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Phase Transitions

This paper presents a selective review of some of IBM's major contributions in the area of phase transitions during the last twenty-five years. It is separated into three main sections covering ferroelectric and structural transitions, magnetism, and nonequilibrium phase transitions.

Introduction

This article has a dual purpose: to give the reader a historical perspective on the early work carried out by IBM and to introduce to him some of the most interesting and challenging new areas of research. The choice to emphasize these areas reflects the particular interests of the authors.

Ferroelectric and structural transitions

• *Early work in ferroelectricity*

The first paper in the first issue of the *IBM Journal of Research and Development* and its associated cover picture were products of IBM's early work on ferroelectricity. It is, therefore, appropriate to return to this field in this anniversary issue. IBM's original interest in ferroelectricity arose from the possibility of using reversible polarization in computer memories. $BaTiO_3$ was investigated in detail as a candidate at IBM, Bell Laboratories, and a number of other institutions in the first attempt to make an integrated solid state memory, in which a whole array of bits would be located in one crystal. The work at IBM, carried out under the leadership of Young, who started work on ferroelectricity in 1950, concentrated on studies of the polarization reversal mechanism in $BaTiO_3$ and on broader phenomenological characterizations of $BaTiO_3$. Much of this work, associated with the names of Young, Drougard, Huibregtse, Karan, Landauer, Triebwasser, and others, has become part of the textbooks [1]. The same can be said for work on TGS, $KNbO_3$, and solid solutions of $K(Nb,Ta)O_3$ by Triebwasser [2]. The phase diagram he constructed for the latter is still used for technological applications and fundamental studies. Detailed study of the ferroelectric transition played a prominent part in this early work, *e.g.*, [3]. We give further attention to only one of the papers stemming from the end of this early period [4]. Triebwasser showed that electric dc fields, applied to $BaTiO_3$, result in space-charge motion, and that this results in spatial nonuniformity of the electric field. (Very recently, the dynamics of space charge in $KTaO_3$ at low temperatures has been explored experimentally by Höchli and explained in terms of Nordheim-Fowler tunneling [5, 6].) Many of the proposals for ferroelectric applications, particularly for light modulation, ignore the space-charge drift problem.

In the second half of the 1950s the character of ferroelectric work, and to a large extent the membership of the ferroelectric community, underwent major changes both in application emphasis and in the fundamental studies. The original hopes for an electrically addressed memory technology remained unfulfilled. Despite that, proposals for other types of storage using ferroelectric materials continued to appear, including later IBM work on sandwiches of photoconductors and ferroelectrics addressed through a deflected light beam [7]. A number of laboratories also investigated digital holographic memories utilizing ferroelectric materials as reversible storage media. A somewhat pessimistic assessment of these possibilities, representative of the judgment of many IBM technologists, has been given by Barrekette [8] and by Landauer [9].

After the realization of the laser, the applied work in many laboratories turned to the utilization of the nonlin-

ear dielectric behavior of ferroelectrics for light modulation. In IBM, KDP (KH_2PO_4) crystals were utilized in a multistage digital light deflector capable of accurate high-speed random access to any one of many spots, under digital control [10].

The theory of ferroelectricity also underwent a serious transition in the late fifties. Until that time it had either been phenomenological or consisted of attempts at a microscopic theory that stressed the atomic composition of the crystal. It was hoped that the theory would provide some guidance in the search for further ferroelectric materials. As an example, Triebwasser's theory [11] of $BaTiO_3$ attempted to explain all aspects of the full temperature-dependent free-energy function from first principles. In 1969 Cochran [12] published his soft-mode concept and shortly thereafter elaborated on it in detail [13]. He pointed out that at a second-order ferroelectric transition where the dielectric constants diverge there must be a transverse optical lattice vibration mode whose frequency goes to zero as the transition is approached. This notion turned out to be a tremendous stimulus to ferroelectric theory. This soft-mode concept had been anticipated on a number of earlier occasions [14(a)] but it was Cochran who appreciated the significance of the concept and the need for its detailed exploration.

One of the soft-mode precursors arose in IBM. An unpublished but widely circulated note dated May 6, 1958 presented work by Juretschke, Landauer, and Sorokin, who explained the soft-mode concept, expressing an awareness that these modes might be overdamped. The work by Juretschke *et al.* is partially recapitulated in Ref. [14(b)]. The IBM soft-mode theory was also the basis for further work by Landauer and Thomas on the structure of electromagnetic shock waves formed by propagation in ferroelectrics [15], an abstract of which appeared in print at the same time as [12].

- *Spectroscopic studies of ferroelectrics*

In 1967 the utility of ferroelectrics with the tetragonal tungsten bronze crystal structure, *e.g.* $NaBa_2(NbO_3)_5$, for nonlinear optics was discovered [16]. Large single crystals could be grown [17] and the linear electro-optic coefficient was considerably larger than those of other state-of-the-art crystals. Extensive experimental work was undertaken involving related crystal systems, solid solution properties, and phase diagrams (so that better crystals would be grown [17]), and the vibrational modes were studied [18].

In 1972, the first work [18] was carried out using polaritons to measure the temperature dependence of the entire dielectric response of a ferroelectric crystal involving high-quality tungsten bronze-type crystals. From these and related measurements on the temperature dependence of the optical index of refraction, it was found that there existed a class of ferroelectric materials that behaved in a qualitatively different fashion from that predicted from Cochran soft-mode theory. These crystals, called dirty displacive ferroelectrics, were characterized by the lack of true translational symmetry. Although their physical properties are now well known, a complete microscopic theory of these materials has not as yet been developed [19].

Nuclear-quadrupole and electron spin-resonance techniques were applied to a number of ferroelectric crystals: $LiNbO_3$ and related materials, the alums, $(NH_4)_2SO_4$, $(NH_4)_2BeF_4$, and others [20]. These techniques and similar work at Cornell on the quadrupole resonance of Nb in $KNbO_3$ were some of the first applications of spectroscopy to microscopic measurements in ferroelectrics.

Most of the work just discussed refers to displacive ferroelectrics. The properties of the order-disorder ferroelectric KDP have been studied extensively at the IBM Zürich Laboratory. Order-disorder transitions are usually described in terms of pseudospin models, whereas anharmonic lattice models are used for displacive transitions. The dynamic behaviors of these transitions are also quite different. In KDP the dominant feature of the dynamic behavior is proton tunneling between equivalent potential minima. The tunneling motion is coupled to optic and acoustic phonon modes. The collective excitations of the coupled tunneling-optic mode problem had already been considered in 1966 by Brout *et al.* [21], following the tunneling suggestion of Blinc [22] and de Gennes' development of it [23]. Consequences of the pseudospin model were further analyzed by Pytte and Thomas [24], who also considered coupling of the heat-diffusion mode to the soft mode that occurs as soon as the order parameter is nonzero [25]. Such a coupling has been recently observed qualitatively in the low-temperature phase of KDP [26]. In KDP, the ferroelectric mode depresses a shear-mode branch, and the final soft mode is an acoustic one along particular directions in momentum space [25, 27]. In recent Brillouin observations [28], a very narrow central peak was found in addition to the soft mode that had been previously reported. Work at IBM Zürich revealed that the central peak of fresh crystals could be substantially decreased by a simple heat treatment [29], and was thus presumably due to structural defects rather than chemical impurities as originally thought [30]. In these annealed crystals the soft acoustic phonon was found to be in excellent agreement with the mean-field description, as the recent renormalization-group considerations suggest it should be [31, 32]. Upon doping KDP with Cr^{5+} on P^{5+}

sites, extrinsic central peak behavior was created and studied in detail by electron paramagnetic resonance (EPR) [33].

The slightly first-order transition of KDP can be made second-order either by application of a suitable electric field or by hydrostatic pressure, in which case a tricritical point is reached. Under an electric field the transition becomes nonsymmetry-breaking but remains an elastic transition. This has the dramatic consequence that critical fluctuations are quenched due to the nonexistence of a soft mode at wavelengths that are short compared to sample dimensions [34, 35]. The transition should then occur exactly as Landau predicted. Only with very excellent samples was it possible to measure meaningfully the integrated intensity decrease that would demonstrate the quenching. Furthermore, the coupling to heat already mentioned [25, 26] is also induced by an electric field. The linewidth of this thermal central peak has recently been measured accurately [36]. One obtains a constant value of the diffusion constant, in close agreement with the background lattice specific heat. This is a strong indication that the critical specific heat follows the Landau behavior.

• *The displacive transitions in $LaAlO_3$ and $SrTiO_3$*

These two double oxides crystallizing in the perovskite structure ABO_3 are traditionally used as model substances for studying structural phase transitions. The perovskite structure can be regarded as composed of positive A ions and negative near-rigid BX_6 octahedra with common anion corners. Thus, the octahedra can rotate about the B ion, the rotation angle being proportional to the oxygen displacement. In $LaAlO_3$ this rotation occurs around a pseudocubic [111] axis, and in $SrTiO_3$ around a tetragonal [100] direction. Because the octahedra share corners, the rotation angles alternate by $\pm\phi$ about the symmetry axis. EPR has played a crucial role in the study of these transitions. The displacements are very small, and EPR is more than an order of magnitude more sensitive than conventional x-ray and neutron diffraction techniques. EPR studies more than two decades ago by Müller in $SrTiO_3$ showed the existence of a cubic-to-tetragonal transition near 100 K and domains below T_c [37]. The EPR of Fe^{3+} disclosed *directly* the basic rotational properties of oxygen octahedra in these compounds, first reported in 1964 in $LaAlO_3$ by Müller *et al.* and then in 1966 in $SrTiO_3$ by Unoki and Sakudo [37]. The angle $\phi(T)$ is the order parameter of these antiferrodistortive transitions and its temperature dependence has been measured by EPR in $LaAlO_3$ and $SrTiO_3$ by Müller *et al.* EPR investigations of Gd^{3+} on La^{3+} sites in $LaAlO_3$ and Gd^{3+} on Sr^{2+} sites in $SrTiO_3$, together with the Fe^{3+} data, allowed assignment of the low-temperature structures as $R\bar{3}c$ and I4mcm, respectively. These are the first two structures determined by magnetic resonance alone. A Landau free-energy expansion by Thomas and Müller [37, 38] accounted for the second-order nature of the transitions and showed that there are only two possible thermodynamically stable low-temperature phases, which are just those exemplified by $SrTiO_3$ and $LaAlO_3$. The staggered rotation can be described by a wave vector q, which lies at the corner of the Brillouin zone in the cubic phase. Associated with these static displacements are soft optic mode frequencies at the same wave vector. The soft modes of the transitions in $SrTiO_3$ and $LaAlO_3$ have been investigated by inelastic neutron scattering [39] as well as by Raman scattering [40]. The Landau theory of Slonczewski and Thomas was able to account for the observations in a phenomenological way [38].

The simplicity of the soft-mode eigenvectors in both $SrTiO_3$ and $LaAlO_3$—*i.e.*, the fact that only the oxygen ions move—has allowed Pytte and Feder [37] to analyze all of the dynamic variables in these two crystal classes *via* a simple microscopic Hamiltonian. This Hamiltonian was treated in a self-consistent mean-field approximation and yielded good results in comparison with experiment. It was further expanded to include elastic strain interactions by Feder and Pytte [37], resulting in a total of five independent parameters. The theory successfully accounts for all aspects of the transition dynamics except the central mode and critical exponents near T_c. This represented the first explicit calculation from a microscopic model of the soft-mode frequencies, soft-mode distortions, strain distortions, and elastic constants associated with a displacive phase transition. An analogous theory has been formulated for perovskite ferroelectrics [37].

• *Improper ferroelectrics*

Generally, soft optic mode frequencies at wave vectors $q \neq 0$ give rise to structural transitions that are not ferroelectric. However, there is a class of materials with transitions of this type which are simultaneously ferroelectric, *e.g.*, gadolinium molybdate [41] $Gd(MoO_4)_3$ and isostructural materials with Sm, Eu, Tb, and Dy. Investigations of the dielectric, optical, and mechanical behavior of these materials have revealed several unique and potentially useful properties. A spontaneous strain appears coincident with the spontaneous polarization, and polarization and strain states of opposite polarity can be induced by either applied electric fields or mechanical stress. Observations on the dielectric response of *unclamped versus clamped* crystals led Cross, Fouskova, and Cummins [41] to suggest that the transformation was driven by an *elastic instability* and that the polarization

was an incidental but necessary consequence of the resulting strain. Thus this substance was at first termed *ferroelastic*.

This proposal was, however, not entirely satisfying because a proposed elastic instability in the paraelectric phase was not observed. The similarity of the elastic data to those for $SiTiO_3$ led Pytte [42] to propose an alternate model in which the essential driving instability involved atomic displacements associated with a normal phonon mode with finite wave vector. In this model, both the polarization and the strain arise indirectly as a result of anharmonic coupling. The model was able to account for all observed data, the 90° switching, and the dielectric and acoustic data; this was later confirmed by neutron scattering experiments [41]. The discontinuous behavior of the elastic constants expected from this model has been verified in detail [43]. Similar models were proposed independently by Levanyuk and Sannikov and by Aizu [41]. The study of these types of transitions has developed into an important subfield of ferroelectricity, now generally known as *improper ferroelectrics* [44].

• *Jahn-Teller transitions*

The cooperative Jahn-Teller effect is a phase transition driven by the interaction between degenerate orbital electronic states and the crystal lattice. It involves the simultaneous splitting of the electronic states and a symmetry-lowering distortion of the lattice. Recent advances in the understanding of this effect have been spectacular both because of the discovery of a family of transparent rare earth compounds in which it is easy to measure the changes in energy of the electronic states and because of the increasing use which has been made of ultrasonic techniques for investigating lattice distortions. In most materials the coupling is predominantly to a strain, and the ultrasonic method provides a direct observation of the softening of the appropriate elastic constant near the transition temperature.

Of these materials, $DyVO_4$ and $TbVO_4$ have been most extensively studied [45]. A description of the Jahn-Teller transitions in these materials has been given by Pytte and Stevens [46] and Elliott *et al.* [47] based on a semiclassical tunneling model. The model leads to a good understanding of why $DyVO_4$ and $TbVO_4$ undergo their respective phase changes, explains their unusual paramagnetic properties, and predicts that their respective elastic constants, C_{11}-C_{12} and C_{44}, should vanish at the transition temperature.

The fact that all Jahn-Teller systems should show large ultrasonic anomalies was pointed out by Pytte and independently by Kataoka and Kanamori [45]. These authors emphasize that if the transition is second-order and if there is any finite coupling to the strain, the soft mode of the system is the strain mode. The first experimental observation of the soft strain mode in $DyVO_4$ was made by Melcher and Scott [45]. The dependence of thermodynamic variables such as the elastic constant on the measuring frequency for Jahn-Teller systems was pointed out by Pytte [45] and was observed experimentally in $TbVO_4$ and $TmVO_4$ [45].

The relaxation rate for a degenerate mode gives rise to a central peak in the dynamic structure factor which is expected to show critical narrowing as the transition point is approached. This was predicted by Sandercock *et al.* and Pytte [45] and has been observed in $PrAlO_3$ by Kjems *et al.* [45].

The rare-earth pnictides, of general formula RX, where R is any Re ion and X is N, P, As, or Sb, are metals or semimetals which crystallize with the cubic NaCl structure. These materials are known to distort either tetragonally or trigonally at low temperature and to order magnetically simultaneously or nearly simultaneously with the structural transition. The type of distortion and direction of magnetic ordering in these materials is well described by the tunneling model of Stevens and Pytte [48]. Englman [49] has discussed the way in which strong anharmonic interactions can lead to the localized distortion picture. An extension of theories of this type (with strong anharmonic forces) has been used by Englman and Halperin and by Thomas and Müller [45] to study compounds of transition metals.

• *Spin-Peierls transitions*

There has been much interest recently in the unusual electrical conducting properties of quasi-one-dimensional systems such as tetrathiafulvalene tetracyanoquinodimethane. Several of these materials seem to undergo a Peierls transition [50] to an insulating ground state. A magnetic analog has also been discussed theoretically [51, 52] for antiferromagnetic chains. At this transition the spin-lattice system dimerizes and the material undergoes a second-order transition to a singlet ground state with a magnetic gap. The theory leads to a model formally similar to the electron-phonon interaction model that gives rise to the Peierls transition. On the basis of this formal similarity, Pytte named the dimerization transition in linear antiferromagnetic chains a spin-Peierls transition. In this theory the distortion is described by a gap equation of the same form as in the BCS theory of superconductivity.

A number of such transitions have recently been observed [53] and their study remains an active field.

Generally good agreement is obtained with the predictions of mean-field theory. An improved treatment of the pseudofermion interaction has recently been given by Cross and Fisher [54].

• *Critical behavior of displacive phase transitions*

Very accurate EPR measurements of the temperature dependence of the order parameter by Müller and Berlinger [37] revealed in both $SrTiO_3$ and $LaAlO_3$ a strong deviation from the square root dependence expected from mean-field theory. The exponent was found to be close to 1/3, as found in magnetic systems near the transition point when critical fluctuations are important. These EPR results opened up a whole new field in the study of critical phenomena. Up to this point it had been generally assumed that structural transitions like ferroelectric transitions could be well described by mean-field Landau theories. Subsequent studies on $SrTiO_3$ and $LaAlO_3$ have revealed a variety of interesting critical behaviors. Thus, the uniaxial Lifshitz point and behaviors in the same universality class as the magnetic Ising, XY, and Heisenberg models, as well as the three-state Potts model, are all observed in these materials. Bicritical, tricritical, and tetracritical points are also realized where internal and external interactions compete. This great variety of multicritical behaviors results from the fact that the stress-temperature interactions, and thus the phase diagrams, are unusually rich in these high-symmetry systems [55]. The realization of a tricritical Lifshitz point marks a still higher degree of sophistication as it consists of a simultaneous combination of two types of multicritical behavior: Lifshitz and tricritical.

The temperature-stress phase diagrams of $SrTiO_3$ and $LaAlO_3$ have been studied by Bruce and Aharony [55–57] for stress along the [100] direction. The system has a topology like the uniaxial antiferromagnet near the antiferromagnetic spin-flop bicritical point [54, 56]. Below T_c, $p[100] < 0$ yields an $n = 1$ Ising-type phase boundary. For $p[100] > 0$, two kinds of monodomains along [010] and [001] are formed and thus an $n = 2$, XY second-order boundary is obtained. EPR linewidth measurements were carried out by Müller and Berlinger [56] on high-quality polydomain samples to obtain the Heisenberg behavior. Application of definite stresses to such samples reproduced monodomain $n = 1$ Ising and $n = 2$ XY-model behavior. These experiments verified the predicted phase diagram and critical behavior.

A different critical behavior is obtained in those perovskite crystals exhibiting first-order antiferrodistortive phase transitions due to cubic order-parameter fluctuations. In this case, a continuous phase transition can be re-established by an anisotropic stress that favors the ordering of a single component of the order parameter when it exceeds a certain tricritical value [57]. Examples are $KMnF_2$ and $RbCaF_3$, which are both weakly first-order due to fluctuations in the absence of an external stress but show the same low-temperature phase as $SrTiO_3$. However, in these crystals the dispersion of the soft antiferrodistortive R_{25} mode is flat from the R to the M points of the Brillouin zone. Due to the spatial anisotropy, the associated exponents at the tricritical point that are induced at sufficiently high stress are quite different from those of the simple spatially isotropic three-dimensional Ising model. The resulting critical behavior is referred to as that of a Lifshitz system [57]. This behavior has been observed in $RbCaF_3$ by monitoring the EPR lines of Gd^{3+} on a Ca^{2+} site [58]. The first-order transition at zero stress becomes second-order at a critical stress and temperature. Near this tricritical point, the exponent of the temperature dependence of the rotational order parameter is $\beta = 0.18 \pm 0.02$, in good agreement with the predicted theoretical value for tricritical and normal Lifshitz behavior, which in both these cases is $\beta = 0.20$. Furthermore, a hydrostatic pressure experiment confirmed that the transition remained first-order under the symmetry-conserving field [59].

Stress along the [111] diagonal in $SrTiO_3$ leads to a rather more complicated phase diagram. At stress p (>0), one first observes a second-order transition from the "pseudocubic" phase into a trigonal phase at temperature $T_1(p)$, and then, at $T_2(p)$, a first-order transition into a "pseudotetragonal" phase. For $p < 0$ there is a direct second-order pseudocubic-to-pseudotetragonal transition. The point $p = 0$, $T = T_1(0) = T_2(0)$ is thus bicritical. This phase diagram, first observed by Müller, Berlinger, and Slonczewski [60] by means of EPR, has been accounted for by the Landau theory and was later confirmed experimentally by neutron scattering [61]. Slonczewski used the Landau theory to analyze the stress and temperature dependences of fluorescence in $SrTiO_3$:Cr^{3+} and was able to quantitatively fit the experimental results [62, 63]. A renormalization-group study of this phase diagram showed [55, 56] that the transition at $T_1(p)$ is Ising-like, while that at the bicritical point, $T_1(0) = T_2(0)$, is Heisenberg-like [55, 56]. The Ising behavior at $T_1(p)$ has been verified by EPR and yielded an order parameter exponent $\beta = 0.32 \pm 0.02$, in agreement with the Ising model prediction [55]. The transition at $T_2(p)$ was described by the three-state Potts model in which the order parameter is reorientable but not reversible [56, 64]. Renormalization-group studies [65] indicated a first-order transition for the three-state Potts model and predicted that the discontinuity in the magnetization at the first-order transition should be described by a critical exponent $\delta^* \approx 0.6$, as quite distinct from the mean-field value

$\delta = 1.0$. This prediction was verified by EPR measurements [66]. The non-mean-field value of δ^*, which agrees remarkably well with renormalization-group predictions, shows that one is indeed in the fluctuation-dominated region.

Classical models suffice for studying critical behavior of phase transitions at finite temperatures since quantum effects play essentially no role. However, in cases of transitions at or near absolute zero, quantum mechanical effects can become very important. In $SrTiO_3$ low-temperature quantum mechanical fluctuations prevent it from becoming ferroelectric, and occupied acoustic modes are strongly mixed. The dielectric constant rises on cooling to 4 K but remains temperature-independent down to 30 mK. Consequently, $SrTiO_3$ has been termed a *quantum paraelectric* [67]. The quantum behavior of displacive transitions has been studied theoretically by Schneider *et al.* [68], and their predictions have been verified experimentally by Höchli *et al.* [69], who studied the ferroelectric transition in $KTa_{1-x}Nb_xO_3$ (KTN) as a function of x. The theory predicts that the spontaneous polarization, inverse dielectric constant, and critical transition temperature will show critical behavior as a function of x. Due to quantum fluctuations, the critical dimension at and above which mean-field critical behavior is obtained changes from its usual value such that the predicted exponents are all mean-field-like. The exponents obtained for KTN by dielectric and elastic constant measurements are in good agreement with the predicted values. As a function of temperature, the dielectric susceptibility diverges in the quantum limit with an exponent $\gamma' = 2$, as confirmed in recent experiments on KTN [70].

Only static critical behavior has been discussed so far. Sufficiently close to T_c the dynamic behavior also becomes universal, and the distinction between displacive and order-disorder transitions disappears. In both cases the critical dynamics is described by slow relaxation of large ordered clusters. In the last few years it has gradually come to be appreciated that the dynamic behavior of systems undergoing displacive structural phase transitions may differ in a qualitatively striking fashion from that suggested by the long-serving phenomenology of the "soft mode." The recent activity may be traced to the observation [71] that the spectral function of the critical degrees of freedom in $SrTiO_3$ evolves, as $T \to T_c^+$, from the simple form expected for a softening quasi-harmonic phonon, to a more complex form. That is, a central peak appears and grows critically in intensity, while the phonon resonance continues to soften, but attains, at T_c, a finite limiting frequency ω_∞ [71]. This central peak has also been studied extensively by Schneider and Stoll [72] by computer simulations. These computer experiments clearly revealed the occurrence of a central peak that became critical close to T_c, while the phonon soft mode was found to saturate, and the formation of clusters was discovered in which the average displacement was nonzero. From these observations a new view [72, 73] of the physics of displacive phase transitions emerged: With the onset of criticality, the growth in correlations drives a crossover from a weakly anharmonic ("displacive") regime to a strongly anharmonic ("order-disorder") regime, whose short-range order is manifested in clusters in which the average value of the ordering variable is nonzero for a time long in comparison with typical inverse phonon frequencies. The central peak may thus be regarded as the short-range-order-induced dynamic precursor of the Bragg peak to appear below T_c, while the phonon sideband reflects quasi-harmonic oscillations about the distorted quasi-equilibrium positions set by the distribution of cluster coordinates. This picture, conceptually very appealing, has received direct support from EPR experiments on $SrTiO_3$ [74]. Near but above the transition temperature T_c, the oxygen octahedra in $SrTiO_3$ are found to oscillate about quasi-equilibrium positions displaced from the high-symmetry position [74]. The phonon is stabilized by the short-range order in much the same way as the low-temperature-phase phonon is stabilized by the true long-range order. From this, one can estimate the limiting frequency ω_∞ close to T_c. The striking accord of the experimental and theoretical values constitutes strong evidence for the overall coherence of this picture of the dynamic behavior of displacive phase transitions.

More recently, Bruce, Schneider, and Stoll [75] have used renormalization-group methods to calculate the critical distribution functions for large *groups* of ordering coordinates in two- and three-dimensional systems undergoing structural phase transitions. In two dimensions the distribution function shows clear evidence of well-defined clusters of precursor order and cluster walls; *i.e.*, the asymptotic collective behavior is *always* order-disorder rather than displacive. However, in three dimensions the order-disorder component of the asymptotic behavior is markedly weaker.

From this review, it should be clear that displacive phase transitions exhibit an extraordinary variety of interesting critical behaviors, both static and dynamic, which has permitted a number of detailed comparisons of experimental data, primarily EPR, with predictions of recent renormalization-group calculations.

Magnetism

Since magnetic cores were the primary computer memory elements during the fifties and early sixties, it was natural that one of IBM's major research efforts should involve

magnetism and magnetic materials. In an effort to optimize core performance, work in the early fifties focused on the development and processing of ferrite compositions. A study of the Cu-Mn ferrite system by Brownlow demonstrated that cores of these materials cooled in an oxidizing atmosphere formed an oxygen-rich phase on the surface that stressed the core and improved loop squareness [76]. This work was significant because it enabled IBM to use a substitute material for the Mg-Mn ferrite core in use at that time.

The latter half of the fifties could be described as the beginning of fundamental research on magnetism and magnetic materials in IBM. During this period the origins of the anisotropy in cobalt-substituted magnetites and manganese ferrite as a function of stoichiometry were examined. Although the magnetization and ordering temperatures of the common ferrites were rather well understood in terms of Néel theory in the late fifties, the relationship of the stiffness of the magnetization to certain crystallographic directions was not. IBM's contributions at that time were highly significant in developing a fundamental understanding of the magnetocrystalline anisotropy of ferrites. By measuring the anisotropy of single-crystal ferrites, the contributions (and their temperature dependences) of Co^{2+}, Mn^{2+}, and Fe^{2+} to the magnetocrystalline anisotropy were observed for the first time [77, 78]. This led to a theoretical treatment in which ionic contributions to the anisotropy were related to the trigonal field seen by the B-site cations [79]. The electronic state of Co^{2+} was shown to differ fundamentally from those of other 3d-shell magnetic ions (Fe^{2+}, Ni^{2+}, Fe^{3+}, etc.) due to the fact that the orbital momentum of Co^{2+} is not quenched. This model is still used to explain the unusual contributions of the Co ion to the anisotropy and the large magnetostrictions of ferrite spinels.

About 1958 a program was initiated to study a newly discovered [80, 81] class of insulating ferrimagnetic compounds, the garnet materials. The initial work was concerned mainly with the correlation between composition and compensation temperature. Perhaps the most important contributions came from work on resonance relaxation [82], which showed by linewidth measurements of yttrium iron garnet doped with various rare earth ions [83] that although the relaxation occurred through the rare earth ions, it could not be explained by the various relaxation theories known at that time. Thus, empirical relationships were formulated which subsequently proved very useful in our understanding of the damping process in garnet bubble materials. Most of the fundamental garnet research ended in 1965, but the experience and information gained served as an extremely valuable entry into magnetic bubble technology around 1969.

In the early sixties, when it was clear that ferrite cores would be replaced by semiconductors, the magnetism effort changed direction. Emphasis shifted toward new materials, particularly those having unique magnetic, magneto-optical, and transport properties. The compound EuO had just been discovered to order ferromagnetically with a Hund's-rule coupled-spin-only ground state of $^8S_{7/2}$. The magnetic exchange in the semiconducting compound was considered to be based on a vertical 4f-5d transition to a neighboring Eu ion. This simple Heisenberg ferromagnet and the related EuS, EuSe, and EuTe compounds provided a rare opportunity for the study of interrelationships between magnetic and transport properties. Several significant contributions to an understanding of the fundamental interactions in ferromagnetic semiconductors grew out of the research in IBM. Among the more significant was the realization by Methfessel *et al.* [84] that the 4f level must lie in the forbidden gap. Based on absorption measurements, the first correct energy level diagram was constructed. McGuire *et al.* [85] interpreted the magnetic properties of the nearly ideal Heisenberg-type ferromagnets in the molecular-field approach by considering nearest and next-nearest neighbors only.

The first successful doping experiments were done by Holtzberg *et al.* [86] and showed that the dominant exchange interaction in these compounds, as in pure rare-earth metals, was via the polarization of conduction electrons for the ferromagnetic members of the series. These results led to studies on the effect of magnetic order on transport properties and the discovery of giant magnetoresistance effects near the magnetic-ordering temperature [87].

Esaki *et al.* studied tunneling into the empty conduction band of EuS [88]. Later Thompson *et al.* studied tunneling in Schottky barriers of EuS:Eu against In as a function of magnetic ordering [89].

The europium monochalcogenides, as with most of the rare-earth monochalgocenides, were characterized by their highly localized and well-screened 4f electrons. As a consequence, the moments developed in these compounds were essentially those of the free ion values. This view was somewhat shaken by the observation by Jayaraman *et al.* [90] of anomalous volume and resistivity effects in SmS under rather moderate pressures. At 6.5 kbars, the semiconducting black SmS undergoes a first-order symmetry-preserved 18% volume collapse to a gold-colored metallic phase. SmS has since become the prototypical intermediate valence compound. The intermediate valence state is characterized as a spatially homogeneous state in which Sm^{2+} and Sm^{3+} are simulta-

neously present; it is reflected in the intermediate value of the lattice constant. Optical absorption measurements by Holtzberg and Torrance [91] on thin films of SmS served to characterize the energy levels of the narrow-band semiconductor. Laser-induced phase transitions in the surface of SmS crystals have been studied by Pohl *et al.* [92].

The difficulties of studying SmS in the collapsed phase were obviated when similar transitions to the collapsed phase were found upon anion and cation doping by Holtzberg [93]. A number of significant experimental papers followed which served to establish the physical characteristics of the intermediate valence state in $Sm_{1-x}Y_x$. These included XPS studies [94], measurement of the magnetic properties [95], Raman and infrared spectroscopic studies [96], measurement of transport properties [97], Mossbauer studies [98], and specific heat [99] and ultrasonic attenuation [100] measurements, as well as neutron scattering studies [101] of the phonon dispersion. Pohl detected a continuous valence transition in $Sm_{1-x}La_x$ at $x = 0.27$ by means of optical reflectivity measurements under hydrostatic pressure [102].

In the early sixties, in efforts to understand the relation between quantum and thermal fluctuations in magnetic systems and at the same time to assess the validity of various approximation methods of many-body theory, a series of attempts were made at the IBM Thomas J. Watson Research Center to find exact properties of certain one-dimensional many-body systems. Lieb, Schultz, and Mattis [103] found the exact solution for what they called the one-dimensional XY model. They showed that while thermal fluctuations at any finite temperature would destroy long-range order, only the complete disappearance of quantum mechanical fluctuations would have a similar effect. Schultz applied these ideas to the one-dimensional gas of impenetrable bosons [104], while Lieb and Liniger [105, 106] found exact ground-state properties of the one-dimensional gas of *penetrable* bosons. Schultz, Mattis, and Lieb [107] also found that Onsager's famous exact solution of the two-dimensional Ising model (classical, spin-1/2) could be reformulated in terms of the ground-state problem of (essentially) the one-dimensional XY model, *i.e.*, a problem of many spinless fermions. Generalizations have since often been exploited, especially in relating the statistical mechanics of classical spin systems in d dimensions to quantum ground-state problems in $d - 1$ dimensions. The mushrooming of interest in one-dimensional physics that accompanied the discovery of quasi-one-dimensional systems in the seventies built heavily on this body of work.

The effect of correlation on the ferromagnetism of 3d transition metals has been considered in a series of papers by Gutzwiller [108–110] starting in the early sixties. Up to this point, the main attempt to explain ferromagnetism in metals was based on the collective electron theory of ferromagnetism [111], a theory which especially failed in the limit of large spacing between the lattice sites. To deal with this problem a new approach was proposed by Gutzwiller in which a correlated wave function for the electrons in the 3d band was proposed as an approximation to the ground state. This approach was used to study mechanisms which tend to favor a ferromagnetic ground state. This work preceded similar independent work by Hubbard [112].

First-principle calculations of the magnetic properties of the 3d and 4d transition metals have been performed by Janak *et al.* [113–115] using spin-polarized self-consistent band theory. This work gives the most systematic and accurate study of the ground-state properties of the metallic elements; only the atomic number is specified. The spin susceptibilities as enhanced by electron-electron interactions were calculated for 32 elements [114]. In order for magnetism to occur, both a large density of states and a large exchange-correlation integral are required. These calculations show where magnetism occurs (Fe, Co, Ni) and in which elements there is a strong tendency toward magnetism (Sc, Pd). Further, the magnetic ordering produces a giant internal pressure [113] that gives rise to important changes in lattice constants and bulk moduli. First-principle calculations of the hyperfine fields and their pressure derivatives in Fe, Co, and Ni have also been carried out [114] in which the results are in good agreement with the experimental values. Calculated photoemission properties are also in good agreement with experimental results [116].

The development of a satisfactory theory of ferromagnetic metals has remained a difficult problem. Some data are readily interpretable in terms of a band-theory (itinerant-electron) model, while other data are interpretable in terms of a localized-electron model. A new formalism developed by Hubbard [117, 118] is capable of reconciling to a considerable extent the localized and itinerant electron models of ferromagnetic metals. The results as applied to iron explain why the Curie temperature of iron is so low in spite of the largeness of the exchange fields (~1–2 eV) and indicate why iron seems in some experiments to behave very much like a Heisenberg model of localized spins. The Curie temperature, the magnetization curve, the paramagnetic susceptibility, and the effective interatomic exchange coupling have been calculated for iron [118].

Recent work at the IBM Zürich laboratory has concentrated on the study of antiferromagnetic insulators well described by anisotropic Heisenberg exchange models. These are rewarding systems because of the variety of multicritical points in the experimentally easily accessible space of uniform field and temperature. Detailed studies of the phase diagrams of uniaxial antiferromagnets [119] were carried out by Blazey, Rohrer, *et al.* and were compared with a molecular-field treatment by Rohrer and Thomas [120]. This phase diagram has been confirmed by acoustic measurements [121]. Other studies dealt with the softening of the antiferromagnetic resonance modes and the relaxation mode near the first-order spin-flop transition, with particular emphasis on the critical point and the bicritical point [122]. The antiferromagnetic systems studied at Zürich have proved an ideal testing ground for many of the predictions of renormalization-group theory as it applies to multicritical points. These experiments have allowed the determination of new sets of critical exponents and the study of crossover behavior from one set of critical behavior to another.

A weakly anisotropic uniaxial antiferromagnet exhibits a very complicated phase diagram as a function of T, $H_{\parallel}$, and $H_{\perp}$, including a first-order spin-flop transition and both bicritical and tetracritical points. Experimental work on $GdAlO_3$ provided the first confirmation [123] of the predictions of renormalization-group studies [124] of the anisotropy crossover exponent, the orientation of the scaling axes near the bicritical point, as well as several exponent relations. Further, the critical behavior near the tetracritical point and the crossover to different critical behavior as one moves away from the tetracritical point in different directions in $H_{\parallel}$, $H_{\perp}$, T space have been determined experimentally to a very high degree of accuracy [125], which has prompted further theoretical studies of these phase transitions.

The dimensionality of a physical system is a central parameter in the theory of phase transitions. One result of the theory is that for two- or three-component order parameters (the planar and Heisenberg interactions, respectively), there can be no long-range order in one and two dimensions. The only experiment on a macroscopic and truly low-dimensional object was performed by Pomerantz and collaborators [126], who constructed a large-area 2d magnet that was one magnetic atom thick. Magnetic order was observed in this material below 2 K. The presence of weak anisotropy and the finite area of the sample were sufficient to violate the assumptions of theory, suggesting that the emphasis of theory should be on the inevitable, albeit small, effects of anisotropy and finiteness of samples.

Much of the recent work at Yorktown has concentrated on the study of amorphous and other random magnetic systems. Effects of disorder (defects, grain boundaries, alloys, amorphous structures) in modifying the properties of ideal crystalline solids have been studied since the earliest attempts to understand condensed matter. In the last ten years, the growing realization that disorder can also lead to entirely new phenomena has made this an extremely active field. In critical phenomena, the most surprising novelty has been the spin glass, a magnetic material in which the spins freeze at low temperatures. Edwards and Anderson (EA) [127] proposed a mean-field theory for this transition in which they introduced a new spin-glass order parameter and a novel technique to deal with the random ordering (the so-called replica method). Sherrington and Kirkpatrick (SK) [128] introduced an infinite-range model for spin glasses for which the EA mean-field theory should be exact. They obtained a phase diagram showing second-order transition lines between the new spin-glass phase and either paramagnetic or conventionally ordered phases, plus a novel multicritical point where all these phases coexist.

Although the EA and SK models are highly simplified, they have proved a useful guide to experimentalists. For example, Mizoguchi *et al.* [129] used a SQUID technique to make dc measurements of susceptibility in fields as low as 80 A/m (0.1 Oe) on amorphous films of Gd-Cu and Gd-Al. Sharp cusps identifying the spin-glass transition were seen in both systems at Gd concentrations below roughly 0.40. The overall phase diagram found for this amorphous alloy system was similar to that obtained by Sherrington and Kirkpatrick. The SK model has attracted considerable theoretical interest, both because of the novelty of the replica procedure and because of the acknowledged deficiencies of the resulting mean-field-like solution at low temperatures. The most glaring difficulty is the untenable prediction of a finite negative entropy at $T = 0$. Further, Alameida and Thouless [130] and Pytte and Rudnick [131] showed the EA and SK solutions to be dynamically unstable. An extended mean-field theory, using no replicas but incorporating random nonlinear "cavity fields," was developed by Thouless, Anderson, and Palmer [132]. They also found corrections to the SK solution below the transition temperature and were able, with some additional assumptions, to estimate low-temperature properties. In particular, they predicted $C \propto T^2$, $\chi \propto T$. Both agree (to within 20% in the coefficients) with Monte Carlo simulations [133].

In all of the above work, the simplest possible spin-glass Hamiltonians were studied, allowing only random exchange interactions. A more realistic model was introduced by Harris, Plischke, and Zuckermann (HPZ) [134].

They focused on the consequences of the structural disorder in amorphous films and postulated the existence of strong local anisotropy fields with random orientations. Within mean-field theory this model gives rise to a ferromagnetic phase transition with a greatly reduced transition temperature and magnetization. This model has been used extensively to describe the magnetic properties of rare-earth amorphous alloys [135]. An extensive series of experiments on the Dy-Cu amorphous system, for which the HPZ model is quite appropriate, were carried out by Coey and von Molnar [136–138], who observed a specific heat linear in temperature. The magnetic entropy at the temperature of the susceptibility maximum was found to be roughly R ln 2 per Dy ion, confirming that only two states per spin contribute to any ordering. Theoretical study of the HPZ model by Pelcovits, Pytte, and Rudnick [139–142] produced the surprising prediction that the ferromagnetic phase is never stable in a three-dimensional system, in disagreement with the mean-field results and existing computer simulations [143]. For this model, long-range magnetic order is not possible below four dimensions. Further measurements [138] on Dy-Cu films with 40 to 50 percent Dy fraction gave qualitative support to this prediction. Jayaprakash and Kirkpatrick [144] considered a limiting case (approximately true in Dy-Cu) by computer simulation. Even for nearly pure Dy films, their calculations showed that the random anisotropy caused the ground state to be nonmagnetic. Very recently, Aharony and Pytte [145] have shown that below four dimensions this model undergoes a phase transition in which the magnetic susceptibility becomes infinite at the transition and remains infinite at all lower temperatures, while the magnetization remains equal to zero. In this phase the pair-spin correlation function exhibits power-law decay rather than the usual exponential decay.

Critical slowing-down as the spin-glass transition is approached from higher temperature was identified by Salamon [146] in a wide range of materials. Kirkpatrick [147] showed that such critical slowing-down is indeed present in Ising spin-glass models, and that a simple pole, rather than some other power-law singularity, is the expected mean-field limiting behavior. Measurements of the electron spin resonance (ESR) in Gd-Al at several frequencies by Malozemoff and collaborators at Ohio State [148] subsequently confirmed that the line shift and broadening are principally a dynamic effect, although other relaxation mechanisms are seen at and below T_{sg}. It is at these lower temperatures that the long-time "glassy" decays are most prominent. Detailed measurements of such relaxation times were carried out by the Yorktown group in collaboration with several visitors from European laboratories [149].

The more conventional critical and multicritical points are sometimes also changed dramatically by randomness. An important distinction is between the effects of random exchange interactions, which usually leave critical properties unchanged, and those of random fields, which affect critical exponents and change the upper critical dimension [150]. Thus, a random-field Ising system at $d = 3$ is expected to exhibit the critical behavior of the pure system at $1 < d < 2$. Experiments [151] on the system $GdAlO_3$:La were the first to verify such random-field critical and multicritical behavior. In particular, they gave new random-field critical exponents still not accessible to theory, and confirmed predicted [152] nontrivial changes of the magnetic phase diagram.

Phase transitions in excited systems far from equilibrium

Phase transitions and cooperative phenomena are not limited to systems in thermodynamic equilibrium. Similar phenomena occur in systems subject to a continuing influx of energy and exhibiting some active kinetic process. The analogy between the hysteresis in arc lamps and hysteresis in ferromagnetism was already appreciated by the turn of the century. In the early days of digital computer development these analogies became particularly clear. As an illustration consider two systems: a magnetic core and a transistor circuit, both of them bistable, and both used to hold information. Both systems go through a bifurcation, or second-order transition, as temperature is lowered in the magnetic case, and as the power supply voltage is increased in the circuit case. In the magnetic system fluctuations are important, whereas in the latter case mean-field theory is exact. An introductory overview was recently provided by Landauer [153]. First- and second-order transitions and all the concomitant phenomenology—hysteresis, nucleated transitions, domain walls, critical fluctuations, soft modes, divergent susceptibilities, etc.—turn up in these dissipative systems. They are realized in lasers, hydronamics, electrical circuits, biological and open chemical systems with a continual supply of new reactants and a continual withdrawal of the exhausted products. A recent review has been given by Haken [154].

It seems particularly significant, in retrospect, that two of the key pioneers in the development of computers, Turing and von Neumann, both made perceptive contributions to the understanding of the kinetics of multistable systems. Turing, aware of the way information was handled in computer circuits, asked how chemical control might be exercised in morphogenesis, *i.e.*, in the determination of differentiated structure via symmetry breaking, during biological development [155]. This led him to a pioneering discussion of the fact that open chemical

systems can exhibit multistability, waves, and oscillations. A more applied contribution was made by von Neumann [156], and independently by Goto [157], who recognized that parametrically excited nonlinear circuits could be used to perform all computer functions. Von Neumann's patent, assigned by him to IBM, involved taking circuits back and forth across a bifurcation point. Near such a symmetry-breaking threshold, systems have a "divergent susceptibility," which is to say that they are easily influenced by external signals. This invention has led to major development efforts within IBM and elsewhere, and to construction of actual working computers in Japan.

Similarities between stability and instability in active systems on the one hand, and particles moving in potentials on the other, are basic to much of the theory of nonlinear oscillations and are implicit in the use of Lyapunov functions. A particularly elegant and highly developed version of such techniques, arising out of the analysis of multistable computer circuits, is due to Brayton and Moser [158]. By contrast, however, the genuinely novel parts of the modern theory of multistable dissipative systems, and the transitions they permit, come from our ability to go beyond deterministic descriptions, to include the role of noise or fluctuations. An early start in this direction was made by Landauer [159], who in 1961 pointed out that in a bistable circuit, as in an asymmetric bistable potential well, one can ask about the relative probability with which the two locally favored states are occupied and about the speed with which the system relaxes to this steady state distribution. The paper contains the sentence "The second class of devices consists of structures which are in a steady (time invariant) state, but in a dissipative one, while holding on to information." The closely related expression "dissipative structure" later became popular through its use by Prigogine and his collaborators [160a]. Landauer's qualitative point [159] was soon put forth in the form of a detailed quantitative theory for bistable tunnel diode circuits [160b], in a paper asking how small a tunnel diode can be and still be used to hold information reliably. It took well over a decade before this general field became fashionable, and before the content of Ref. [159] was restated in the language of a chemical reaction [161].

The aforementioned early paper [160b] brought out a point which has been understood and emphasized only recently: The controlling influence of noise on questions of relative stability (*i.e.*, which is the more likely state) in these active systems [162, 163]. This is now also recognized to be true in many equilibrium first-order phase transitions.

Up to this point we have emphasized systems with essentially only one degree of freedom which have a threshold at which the original physical symmetry is broken. Such symmetry-breaking thresholds also occur, in spatially extended systems that can respond in a nonuniform way, in space and/or time, to a uniform excitation. Haken reviews such systems [154] and shows, for example, that the Ginzburg-Landau equations of superconductivity can be rediscovered in the laser. However, instabilities producing spatial symmetry breaking do not occur only in systems permitting phase separation or in highly excited systems. Rayleigh and later Bohr [164], in classic papers, studied the breakup into drops of a thin stream of liquid under the influence of surface tension. The motion of the stream is incidental and is only required to produce a fresh uncontaminated surface. This instability has become the basis for ink jet printing, discussed in detail in a series of recently published papers [165].

Instabilities leading to spatial nonuniformity in initially uniform systems are, however, particularly likely to be found in highly excited systems. The breakup of intense laser beams, to form filaments, in the case of media whose refractive index increases with light intensity, is a well-studied example [166]. In that case the light can create its own high-index regions of geometrical confinement. Instabilities due to self-heating in temperature-dependent conductors constitute another example [167]. Instabilities in rotating disks of the type used as magnetic storage media have been studied in detail by Stahl and Iwan [168].

The Gunn effect [169] is an instability found in n-type GaAs under high electric fields when transfer of energetic electrons from the normal conduction band to a higher-lying band reduces their mobility, resulting in a negative differential resistance. The time evolution of the initial departure from a spatially uniform conducting state was considered by Pytte and Thomas [170], and it was pointed out that near the onset of the Gunn instability the plasma frequency is purely imaginary and goes to zero at the critical field, just as a soft-mode frequency does. Viewed simply, charges in a conductor are known to decay as $\exp(-\sigma t/\epsilon)$, where σ is the conductivity. When considering small departures from a uniform initial state, it is the differential conductivity that counts, and that determines the stability or instability. This initial observation by Pytte and Thomas led to a great many further treatments of current instabilities; see for example [171].

More complex space- and time-dependent dissipative structures occur in homogeneous current-driven superconducting filaments that are close to their transition

temperatures where heating can be kept small. Extensive studies of phase slip centers, *i.e.*, spontaneous weak links, have been carried out at the IBM Zürich laboratory by Baratoff [172, 173]. These phase-slip centers have been shown to form spontaneously and oscillate synchronously at the Josephson frequency [173].

At the San Jose Research laboratory, there has been a continuing interest in the thermodynamics, structure, and phase stability of the fluid state [174–176]. Abraham, Barker, and Henderson have pioneered the application of the Monte Carlo computer simulation method of classical statistical mechanics for the study of the microscopic properties of the nonuniform fluid state, such as surfaces, interfaces, and physical clusters of nucleation phenomena [177–181].

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A version of this manuscript with a more complete list of references is available from the authors.

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