

SESSION VII—SUMMARY AND REVIEW OF THE CONFERENCE

Summary and Review

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I have been asked to summarize this conference. I shall do this by classifying the various contributions and by picking out points that especially interested me.

I want to make a classification very much cruder and coarser than the one used previously.¹ The transitions discussed here fall into three cases: (1) the narrow-band case, (2) the wide-band case, and (3) those substances containing transition metals where the categorization of the metal–nonmetal (M–NM) transition must be done almost on a compound-by-compound basis.

What does one mean by wide- and narrow-band cases? As far as metals are concerned, it really doesn't make any difference. Metals are metals. We can agree when something is metallic in character simply by looking at the transport properties, the optical properties, or a variety of other indicators. The narrow-band case gets distinguished from the wide-band case when one begins to look at the insulating state, or the nonconducting side of the transition. There we think we understand very well what wide-band insulators are, such as, say, the covalently bonded semiconductors. We also have a pretty good idea of what the narrow-band insulators are, although generally those are the materials about which we say that band theory breaks down. It does not seem entirely satisfactory to use a band-theory classification when the band theory is supposed to break down.

Let me start with the narrow-band case by recalling the talks that started the conference. Professor Mott's talk was largely concerned with the narrow-band case. Dr. Kasuya made an extremely interesting discussion of europium chalcogenide-based alloys, in which, instead of having impurity states of the ordinary type that we have in semiconductors, we have magnetic impurity states. The fact that these impurity states have a magnetic moment is of profound importance for discussing the over-all properties. There, in contrast to many other cases, the band narrows as the temperature rises because the spin disorder, in effect, reduces the number of neighbors to which a given electron associated with a magnetic impurity state can couple. Dr. Methfessel commented in the discussion that

magnetic polarons could give a good account of the temperature dependence of the conductivity for the more concentrated alloys. These substances present a marvelously interesting system for further investigation. Franck's paper on transitions in liquid mercury belongs in this category of narrow bands. Thompson's and Mahaffey's discussions of metal–ammonia solutions, the papers on theory, for the most part concerned with the Hubbard model, by Kemeny, Lange, Pratt and Caron, Horwitz, and Edwards, and then the papers on the doped semiconductors by March, Holcomb, Mikoshiba, and Jérôme, all focused in considerable measure on the narrow-band aspect.

The broad-band case was represented by the review of the excitonic insulator given by Halperin, the singular case of grey tin discussed by Sherrington, the bismuth–antimony alloys discussed by Lerner, the band structure calculation on the pressure dependence of the energy bands of the alkaline-earth metals by Vasvari, and the interesting alloys cesium–gold and lithium–silver by Amar. Then the mixed case of the transition-metal oxides, sulfides, etc., was reviewed in detail by Adler and specific substances were discussed by Barker, Powell, Hyland, Hanamura, and Sparks. The papers of Professor Mott, of Dr. Halperin, and of Dr. Adler by and large make a systematic review of those same areas unnecessary, and to some extent justify my picking out only particular points.

In the narrow-band case, we are used to thinking of a metal–nonmetal transition occurring as we vary some parameter; in particular, the variation of separation of impurities in semiconductors has been most frequently discussed. Professor Mott emphasized that we could in fact keep the impurity separation fixed and vary the degree of randomness of the potential fluctuations that are seen by individual electrons. Professor Mott showed a slide² in which the activation energy was plotted as a function of the impurity separation. There were a whole series of traces taken from the experimental data in which the parameterization of each trace was given by the compensation. As the compensation systematically increased there must have been a transition at some as yet undetermined compensation below the 0.8 value at which (in the

¹ M. H. Cohen, *Bull. Am. Phys. Soc.* **12**, 187 (1967).

² N. F. Mott, *Rev. Mod. Phys.* **40**, 677 (1968), Fig. 6.

region that would have been metallic before) we found a definite activation energy. This suggests a transition of the Anderson sort. In other words, the band is simply torn up into localized states by the randomness of the potential. This is an extremely interesting thing and one that should be borne in mind whenever one tries to carry over arguments that relate to essentially periodic structures to a discussion of materials where the arrangement of impurities is random. There are many such substances where we see metal-nonmetal transitions, e.g., the sodium tungstate bronzes. From the recent work on rhenium trioxide by Feinleib *et al.*,³ one can easily imagine transition metal alloys based on tungsten trioxide where one would see a similar transition and where the randomness may play an essential role.

Another system in which this kind of randomness occurs is in the metal-ammonia solutions, where one sees a well-defined metal-nonmetal transition as discussed by Thompson. But here the structure is not tied down. The structure can readjust itself so as to minimize its free energy as the concentration and temperature vary. One does not have anything like the rigid framework that exists for the impure semiconductors. As a consequence one finds somewhat the reverse occurring. That is, the phase diagram in the temperature-concentration plane shows a phase separation curve and, insofar as we can determine, the locus of the metal-nonmetal transition appears to go rather near the consolute point of this phase separation curve. But it turns out, as emphasized by Thompson, that the concentrations at which the metal-nonmetal transitions occur are somewhat lower at higher temperatures. Since an increase in temperature increases the randomness, this is a case where the effect of randomness apparently is somewhat different than in the semiconductors. This may have to do with the fact that the overlap integral tends to get rather large as individual cavities approach one another, so possibly this is simply a consequence of an increased average overlap with increasing temperature.

The beautiful results in the paper by Franck and Hensel on the pressure dependence of the resistivity in liquid mercury and in cesium-doped mercury raise another chicken and egg question. As mentioned before, the locus of the metal-nonmetal transition in metal-ammonia solutions appears to go rather near the consolute point. Professor Mott⁴ and Professor Krumhansl⁵ pointed out quite a bit earlier that there may be a significant correlation between the metal-nonmetal transition and the phase separation. That is, the anomalous part of the free energy which is responsible for the phase separation may well come from the metal-

nonmetal transition or alternatively the phase separation simply disrupts the structures in such a way that one gets a metal-nonmetal transition. The data of Franck and Hensel show a very similar correlation. The temperature range was fairly limited, but a locus of metal-nonmetal transitions in the vapor phase would surely come rather close to the critical point. There seems to be a good correlation between the phase separation which we call condensation and the metal-nonmetal transition. So one raises the question, with Krumhansl particularly, as to whether a part of the driving free energy for the condensation does not come from the metal-nonmetal transition. This question was raised again in discussion by Cutler, who called attention to a similar correlation between a phase separation in liquid semiconductors (in the tellurium-thallium system) and the metal-nonmetal transition. This is a point towards which more experimental work could be directed.

The metal-ammonia solutions form a very old and very rich field. It is perhaps the oldest field discussed at this conference. The quantitative data go back perhaps 100 years in this area. Professor Onsager suggested the possibility that the dielectron, that is, a cavity containing two electrons, may be responsible for a number of the anomalous properties of the solutions in the low concentration region and may also play an interesting role in the metal-nonmetal transition. This may be. It depends on the way one reads the experimental data and, without attempting to contradict Professor Onsager, let me say that I read the experimental data somewhat differently. Emphasizing the optical absorption, I note that in the region in which diamagnetic species appear to be forming very rapidly (the susceptibility is rapidly reduced) one notices that the optical absorption changes neither in frequency nor in oscillator strength to any appreciable degree. The detailed calculations of Land and O'Reilly⁶ give a 1-eV instability of the dielectron cavity relative to two separate, one-electron cavities, primarily because of the electron-electron repulsion. So I prefer to discuss the metal-ammonia solutions within the framework of a model in which the one-electron cavities, although they rearrange themselves and associate and form complex structures, at least preserve their integrity past the metal-nonmetal transition. Professor Thompson mentioned that in a more concentrated range the transport properties could be explained to some extent by supposing that the electrons had become very nearly free, giving quantitative agreement in a simple calculation. This is a little puzzling to me. The remark may well be completely correct, but at least in the lower concentration region or in the concentration region around 8 MPM, there is essentially no apparent loss of the excess volume associated with the cavity, so the cavity structure appears still to be there. Another

³J. Feinleib, W. J. Scouler, and A. Ferretti, *Phys. Rev.* **165**, 765 (1968).

⁴N. F. Mott, *Phil. Mag.* **6**, 287 (1961).

⁵J. A. Krumhansl, in *Physics of Solids at High Pressures*, C. T. Tomizuka and R. M. Emrick, Eds. (Academic Press Inc., New York, 1965), p. 425.

⁶R. H. Land and D. E. O'Reilly, *J. Chem. Phys.* **46**, 4496 (1967).

possibility as to the origin of the nearly free-electron behavior can be raised. It is simply that the band which we think of as a tight-binding band has already overlapped with the band which comes from the excited state of the electron in the ammonia cavity that is responsible for the optical absorption, and that this band in turn overlaps with the continuum. We would then have a normal simple metallic-band structure without loss of the cavity, and without loss of the excess volume. This would explain why the peak in the optical absorption appears to be gone at that concentration. This does not preclude the disappearance of the cavities at still higher concentrations.

Regarding the theoretical papers, it was encouraging that Dr. Arai attempted to go beyond the Hubbard model by taking much more explicit account of the actual interactions that occur in these materials. That is, we did see matrix elements of e^2/r_{12} written down. Nevertheless, as pointed out by Lange, it is really important to find the physical content of the Hubbard model in a quantitative sense. This is distinct from spurious effects introduced by faulty analysis of the model itself. Edwards' paper illustrated this point very well by demonstrating that one of the things we thought we understood, namely the metallic state, was not properly described within the framework of the Hubbard model if one uses the decoupling scheme that Hubbard used. Lange, of course, took the very solid point of view that one simply goes ahead and does a proper perturbation analysis to first and possibly to second order in the coupling constant (that is, in the hopping integral). I hope he will not stop with first order and we will at least see whether we can get some of the superexchange interactions, some of the magnetic effects, taken into account within this same framework. Edwards and Horwitz applied somewhat more conventional and less special many-body techniques to the Hubbard model than did Hubbard himself. They arrived at what I regard as interesting and sensible results relevant to the problem of the metal–nonmetal transition. This suggests that the conventional wisdom within the framework of many-body theory is by no means exhausted as far as its applicability to the Hubbard model is concerned. I do not think we have to become more sophisticated than we are, as far as handling the many-body problem is concerned, to resolve a number of the difficulties that now exist. As Kemeny has emphasized, the electron–hole short-range correlation is really very important, and there are very powerful ways of taking this into account.

What I have in mind has been discovered independently by Garland, Rajagopal, and myself, and essentially represents a very simple self-consistent-field generalization of the ladder-bubble approximation. If one makes the transformation that Kemeny used, where one talks about up-spins as electrons and down-spins as holes, then the remarks that I am going to make are quite pertinent to nearly half-filled bands. If

one writes down just symbolically an expression for the self energy Σ , or the mass operator as it was called, $\Sigma = V_H + vG\Gamma$, there will be a Hartree term V_H (omitting all integrals, and i 's and h 's and things like that) and something like a Hartree–Fock exchange, $vG\Gamma$, where v is the bare Coulomb interaction and G replaces the occupation number for many-body problems. It would be just the Hartree–Fock exchange were it not for the vertex correction Γ which hides all the many-body effects. Now one can write down an equation for the vertex function $\Gamma = \epsilon^{-1} + vG\Gamma G\Gamma + O(d\Gamma/dV_{\text{ext}})$ in which the leading term involves the microscopic dielectric function ϵ . If we only kept that term, we would simply have dynamically screened exchange in Σ . However, the term $vG\Gamma G\Gamma$ is essential in the present context. The remaining term in Γ involves a second-order vertex function (a functional derivative of the vertex function with respect to an external field). If one neglects that term, one has still taken into account self-consistently and completely all electron–hole pair-correlation effects, including the type of long-range pair-correlation effects that give rise to screening in metals and the type of short-range electron–hole interactions that give rise to excitons, spin waves, magnetic transitions, and other things of that sort. The equation for Γ can now be solved formally giving $R^{-1}\epsilon^{-1}$, where $R = 1 + vG \times G\Gamma$. The details are not important; it is just that ϵ^{-1} takes care of screening and R^{-1} takes care of short-range correlations such as arise from repeated scattering of a given electron by a given hole. Rajgopal and others have developed double dispersion relations for the description of vertex functions as well as sum rules on the spectral density functions entering them so that it is possible to make some fairly consistent and not too complicated arguments about R itself. Somebody should look at these more complex vertex corrections with an eye toward extracting some information about the metal–nonmetal transition. The work of Dr. Horwitz was an analysis of terms in R^{-1} ; the pole that he talked about corresponds to poles in R^{-1} , and there are systematic techniques for analyzing it self-consistently. The self-consistency is extremely important, as in connection with Dr. Horwitz's paper, in relation to the strength of the poles themselves.

It has been stressed repeatedly that the ground state can not be described within the band model in the low-density limit, and this is probably right because of degeneracy. But that does not mean that one has to eschew, for simple-minded arguments, all aspects of the band picture. It is possible to make a simple quasi-particle band model as discussed by several authors, which will help one to see what is going on. This was implicit in Dr. Kemeny's talk, and I want to make it more explicit.

Suppose we start with a band as in Fig. 1(a); we can even think in one dimension, but I do not intend this to be a discussion in one dimension. Now we increase the separation between the atoms, the band

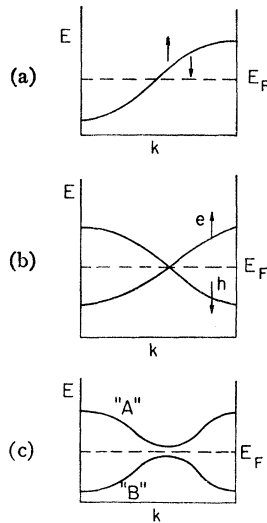


FIG. 1. Quasiparticle band scheme valid for the metallic and the nonmetallic states. (a) Energy E vs wave number k schematically for a nonmagnetic metal. The spin-up (\uparrow) and spin-down (\downarrow) bands are degenerate. E_F is the Fermi energy appropriate to a half-filled band. (b) The same with the spin-down band replotted as a hole (h) band and the spin-up band left as an electron (e) band. (c) Quasiparticle bands after electron-hole pairs condense, lifting degeneracy at the Fermi energy to give a nonmetallic state. The designations A and B are discussed in the text.

flattens and something is going to happen. Figure 1(a) shows both up-spin and down-spin bands, assuming a nonmagnetic state so that they are degenerate. If we follow Kemeny it is easier to describe what is going to happen by replotting the bands [Fig. 1(b)] as an electron band for up-spin and a hole band, in which I reflect the energy about the Fermi energy (assumed at the midpoint), for the down-spin band. With Herring,⁷ I suppose that the system can be at a temperature T which is smaller than the metal-nonmetal transition temperature but greater than any magnetic-ordering temperature. I suppose, for the sake of argument and not because I really believe it, that this is the case so that I do not have to worry about the spins. The type of bound state that Dr. Kemeny was talking about involves, basically, a mixing between the electrons and the holes. That is, we find an electron of up-spin and a hole of down-spin on the same site. With a weak interaction this mixing lifts the degeneracy in the neighborhood of the crossover, and we get a splitting in the band structure, Fig. 1(c). Thus, one can continue with the band scheme as long as one reinterprets the band picture properly on both sides of the transition. "A" marks the band for propagation of a hole at low k and an electron at high k ; "B" marks the band for propagation of an electron at low k and a hole at high k , and at the Fermi surface we have a gap and a gradual transition from electron to hole character.

⁷ C. Herring, in *Magnetism*, G. T. Rado and H. Suhl, Eds. (Academic Press Inc., New York, 1966), Vol. IV.

This is essentially identical to the picture of the excitonic insulator that was discussed, and is very similar to what occurs in superconductivity. The essential point in both cases is that one can use a simple band model as far as the one-electron excitations are concerned. Although straight-forwardly applied band theory gives the wrong answer as to whether a metal is an insulator or a conductor, a small twist following the suggestions of Kemeny can describe the whole thing within a somewhat generalized band picture. What would spoil this picture, of course, would be any kind of polaron effect (which we would expect to be very strong when we get to the narrow band limit). There, bringing in additional coordinates requires that the phonons be included from the beginning.

The wide-band case involves the relationship between phonon instabilities and the metal-nonmetal transition. Proffessor Mott discussed the order of the transition, revised his first arguments, and came out in favor of a higher-order transition on the argument that in the excitonic binding energy, schematically $e^2/\epsilon r$, ϵ tends to infinity on approaching the transition, giving essentially a zero binding energy. Although the remark was not made explicitly, let me do so since I will come back to this several times: *When the frequency of an exciton tends to zero, then indeed the static dielectric constant must tend to infinity.* This is completely equivalent to the polarization catastrophe that was much discussed during the early days when ferroelectricity was an exciting and novel subject. This leads to a point stressed by Halperin, by Sherrington and Kohn, and most explicitly and beautifully by Hanamura: that is, that phonons must be considered at the beginning. Excitons are, in fact, simply charge density waves; a wave-like disturbance in which an electron and a hole are coupled. That means taking charge from one region and replacing it in another. The charge density wave produces an electrostatic potential with which the ion cores can interact, giving a strong exciton-phonon coupling. This can be discussed from a slightly different point of view⁸ which makes explicit the relationship between phonon instabilities, exciton instabilities, and the infinities in the dielectric constant. An exact form for the analog of the Born-Mayer constants can be written down, even in a situation in which the Born-Oppenheimer approximation breaks down. One has the possibility that the C_{ij} are complex in that case. C_{ij} is given by

$$C_{ij} = (\partial^2/\partial R_i \partial R_j) V_i v^{-1} \epsilon^{-1} V_j,$$

where R_i and R_j give the positions of the i th and j th atoms, respectively, and V_i is the exact electron-bare nucleon potential. The operator v^{-1} is the inverse of $|r-r'|^{-1}$, $(4\pi)^{-1}\nabla^2$, and ϵ^{-1} is the inverse of the microscopic dielectric function ϵ of the electrons. Integration

⁸ M. H. Cohen, R. M. Martin, and R. Pick (to be published).

over the electronic coordinates is implied. One can go ahead by means of less secure arguments close to those used for doing the pseudopotential theory of the lattice-vibration spectrum of simple metals in recent years. One can replace V_i by a bare ion pseudopotential and similarly V_j . Whereas ϵ was the entire dielectric function of all the electrons including the core electrons, one now uses just the dielectric function of the valence electrons. This approximation would work rather well in materials of high valence where the cores are very tightly bound and rather small in extent. Now ϵ has two parts, $\epsilon = \epsilon_d + \epsilon_{od}$. ϵ_d is the part given by a random phase approximation, in other words, by neglecting Umklapp terms and local field corrections; ϵ_d is diagonal in the wave number. The other terms ϵ_{od} are off-diagonal in the wave number. These take into account Umklapp processes in the motion of the electrons and so on. The processes that give rise to this are responsible for building up the covalent bond, as Phillips⁹ has emphasized in his recent discussion of covalent bonds. One can essentially make a kind of justification of Phillips' recent arguments by a sum rule (indicated schematically)

$$\lim_{q \rightarrow 0} [A\epsilon_d^{-1} + \Sigma B\epsilon_{od}^{-1}] = 0.$$

This is not to be confused with the translational invariance requirement which is already satisfied precisely at $q=0$. This is separate and distinct, and refers to the requirement that the limiting value of the frequency as q tends to zero must be zero for the acoustic modes. One can then make an argument that Phillips' bond charges are related to terms in ϵ_{od}^{-1} so that one can construct a lattice-vibration theory in which one simply takes the usual diagonal part of ϵ^{-1} to screen the pseudopotentials, and adds to that bond charges of appropriate magnitude at points halfway between the atoms. The size of the bond charge is obtained from the dielectric function according to Phillips' prescription. Richard Martin¹⁰ has developed a theory of lattice vibrations along these lines and has been able to fit the lattice-vibration spectrum for silicon quantitatively in all directions for which the measurements have been made.

Grey tin is extremely interesting from this point of view. As Liu and Brust¹¹ have shown, $\epsilon = \text{constant} + O(q^{-1})$ for small q . The constant term would give the bond charge in Phillips' theory, but the whole picture becomes uncertain because of the q^{-1} term arising from the contact between valence and conduction bands. The infinity in the dielectric function for zero frequency and wave number does suggest $q=0$ exciton condensation, as already discussed in the Conference, but one has to worry just as seriously about the elastic constants and the velocity of sound. One must get phonon

instabilities simultaneously. That can be made explicit for grey tin and the other cases, the excitonic insulators. When one has excitons, one has an infinite dielectric function. When one has an infinite dielectric function, one has a set of vanishing force constants (zero frequencies for some phonon or phonons) and therefore phonon instabilities. In the present point of view, it is necessary to do completely self-consistent calculations which include both the influence of the excitonic instability on the phonon frequencies and the influence of the phonon frequencies on the excitonic instability.

The grey tin problem is particularly interesting because of the way its anomalous band structure forces a singularity in the dielectric function. Possibly a lattice distortion accompanies the excitonic-insulator transition. Perhaps there will not be for the following reason. Displacive transitions arising from phonon instabilities have been likened to Jahn-Teller transitions. Suppose one has a displacive transition which carries one from a metallic to a nonmetallic state. Whereas before the transition the electron states just below the Fermi energy are degenerate with the hole states just above, that degeneracy is lifted completely by the distortion, just as in the atomic or molecular Jahn-Teller effect. In the case of grey tin, the degeneracy is forced by symmetry considerations that involve the spin-orbit coupling in an essential way. In the corresponding case of an atom or ion having a ground state of the same symmetry as the Γ_8 state responsible for contact of valence and conduction bands in grey tin, no static distortion occurs. Instead, a large spin-orbit coupling leads to the dynamic Jahn-Teller effect in which the axis of distortion of the crystal rotates. In grey tin, we therefore expect no static distortion, but a modification of the acoustic modes instead. Clearly, no theory of an excitonic-insulator phase of grey tin can be constructed without including electron-phonon coupling from the start.

Adler gave an excellent summary and analysis of the present situation of the transition metal oxides. There are two obvious points on which further work is necessary. First, it was shown repeatedly by the experimental talks that there must be more work on specimen preparation. The tests for metallic or nonmetallic concentration, whether we have polarons present or not, depend in an essential way on the quality of the specimen. A clarification of the experimental situation often requires improvement of the quality of the specimens. So, for the lowly art of specimen preparation, I hold out the highest of praise. As far as characterization of the state is concerned, it is easy to do this on the metallic side. One measures the transport properties, and most of us can agree on what is metallic and what is nonmetallic behavior of a transport property. Magnetic structure, etc., is very important. It is essential to have all measurements made on the same or as nearly similar as possible specimens. In other

⁹ J. C. Phillips, *Phys. Rev. Letters* **19**, 415 (1967); *Phys. Rev.* **166**, 832 (1968).

¹⁰ R. M. Martin (to be published).

¹¹ L. Liu and D. Brust, *Phys. Rev. Letters* **20**, 651 (1968).

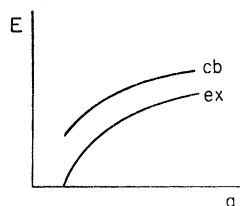


FIG. 2. The energy E of the bottoms of the conduction band (cb) and the Frenkel exciton band (ex) as functions of lattice constant a for the tight-binding case.

words, for one investigator to focus experimentally on one type of measurement is unfortunate in this particular subject. A concerted broad-range attack is needed until one can prepare or buy specimens in a routine fashion that one knows are largely identical in character. The progress made on conventional semiconductors counterpoints these remarks dramatically.

I was pleased to see at least one band structure calculation shown in detail at this conference, the band structures of the alkaline-earth metals presented by Dr. Vasvari. We need a great many more band structures, and we need more than one individual or more than one group making the band structure calculations. Often progress on band structure calculations in complicated substances has been made only after disputes between different groups have been resolved. The techniques for calculating band structures have now proceeded to the point where one can tackle quite complex structures and quite complex materials. The degree of precision that has been achieved is, in fact, scarcely necessary for the problems that we have here. Indeed, the power of the band structure calculations has developed far beyond our understanding of the crystal potential that enters them. To do band structure calculations alone for that reason is not terribly fruitful particularly in these transition metal oxides where we do not know the degree of ionicity and there are serious problems of self-consistency. They have to go hand-in-hand with the kind of systematic and careful experimental analysis of the optical constants that we have seen develop in the group IV semiconductors and spread throughout the nearby portion of the inorganic compendium. Here we can also carry out Fermi surface studies on those metallic compounds for which crystals of suitable quality can be prepared.

As to general comments, first, regarding the question of the relation of the dielectric constant to the metal-nonmetal transition, there is a paper by Herzfeld¹² in 1927 in which he says (he talks about the refractive index instead of dielectric constant) that when the dielectric constant goes to infinity perhaps the bound electron becomes free and we get a metal-nonmetal transition. In addition, he commented in the same paper on the metal-ammonia solutions. The degree of

sophistication then extant was such that these remarks were not picked up at the time, and they have become lost. I found out about it because Professor Herzfeld wrote me a charming letter when he discovered that I was going to give a review talk on metal-nonmetal transitions at an American Physical Society meeting last year.¹ I am grateful to him.

Dr. Hyland mentioned that Professor Fröhlich had emphasized that a ferroelectric phase may, in fact, precede the metallic phase as one passes from the insulating to the metallic phase in a metal-to-nonmetal transition. This notion is really identical with that of the excitonic insulator. Suppose, for example, one takes a narrow-band case where one has a Frenkel exciton as in Fig. 2. Let us suppose the frequency of the Frenkel exciton goes to zero as the lattice constant a decreases. This would correspond precisely to the Lorentz or ferroelectric catastrophe in the dielectric function in the tight-binding approximation. Suppose one has several species of atoms or ions of density N_i , polarizability α_i , the dielectric function ϵ is

$$\epsilon = [1 + \frac{8}{3}\pi \sum_i N_i \alpha_i] / [1 - \frac{4}{3}\pi \sum_i N_i \alpha_i].$$

ϵ goes to infinity just at the point that the frequency of the Frenkel exciton goes to zero. As mentioned before, at that point one must also have a phonon instability. In this case, there would be an instability in the transverse optical mode. One gets a conventional ferroelectric with a displacive transition plus an electronic polarization out of the excitonic instability. If it is a finite q exciton whose frequency goes to zero, one gets the antiferroelectric phase that was discussed, using the very word *antiferroelectric*, by Dr. Halperin. The development of the notion of the excitonic insulator fits in very well with a fairly coherent and consistent series of developments in the recent history of physics; it ties a lot of these together and makes the proper connection to the metal-nonmetal transition.

As to impure semiconductors, we have just heard about them and the subject is fresh in our minds. The model Dr. Mikoshiba introduced, as well as a related one talked about by Dr. Holcomb, in fact, is quite close to the models that Professor Thompson and myself have been studying for the metal-ammonia solutions. In both groups of substances in the transition region between what is clearly nonmetallic and what is clearly metallic the randomness in the structure plays an essential role.

I am grateful to the National Aeronautics and Space Administration for support of my work on the metal-nonmetal transition and to the Advanced Research Projects Agency for general support of materials research at the University of Chicago.

¹² K. F. Herzfeld, Phys. Rev. **29**, 701 (1927).