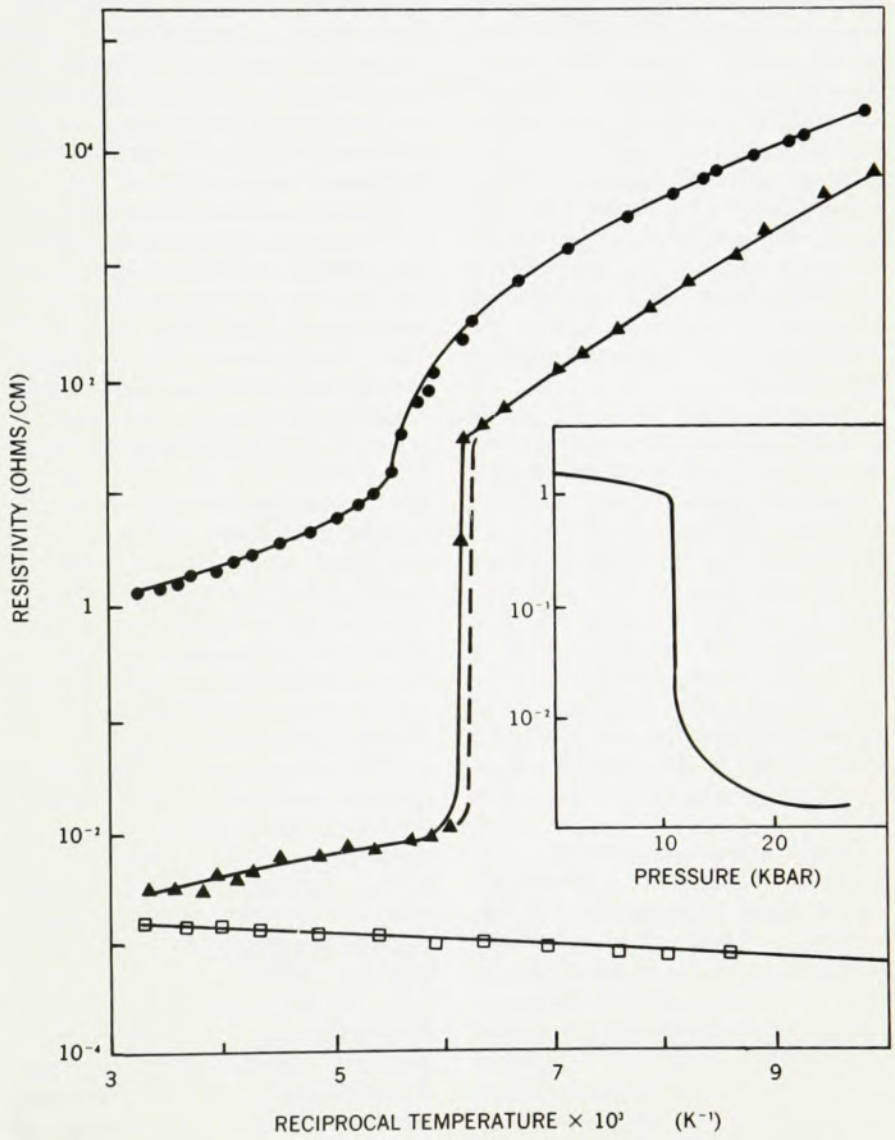
Magnetic Semiconductors Intrigue Both Scientists and Engineers

A confluence of magneticians and semiconductor specialists has been taking place over the past few years as a result both of studies on magnetic chalcogenides and of the realization that transition-metal oxides and sulfides provide an opportunity to study electrons in solids that conform neither to the localized description of crystal-field theory nor to the uncorrelated description of broad-band theory. In addition, the search for new classes of materials for optical, electronic and electrical applications makes magnetic semiconductors of potential interest to engineers. It was therefore fitting that a symposium on magnetic semiconductors was held at the IBM Research Center in Yorktown Heights, N. Y., on 13 and 14 Nov., just before the annual meeting on Magnetism and Magnetic Materials.

There are three kinds of magnetic semiconductors; they may have localized cationic spins and broad-band charge carriers, localized cationic spins and small-polaron charge carriers, or half-filled bands that are split in two by electron correlations that simultaneously introduce measurable cationic spins. Of the compounds discussed in this symposium, the europium salts EuX (where X is oxygen, sulfur, selenium or tellurium) and the ferromagnetic $A^{2+}[Cr_2]X_4$ chromium spinels (where A is cadmium or mercury and X is sulfur, selenium or tellurium) belong to the first category. Ferrimagnetic $Fe^{3+}[Ni^{2+}_{1-x}Fe^{2+}_{x}Fe^{3+}]O_4$, where x is less than 0.6, contains small polarons, whereas the mobile charge carriers in ferrimagnetic $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$ and ferromagnetic $La_{0.7}Ca_{0.3}MnO_3$ are probably intermediate between small polarons and itinerant electrons. Antiferromagnetic nickel disulfide belongs to the third category.

Europium chalcogenides. The europium compounds EuX all crystallize with the rocksalt structure. Although europium oxide and europium sulfide are ferromagnetic, europium selenide is metamagnetic and europium telluride is antiferromagnetic but becomes paramagnetic in high (about 80 kilo-oersteds) applied magnetic fields. C. Kuznia (Siemens) presented the magnetic phase diagram of EuSe, which has two types of antiferromagnetic order as well as a transition to ferromagnetism in relatively low applied fields.

Tadeo Kasuya (IBM and Tohoku University) discussed the microscopic origins of the superexchange interactions that order the localized spins ($S = 7/2$) at the Eu^{2+} ions. Following an earlier qualitative suggestion,[1] he estimated the magnitude of the coupling due to a 4f–5d electron transfer from one europium ion to its neighbor. Although the calculation requires sixth-order perturbation theory, he claims quantitative results for the positive Eu^{2+}–Eu^{2+} interaction. He also showed that the



RESISTIVITY versus reciprocal temperature for $V_{1.92}Cr_{0.08}O_3$ at three different pressures. Corundum phase at 1 bar (dots) has small hexagonal c/a and at 13 kilobars (triangles) has large c/a. Low-temperature monoclinic phase is completely suppressed at 47 kbar (squares). Insert: Resistivity versus pressure at 298 K. Note abrupt change from low c/a to high c/a phase with no change in symmetry.

Eu^{2+}–X–Eu^{2+} interaction contains both positive and negative terms; this situation makes qualitative predictions of its sign unreliable. In fact, the net Eu^{2+}–O–Eu^{2+} interaction is positive, whereas the other Eu^{2+}–X–Eu^{2+} interactions are negative.

The EuX compounds have a $4f^7$ localized-electron level in the energy gap between a filled s,p valence band and an empty conduction band. From optical reflectance data, Carl Pidgeon (National Magnet Laboratory) and William Scouler, Julius Feinleib and John Dimmock (Lincoln Laboratory, MIT) found superlattice splittings of the conduction bands in antiferromagnetic EuTe as well as a transition to paramagnetism when the applied magnetic field H_a is greater than 80 koe. They also observed, for all EuX compounds, that an applied field resolves the reflectivity spectra into right and left circularly polarized components. Above the Curie temperature T_c, the splittings appear to be due to changes in the occupations of the $4f^7$ levels; below T_c additional splittings provide direct evidence for a polarization of the conduction bands. This polarization accounts for the characteristic red shift of the EuX compounds on cooling through T_c.[2]

Dimmock reviewed all the optical data for the EuX compounds and concluded that the fundamental absorption edge is due to the onset of Eu^{2+} transitions of the type $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(T_{2g})$, and that a higher-energy reflectivity peak is primarily due to $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F_J)5d(E_g)$ transitions. However, the position of the 5d (T_{2g}) states relative to the europium 6s band edge, the breadth of the 5d levels and the role played by exciton effects in the 4f to 5d optical transitions remain, in his view, unresolved.

Coupling via mobile electrons. The europium-chalcogenide compounds can be doped with negative-type impurities in a variety of ways, and the gross features of the transport properties are relatively insensitive to the dopant but very dependent on dopant concentration. Stephan Von Molnar reviewed the rather spectacular transport properties that the IBM group has reported previously for n-doped EuX. If the dopant concentration is high enough to produce a degenerate semiconductor, fairly standard broad-band theory accounts well for the transport data. In this case the Rudermann – Kittel – Kasuya – Yosida (RKKY) theory appears to describe, at least qualitatively, an indirect magnetic coupling via the mobile electrons.

For low concentrations of impurities, on the other hand, the problem is more complex. According to the Kasuya model the electrons either move in impurity bands or become trapped at impurity sites, depending on the magnitude of the fluctuations in the impurity energy levels. If the ratio of the average variation in potential W to the impurity bandwidth J is greater than five, then the electrons become trapped.[3] In EuX, mobile d electrons see fluctuating atomic potentials between regions of short-range order; these fluctuations are caused by exchange interactions with the localized $4f^7$ spins. Because these fluctuations are greater near T_c and can be modulated by external magnetic fields, this model can account for the anomalous resistance maximum and for at least part of the giant negative magnetoresistance near T_c.

Michael Oliver, Dimmock and Thomas Reed presented an alternative model to account for large changes in resistivity with temperature and magnetic field below T_c in EuO. Their measurements of conductivity and infrared absorption on the same sample show that the sharp change in resistivity that commences around 50 K is due primarily to changes in carrier concentration and only secondarily to changes in carrier mobility. Therefore they now postulate that the parallel-spin states in the conduction band, which are stabilized at low temperatures by magnetic ordering, fall below the donor levels of nonmagnetic impurity centers as the temperature decreases to below T_c.

Other compounds in which localized spins interact via RKKY coupling through itinerant electrons were also discussed. Moshe Kuznietz (Argonne) reported two new magnetic structures between antiferromagnetic uranium phosphide and ferromagnetic uranium sulfide in the system $UP_{1-x}S_x$, where the occupancy of the conduction band increases with x. Mahendra Mathur and coworkers (Westinghouse) provide evidence, from specific-heat measurements, of ferromagnetic ordering between Mn^{2+} ions in $Sn_{0.97-x}Mn_xTe$, where x is less than 0.1.

Tunneling spectroscopy through ferromagnetic EuS:Eu on superconducting indium was discussed by William Thompson, Fred Holtzberg and Von Molnar.

Chalcogenide chromium spinels. In the chromium spinels $A^{2+}[Cr_2]X_4$, the chromium d orbitals of t_{2g} symmetry are localized and half filled, giving rise to a Cr^{3+} atomic moment of 3 Bohr magnetons μ_B and ferromagnetic 90-deg Cr^{3+}–X–Cr^{3+} interactions. When X is sulfur, selenium or tellurium, this ferromagnetic component dominates the antiferromagnetic Cr^{3+}–Cr^{3+} interactions, and the spinels $A[Cr_2]X_4$, where A is cadmium or mercury and X is sulfur or selenium, are ferromagnetic semiconductors. Although Walther Rehwald[4] has provided a qualitative band scheme for $CdIn_2S_4$, we can not calculate the energies of the d states relative to the s,p band edges in a similar way, but must obtain them from experiment.

After a review of his general theory of spin-disorder scattering of itinerant electrons by localized electrons, Cornelis Haas (University of Groningen) discussed the evidence for believing Cr^{2+} d bands to be below the bottom of the 4s conduction band. He showed that it was by no means convincing. In particular, he pointed out that the lower electron-versus-hole mobility can be expected from spin-disorder scattering, because the electrons occupy primarily cationic orbitals whereas the holes occupy primarily anionic orbitals. Bayram Vural (City College of the City University, New York) echoed this idea; he suggested that the magnetoresistance anomalies he observed in p-type $Cd_{1-x}Ag_x[Cr_2]Se_4$ could be due to interactions of the itinerant holes with magnetic-spin waves. So did D. Kuse (Brown Boveri Research Center), who could infer from the Faraday rotation in $Cd[Cr_2]Se_4$ near the optical absorption edge both above and below T_c, that exchange splitting of the conduction bands dominates any splitting of the valence bands that may occur.

Although an apparent "blue" optical absorption shift below T_c has been reported for $Cd[Cr_2]S_4$,[5] in contrast to the "red" shift found in $Cd[Cr_2]Se_4$ and the ferromagnetic EuX compounds, Stephen Wittekoek and Pietr Bongers (Philips) presented convincing magneto-optical evidence that this "blue" shift is due to the $^4T_{2g}$ absorption band of the Cr^{3+} ions; the conduction-band absorption actually shows a red shift in $Cd[Cr_2]S_4$, as in the other ferromagnetic compounds.

Stuart Berger presented evidence from the RCA Laboratories for the same conclusions. Finally, in the discussion Bongers presented chemical evidence that Cr^{2+} ions may not be stabilized in these spinels. The results are compatible with the existence of Cr^{2+} d bands above the bottom of the 4s conduction band.

Murray Robbins and his coworkers at Bell Telephone Laboratories reported magnetic and crystallographic measurements on the $Cu[Cr_{2-x}V_x]S_4$ metallic system. Their data indicate that, when x is less than 0.35, localized-electron spins at the vanadium ions (lattice parameter increases with x) couple parallel to localized Cr^{3+} ions, whereas if x is greater than 0.375 the vanadium d electrons are itinerant (lattice parameter decreases with x in spite of the larger size of a V^{3+} ion) and their spins are polarized antiparallel. Antiferromagnetic coupling of the itinerant-electron spins seems to argue against the existence of partially filled Cr^{3+} d bands at the top of the valence band, as proposed by F. K. Lotgering and by R. P. Van Stapele,[6] and in favor of partially filled Cu–S d–p bands.[7] However, the character of the states at the top of the valence band in $Cu[Cr_2]X_4$ spinels does not yet appear to be definitively established.

Lionel Friedmann and Avraham Amith (RCA) presented transport data for n-type $Cd[Cr_2]Se_4$ that they interpreted with an ad hoc energy-level scheme.

Localized versus itinerant electrons. At present there are two limiting descriptions of the outer electrons in solids: crystal-field theory and band theory. Crystal-field theory assumes that the outer electrons are localized to discrete atomic positions. Superexchange interactions between immobile localized electrons on neighboring atoms are treated in second- or third-order perturbation theory. Tight-binding band theory, on the other hand, uses first-order perturbation theory. Here the electrostatic energy U required to create polar states is either neglected or incorporated into a much smaller intra-atomic exchange energy.

Difficulty arises as the superexchange perturbation increases: Is there a gradual transition from localized cationic spins to a partially filled band without spontaneous spin polarization, or are there two thermodynamic states, corresponding to localized versus itinerant electrons, with a sharp change in U between them? Some years ago, Nevill Mott[8] argued for a sharp transition between a nonconducting and a conducting state for the case of half-filled bands. Transition-metal oxides and sulfides are particularly suited to an experimental study of this question.

Nickel disulfide has the pyrite structure, and here strong covalent bonding creates a half-filled band of e_g symmetry at Γ. Some samples appear to be metallic and to have no long-range order, whereas others are semiconducting and antiferromagnetic. The compound is interesting because it appears to have a bandwidth that is borderline for the presence of spontaneous magnetism. Julius Hastings and Lester Corliss (Brookhaven) found, unlike those who did a previous neutron-diffraction study, that their semiconducting sample of NiS_2 was antiferromagnetically ordered below 40 K with an atomic moment per nickel atom of $1.17\mu_B$. This value is considerably less that the $2\mu_B$ expected of a localized spin at a Ni^{2+} ion. The paramagnetic susceptibility, although obeying a Curie-Weiss law, has too large an effective moment and paramagnetic Curie temperature to be described by a localized-electron model. This compound provides a clearcut case of band antiferromagnetism, as distinguishable from localized-electron antiferromagnetism.

Above 150 K, V_2O_3 has the corundum structure and its axial ratio c/a exhibits anomalous variations with temperature. The metal–metal interactions are strong enough to form overlapping, itinerant-electron d bands whose relative stabilities are sensitive to the c/a ratio. This phase has been stabilized to lowest temperatures by hydrostatic pressures greater than 26 kilobars, and it is metallic without spontaneous magnetic ordering. Below 150 K and at atmospheric pressure, V_2O_3 is semiconducting and monoclinic.

Although an earlier neutron-diffraction study failed to identify any magnetic peaks in the monoclinic phase, Ralph Moon (Oak Ridge) has used spin flipping of a polarized neutron beam to demonstrate a peculiar antiferromagnetic ordering with a V^{3+}-ion moment of $1.2\mu_B$. Because the monoclinic unit cell contains two molecular units, as does the rhombohedral unit cell, Denis McWhan and T. Maurice Rice (Bell Labs) suspected that the transition in V_2O_3 is a Mott transition. Unpublished lattice-parameter measurements of the system $V_{2-x}Cr_xO_3$ from the MIT Insulation Laboratory show an anomalous variation that indicates localized d electrons may be present at V^{3+} ions in $V_{1.92}Cr_{0.08}O_3$. They therefore subjected a sample with this composition to hydrostatic pressure and found a semiconductor–metallic transition at 10 kbar at room temperature, as illustrated in the figure. The transition does not involve a change of symmetry but a pronounced change in c/a; the semiconducting phase has the smaller c/a.

These findings in $V_{1.92}Cr_{0.08}O_3$ are consistent with the existence of localized d electrons at atmospheric pressure and itinerant electrons in the high-pressure hexagonal phase; it is not, however, correct to conclude that the transition from localized to itinerant electrons is generally first order. The data on NiS_2 illustrate the possibility of a narrow transition range in which band antiferromagnetism may arise. The transitions in V_2O_3 and $V_{1.92}Cr_{0.08}O_3$ are first order only because overlapping d bands change their relative occupations as the c/a ratio changes, which means they do not represent pure Mott transitions.

Small polarons. The charge carriers in oxides may be either itinerant or small-polaron. Small polarons are mobile charge carriers localized to discrete atomic sites for a time long enough that local lattice distortions can occur. Small-polaron conduction is characterized by an activated mobility and a constant number of carriers. Jergen M. Honig (Purdue University) and Hans Frederikse (National Bureau of Standards) reviewed the relations among transport, magnetic and structural properties of a number of oxides. Honig illustrated small-polaron hopping by reviewing his earlier studies on $Pr_{1+x}O_2$. P. Niclau, Ion Bunget, Mihai Rosenberg and I. Belciu (Bucharest) demonstrated small-polaron hopping in $Fe^{3+}[Ni_{1-x}{}^{2+}Fe_x{}^{3+}]O_4$ by correlating transport properties with chemical analysis. They found that the measured Seebeck coefficients began to deviate from the small-polaron formula as x approaches 0.6.

In ferrospinels and ferrogarnets, octahedral sites are of four types, with trigonal fields directed respectively along the four (111) axes to conform with the overall cubic symmetry of the structures. Low concentrations

of Fe^{2+} ions are present as small polarons, and annealing in a magnetic field H_a below T_c can produce a preferential ordering of the Fe^{2+} ions. E. Michael Gyorgy, Joseph Dillon, Jr and Joseph Remeika (Bell Labs) reported experiments on the ferrogarnets $Y_3Fe_{5-\delta}Si_\delta O_{12}$ in which the distribution of Fe^{2+} ions was modulated by light, preferentially by polarized light. The magnetic anisotropy, strain, linear dichroism, coercive force and initial permeability can all be modified by infrared radiation, and with the simple model of Fe^{2+} ion distributions among the four types of octahedral sites, it is possible to account for the first three effects. For the last two, it appears necessary to distinguish between those Fe^{2+} sites very near a Si^{4+} ion and those that are more distant from these impurities.

Hall mobilities are difficult to measure in most transition-metal oxides, and an adequate theory for the small-polaron regime has not yet been established. Nevertheless, Frank Wang (State University of New York, Stony Brook) reported Hall-mobility measurements in single-crystal lithium ferrites, and Willem Siemons (E. I. DuPont de Nemours & Co.) presented Hall and Seebeck voltage data above and below the electron-ordering temperature $T_t = 119$ K for pure single crystals of Fe_3O_4. In Fe_3O_4 charge-carrier density is relatively insensitive to temperature for $T > T_t$ (characteristic of polaron conduction), but showed a discontinuous decrease at T_t. The sign of the Hall coefficient was opposite to that of the Seebeck coefficient, which is not uncommon in magnetic oxides. The Hall mobility is 0.1 cm^2/V-sec for $T > T_t$; this value is in the range where small-polaron hopping gives way to an inactivated tunneling, but is too small for a conventional band model.

If the jump frequency of the mobile electrons is fast relative to the lattice optical frequencies, electron–phonon interactions may be handled in the standard perturbation treatment of band theory. Frederikse chose $LaCoO_3$ to illustrate the complex relationships that can be found between transport and magnetic properties[9] and cited the pioneering work of his group at NBS as an illustration of itinerant-electron behavior in slightly reduced $SrTiO_3$. Honig referred to ReO_3, which is metallic and Pauli paramagnetic, for his illustration of itinerant d electrons that must be described by band theory.

Gen Matsumoto and Kuniro Tsushima (Tokyo) showed that, in the system $La_{1-x}Ca_xMnO_3$, when x is less than 0.1 the mobile holes, which introduce a ferromagnetic double-exchange coupling, are trapped at the eight manganese atoms neighboring a substitutional Ca^{2+} ion. This produces ferromagnetic clusters, but unless x is greater than 0.1 these clusters do not interact to form impurity bands and a long-range ferromagnetic component.

Raphael Tsu, Leo Esaki, and R. Ludeke (IBM) found a prominent peak in the infrared photoconductivity of NiO films at 0.23 eV, which they attributed to a coupling between mobile holes and localized spins.

David Adler (MIT) focused attention on NiO, an antiferromagnetic semiconductor. Considerable controversy has centered around the character of the mobile holes in nonstoichiometric $Ni_{1-\delta}O$. Adler constucted an energy-level scheme from very simple physical arguments. He selected a U of about 13 eV for the energy separation of localized $3d^8$ and $3d^9$ manifolds; in a recent band calculation[10] this energy is incorporated in a much smaller intra-atomic exchange splitting. No resolution of this discrepancy was achieved by the participants. To obtain a convincing number for U remains a central challenge to solid-state theory.

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Phillip Seiden and Siegfried Methfessel of IBM organized the conference.

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