, so that we obtain partially filled $\sigma^*(x^2 - y^2)$ bands of strongly correlated itinerant d electrons and hence the metallic behavior. The half-filled d_{z^2} orbitals of Ni^{2+}, on the other hand, would be localized. A likely origin of the semiconductor-metal transition is the splitting of the $\sigma^*(x^2 - y^2)$ band on lowering the temperature because of strong electron correlations, which in turn may be accentuated by short-range antiferromagnetic ordering d_{z^2} spins.[30]

In spite of the great interest in the 550 K electronic transition of this two-dimensional system, all the electrical measurements have hitherto been carried out on pellets of polycrystalline material. Preliminary measurements on single crystals[31] indicate the occurrence of a sharp transition (in the ab plane) with at least an order of magnitude jump in conductivity. Furthermore, Ni^{3+} ions that are inevitably present (3–9%) in all preparations of La_2NiO_4 seem to influence the structure and properties quite significantly. Samples of La_2NiO_4 annealed in a CO_2 atmosphere at 1400 K (to removed Ni^{3+}) seem to show evidence for long-range antiferromagnetic ordering. In addition, electron diffraction studies show them to have a monoclinic distortion contrary to published crystallographic data. Careful investigations of the electronic and magnetic properties of well-characterized samples of La_2NiO_4 are therefore warranted.

The last type of electronic transition that I shall discuss is the one exhibited by silver chalcogenides, $Ag_{2+\delta}Ch$ (Ch = S, Se, or Te). These compounds transform to a symmetrical phase on heating wherein Ag^+ are randomly distributed, giving rise to superionic conductivity just as AgI. These materials are small-gap semiconductors at room temperature and exhibit interesting electronic behavior as a function of temperature as well as of composition.[32] Thus, in the high temperature phase ($T > 406$ K), $Ag_{2+\delta}Se$ shows metallic behavior of electronic conductivity for high values of X. With decrease in δ, the electronic conductivity shows evidence for an interesting transition (Figure 5), the ionic conductivity of the high temperature phase being essentially independent of δ. The magnitude of change in electronic conductivity at the phase transition is also

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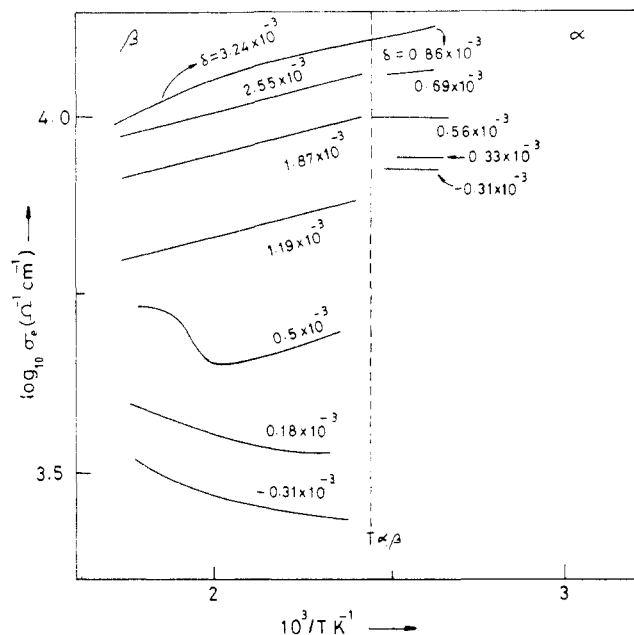
Figure 5. Plot of the logarithm of electronic conductivity against inverse of absolute temperature for various compositions of α- and β-silver selenide. The degree of nonstoichiometry, δ, was determined by solid-state coulometry (taken from ref 32).

determined by stoichiometry. In the low-temperature phase, the material conducts like a semimetal around 400 K and the conductivity decreases substantially at low temperatures, the magnitude of the decrease depending on the value of δ. This behavior as well as the δ-dependent electronic transition in the high-temperature phase is indeed interesting. We are now investigating $Ag_{2+\delta}Te$, which is a p-type material with a small gap (unlike $Ag_{2+\delta}Se$, which is a n-type material), at ordinary temperatures.

Organic Solids and Related Systems

Although phase transitions in organic solids have been reported from time to time, extensive mechanistic studies have not been carried out as in the case of inorganic solids.[2] It was believed until recently by many workers that there are no structural relations between phases in the case of organic solids. Jones et al.,[33] however, have reported that the stress-induced phase transition of 1,8-dichloro-10-methylanthracene proceeds by a diffusionless displacive transition (somewhat similar to a martensitic transition) with definite orientational relationships. The irrational habit plane seems to be composed of close packed planes and the properties of the interface could be formulated in terms of slip dislocations. The reversible topotactic phase transition of 5-methyl-1-thia-5-azoniacyclooctane 1-oxide perchlorate has been explained by Parkinson et al.[34] in terms of recurrent glissile partial dislocations; it was earlier thought[35] that the transition involved a cooperative inversion and rotation of half of the molecular cations. The phase transition of paraterphenyl involving rotational disorder has been elucidated by Ramdas and Thomas[36] by evaluating pairwise interac-

tions between nonbonded atoms.

In this laboratory, we have been studying phase transitions of a variety of organic solids. For example, we have investigated the α–γ–α–β transitions of p-dichlorobenzene by infrared spectroscopy.[37] The γ phase is characterized by unusually high intramolecular vibrations mode frequencies. The α–γ transition shows athermal nucleation behavior as in martensitic transitions; the α–β transition seems to be associated with some disorder. When the asymmetry of the molecules is not too high, organic crystals often exhibit order-disorder transitions (e.g., benzothiophene). We have investigated order–disorder transitions in benzothiophene and other compounds by making use of changes in infrared band intensities and half-widths.[38] Raman spectroscopy would be especially useful in investigating order-disorder transitions.

We have investigated the phase transitions of compounds of the type $(C_nH_{2n+1}NH_3)_2MCl_4$, M = Mn, Fe, Cd, or Cu, which provide interesting model systems to investigate magnetic phenomena in two dimensions. Earlier spectroscopic investigations[39] seemed to indicate that in $(CH_3NH_3)_2MCl_4$, the phase transitions are determined essentially by the motions of the methylammonium groups. We have examined the infrared spectra of several $(C_nH_{2n+1}NH_3)_2MCl_4$ systems through their phase transitions to investigate whether the intramolecular vibration modes show the expected changes.[40] In the high-temperature phase of these solids, the $(CH_3NH_3)^+$ ion has C_{3v} symmetry, but the symmetry goes down to C_1 or C_s in the ordered low-temperature phases. The spectra indeed show the expected site-groups as well as factor-group splittings in the low-temperature phases, the degenerate bending modes of NH_3 and CH_3 being particularly sensitive. The phase transitions of the tetrachlorometallates are similar to those of the corresponding alkylammonium chlorides, $C_nH_{2n+1}NH_3Cl$, thereby establishing that the phase transitions in the former are entirely controlled by the motions of the $(C_nH_{2n+1}NH_3)^+$ group. Accordingly, we find that the $(C_nH_{2n+1}NH_3)_2MBr_4$ system shows transitions similar to those of the chloro compounds.

We have been particularly interested in the study of the plastic states of organic compounds,[41] which are characterized by high values of ΔS of formation from the crystalline state, the ΔS of fusion (plastic–liquid transition) being much smaller. We find that the ΔH as well as the ΔS of the crystal–plastic transition generally decrease as the temperature range of stability of the plastic phase increases; the ΔH and the ΔS of the plastic–liquid transition, on the other hand, increase as the temperature range of stability of the plastic phase increases.[42] Neutron scattering, NMR spectroscopy, and several other techniques have been employed to study molecular reorientation in the plastic state.[41] We

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have employed Raman band shape analysis to obtain rotational correlation function of plastic phases of a few organic compounds.[43] The correlation times are continuous through the plastic–liquid transition.

Molecular dynamics simulation of the plastic state of CH_4 has been carried out by Bounds et al.[44] who have evaluated the static and dynamic structure factors. The crystalline phase of CH_4 described by James and Keenan[45] has been investigated by several techniques. We have carried out a Monte Carlo simulation study[46] on the orientational glasses (or glassy crystalline phases) obtained by annealing or quenching the plastic phase. Different cooling rates lead to different states of the glassy crystalline phase. Temperature variation of the orientational parameter of molecules suggests the presence of a transition between the plastic and glassy crystalline phases.

Phase transitions of hydrogen-bonded solids such as ferroelectric hydrogen phosphates and Rochelle salt have been investigated widely in the literature.[2] We have been recently investigating phase transitions of alkanedioc acids employing vibrational spectroscopy.[38] The phase transition of malonic acid at 360 K is especially interesting. At ordinary temperatures, the unit cell of malonic acid contains two cyclic dimeric rings orthogonal to each other; above 360 K, the two hydrogen-bonded rings become similar as evidenced from IR and Raman spectra.[47,48] Hydrogen bonds in the high-temperature phase are on the average weaker than those in the low-temperature phase. The phase transition occurs at a higher temperature (366 K) in the fully deuterated acid, and the vibrational bands show a positive deuterium isotope effect. It appears that the transition is governed by librational and torsional modes of the hydrogen-bonded rings (around 90 and 50 cm^{-1}, respectively, below the transition temperature), which show a tendency to soften.

Concluding Remarks

The above discussion should serve to indicate the variety of problems in the area of phase transitions that are of relevance to solid-state chemistry. Of course there are other important aspects of phase transitions, such as cooperative Jahn–Teller effect, commensurate–incommensurate structure transitions and transitions in ferroics, that I have not touched upon. Neither have I dealt with technological applications.[2] The main point that I have tried to make is that the study of structural and mechanistic aspects of phase transitions in the solid state constitutes an essential and interesting aspect of the chemistry of solids.[49]

A word about the so-called normal-superionic conducting state transitions would be in order. It seems to be wrong to refer to these transitions as superionic transitions by analogy with the electronic superconducting transitions. While AgI related materials show a marked jump in ionic conductivity at a transition temperature, there are many other superionic materials that do not.[50]

A transition that has eluded a proper understanding and has increasingly become an area of vital interest is the glass transition.[51] Although many models have been proposed, none of them is able to explain all the features of this transition. An interplay of kinetic and thermodynamic effects further complicates the situation. We have recently proposed a cluster model of the glass transition[52] based on the premise that glass is an ensemble of more ordered regions (clusters) embedded in a liquidlike, disordered tissue material. Toward the glass transition, clusters gradually melt and add on to the tissue material. The cluster model making use of the relative size of the cluster as an order parameter seems to explain several features of the transition. Another aspect of the glass transition that is worth noting is that it is not merely characteristic of the normal variety of (positionally disordered) glasses but also of orientationally disordered glasses and dipolar glasses. A satisfactory model would have to account for this feature as well. Some other aspects of phase transitions that deserve attention are transitions in organic solids, deformational mechanisms of phase transitions in complex solids, transitions of orientationally disordered crystals, and transitions involving ordering of defects. Computer simulation studies are bound to be increasingly useful in understanding the nature of many of the solid-state phase transitions.

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