

FIG. 2. Superconducting and ferromagnetic transition temperatures of $(\text{Ce, Gd})\text{Ru}_2$ solid solutions. (a) 0 to 10% GdRu_2 . (b) Ferromagnetic Curie point from 5% to 32% GdRu_2 .

easier one in which to show the occurrence of both. By lowering the temperature of a sample with 8% gadolinium, first the onset of ferromagnetism at the Cpt is observed and then at lower temperatures yet the crystal becomes superconducting. However, at these low temperatures the spontaneous ferromagnetic polarization is more than an order of magnitude larger than any frozen-in flux would be for a typical nonmagnetic superconductor.

The fact that so much flux escapes the sample even though it is superconducting would suggest that the sample never leaves the intermediate state. If, as seems likely, a typical conduction electron in the sample is acted on by the total flux, the London equation $\text{curl } \vec{j} = (1/\lambda c) \vec{B}$ and Maxwell's equations demand that $B \rightarrow 0$ in the

interior of a massive specimen, and only the flux in a shell of order of the penetration depth can escape, giving a negligible total moment. This is, of course, not the case if there is a pattern of superconducting domains whose sizes adjust themselves to yield the observed flux.

We want to thank Dr. A. M. Clogston for many stimulating discussions, and Mrs. V. B. Compton for all the structural work.

¹Matthias, Suhl, and Corenzwit, Phys. Rev. Lett. 1, 92 (1958).

MOBILE AND IMMOBILE EFFECTIVE-MASS-PARTICLE COMPLEXES IN NONMETALLIC SOLIDS

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Quite recently the study of excitons has taken a front-rank position among the techniques for the study of nonmetallic solids.¹ It is the purpose of this note to outline a natural extension of the concept of the exciton, namely to consider bound aggregates of two or more charged particles in a nonmetallic solid, at least two of which are effective-mass particles, i.e., electrons in a conduction band or holes in a valence band. We refer to such aggregates as "effective-mass-particle complexes."² The exciton itself is, of course, the simplest such complex. The choice of nomenclature reflects the restriction of our discussion to those weakly bound complexes for which the well-known effective-mass approximation gives a good description of the "envelope" motion of the electrons and holes. Therefore our conclusions are particularly relevant to those solids (e.g., Ge, GaAs, CdS) for which the only possible excitons are shallow ones. A complex which has as a constituent member an ion fixed in the lattice is localized about the ion and hence is called an immobile complex. On the other hand, a complex consisting entirely of effective-mass particles is obviously a mobile complex.³

We have listed some five types of complexes in Table I, which also contains explanations of the notation. For the sake of simplicity we assume spherical constant-energy surfaces for electrons and holes. In enumerating complexes

in Table I we have omitted those complexes obtained by reversing the sign of all members of a complex, since for simple band models nothing essentially new is obtained by this operation. However, note that for solids with complicated band structures, such as Ge and Si, sign reversal can indeed produce a "new" complex, i.e., one with different energy-level structure.

We are able to describe, without further ado, the electronic structure of the complexes A-E in Table I for limiting values of the ratio of hole to electron effective masses, namely for $m_h/m_e \gg 1$, $=1$, and $\ll 1$. For, in these limits, each complex is analogous, as listed, to either a molecular or polyelectron structure which has already been investigated, at least theoretically, if not experimentally. (An exception is the Type A complex with $m_h/m_e = 1$ for which the author did not find a suitable reference.) The energy level structure of any complex listed in Table I is basically that of its analog. Thus, for those structures analogous to H_2^+ , the gross energy

level scheme is the electronic level scheme of H_2^+ . Each electronic level has a fine structure similar to the vibration-rotation level scheme of H_2^+ . A similar description holds for those complexes analogous to H_2 . Those complexes analogous to H^- have only a single bound state.⁴ The existence or nonexistence of bound, excited states of the polyelectrons which are listed appears not to have been established to date. It is not known whether the complex $\oplus+-$, for $m_h/m_e \ll 1$, is stable. The hole moves in the electrostatic field of a "fixed" dipole determined by \oplus and the instantaneous position of $-$. If the hole is bound,⁵ its orbit moves adiabatically with the electron around the ion. The complex $\oplus+--$, for $m_h/m_e \ll 1$, consists of a hole bound to a Coulomb attractive "center," namely the H^- -like complex $\oplus--$. The corresponding hole levels are the hydrogenic levels modified by the spatial extent of the "center."

The discussion in this note should be applicable quantitatively to the semiconductors GaAs, InAs,

Table I. Some complexes and their properties. Notation: \oplus denotes a positive ion^a fixed in the lattice, $+$ a hole in the valence band, and $-$ and electron in the conduction band. $\oplus+--$ denotes a complex consisting of two electrons and one hole bound to a positive ion, and similarly for other complexes. Units: length, $a_S = \epsilon m a_0/m_e$; energy, $E_S = m_e E_0/m\epsilon^2$. ϵ is the static dielectric constant of the host lattice; m is the mass of the electron in vacuum; m_e is the effective mass of an electron near the minimum of the conduction band; m_h is the effective mass of a hole near the maximum of the valence band; a_0 is the Bohr radius in vacuum, $a_0 = \hbar^2/m_e^2 \approx 0.53 \text{ \AA}$; $E_0 = e^2/2a_0 \approx 13.6 \text{ eV}$; D_0 is the dissociation energy of the complex; $r_{\oplus+}$ is the average separation of \oplus and $+$ in the complex, and similarly for analogous symbols; e^+ is a positron, e^- an electron. $e^+e^+e^-$ and $e^+e^+e^-e^-$ are polyelectrons.^b

Complex	m_h/m_e	Analog	D_0	Average separations
A: $\oplus+-$	$\gg 1$	H_2^+	0.21	$r_{\oplus+} \approx 2$
	$\ll 1$	See text		
B: $\oplus--$		H^-	0.055	
C: $++-$	$\gg 1$	H_2^+	0.21	$r_{\oplus+} \approx 2$
	1	$e^+e^+e^-$	0.0015 ^c	
	$\ll 1$	H^-	$0.055m_h/m_e$	
D: $++--$	$\gg 1$	H_2	0.35	$r_{++} \approx 1.4$
	1	$e^+e^+e^-e^-$	0.010 ^d	$r_{++} = r_{--} \approx 8.5$ ^d
	$\ll 1$	H_2	$0.35m_h/m_e$	$r_{+-} \approx 5.7$
E: $\oplus+--$	$\gg 1$	H_2	0.35	$r_{--} \approx 1.4m_e/m_h$
	1	H^-e^+	0.0050 ^e	$r_{\oplus+} \approx 1.4$
	$\ll 1$	See text		

^aTo avoid complications we assume that the positive ion is such that the lowest state of the \oplus -atom is a shallow, hydrogen-like state. Thus, in Ge \oplus might be a Group V substitutional donor ion.

^bSee reference 3.

^cE. A. Hylleraas, Phys. Rev. **71**, 491 (1947).

^dA. Ore, Phys. Rev. **71**, 914 (1947).

^eA. Ore, Phys. Rev. **83**, 665 (1951).

InP, InSb, and GaSb. In these materials the electron effective mass is isotropic and about an order of magnitude, at least, smaller than the average hole mass. Thus we do not expect the complications in the structure of the valence band to alter drastically the estimated dissociation energies of the various complexes, as given for the limiting case $m_h/m_e \gg 1$, although the detailed structure of the envelope wave functions may be complicated. It may be of practical significance that for these materials the dissociation energies of the "excitonic ion" ++- and the "excitonic molecule" ++- are an appreciable fraction of the binding energy of the exciton itself. The situation in Ge and Si calls for a more refined analysis. Although the "average" electron and hole effective masses are approximately equal, the complications both in conduction and valence band structure are such that the polyelectron model for the complexes is probably too simplified to apply in these materials. In any case, the effective-mass formalism for the study of the complexes is a straightforward extension of Dresselhaus' formalism for the description of the exciton.⁶

Observable effects due to the complexes must be sought in the 1-4°K temperature range where at least some of the complexes will have a dissociation energy many times kT . An experiment of particular interest might be the cyclotron resonance of the excitonic ions ++- or --+ which are both charged and mobile. Probably the most efficient means of generating the complexes are through the excitation of free electron-hole pairs, say by light, and subsequent reactions (exciton formation and interaction of excitons among themselves and with free carriers and with ions). The steady-state density of excitons n_x in equilibrium with electrons and holes of densities n and p , respectively, produced by excitation, is given by $n_x = np\bar{v}\sigma_x\tau_x$, where \bar{v} is the rms relative velocity of electrons and holes, σ_x their cross section for exciton formation, and τ_x the exciton life-time. At helium temperatures, taking $\bar{v} \approx 10^6$ cm/sec and $\sigma_x \approx 10^{-12}$ cm² then $n_x \approx 10^{-8} np\tau_x$. Producing $np \geq 10^{24}$ by light, and assuming⁷ $\tau_x \geq 10^{-8}$ sec, $n_x \geq 10^{10}$ cm⁻³ appears readily obtainable.

In similar fashion, rough estimates can be made for attainable densities of the various complexes listed in Table I.

It has been the purpose of this letter to bring to the attention of solid-state physicists a hitherto unexplored area. Work is continuing on more

accurate, variational calculations of the dissociation energy of some of the complexes.

The author would like to express his indebtedness to Dr. D. O. North, Dr. F. Herman, and Dr. R. H. Parmenter, and to his other colleagues at the RCA Laboratories who have made incisive suggestions both as to technical content and style.

¹See the review article by H. Haken in Halbleiterprobleme, edited by W. Schottky (F. Vieweg und Sohn, Braunschweig, 1958), Vol. 4, for a survey of the exciton problem and a bibliography. For the most recent developments also see the Proceedings of the International Conference on Semiconductors, Rochester, 1958, J. Phys. Chem. Solids (to be published).

²I am indebted to Dr. John Kessler of the RCA Laboratories for assistance in the choice of nomenclature. Dr. Kessler had independently speculated about some of the problems discussed here.

³Mobile complexes are analogous to J. A. Wheeler's "polyelectrons"; see Ann. N. Y. Acad. Sci. 48, 219 (1946). Indeed for the case of simple, spherical bands and equal effective masses for the hole and electron, we are able to utilize already-existing calculations on polyelectrons, as evidenced in Table I.

⁴H. A. Bethe and E. E. Salpeter, Handbuch der Physik (Springer-Verlag, Berlin, 1957), Vol. 35, p. 240. With regard to the complex ++-, the fact that in the H⁻-like limit, $m_h/m_e \ll 1$, there is only one bound state leads to the speculation that for any finite value of m_h/m_e , no matter how large, there are only a finite number of bound states of the corresponding complex. If the speculation is false, it would be of interest to determine the precise value of m_h/m_e at which an infinite number of bound states first appear.

⁵Wallis, Herman, and Milnes have studied the "Energy Levels of an Electron in the Field of a Finite Dipole" [Bull. Am. Phys. Soc. Ser. II, 3, 53, (1958) and to be published]. The authors did not settle the problem of the existence of a bound state in the limiting region where $R/a_0 \ll 1$ (R being the dipole length), which corresponds to the case discussed above. I am indebted to Dr. Wallis for sending me a preprint of the full article.

⁶G. Dresselhaus, J. Phys. Chem. Solids 1, 15 (1956).

⁷Thus the lifetime of the exciton against self-annihilation is assumed to exceed 10^{-8} sec. Its lifetime $\tau_{x,c}$ against any process catalyzed by an "impurity" of density N_C is given by $\tau_{x,c} = (N_C\bar{v}\sigma_C)^{-1} \approx 10^6/N_C$ since $\sigma_C \lesssim 10^{-12}$ cm², the cross section for a Coulomb-attractive reaction at helium temperatures. Chemical purification achieving $N_C \lesssim 10^{14}$ cm⁻³ guarantees that $\tau_{x,c} \gtrsim 10^{-8}$ sec. A likely catalytic process for breakup of the exciton is a charge-exchange reaction in which, for example, the electron member of the exciton is captured by a positive ion, the hole being freed into the valence band. The cross section for this reaction in Ge is estimated to be about 10^{-12} cm². The maximum possible density of excitons $n_{x,max}$ is obtained if the

excitons are in quasi-thermal equilibrium with the free carriers, i. e., if the most likely mode of breakup of the exciton is thermal dissociation. For a given n and p , $n_x, \max \approx (N_x n p / N_v N_C) \exp(E_x/kT) \approx 4 \times 10^{-16} \{ m \times (m_e + m_h) / m_e m_h \}^{3/2} T^{-3/2} n p \exp(E_x/kT)$, where E_x is the binding energy of the exciton, N_x , N_v , N_C are the effective densities of states of the exciton, valence, and conduction bands, respectively, near their respective extrema. Taking $T=4^\circ K$ and assuming that $\{ \}^{3/2} \approx 1$ and that $E_x \approx 10kT \approx 4 \times 10^{-3}$ ev, we obtain $n_x, \max \approx 10^{-12} n p$ under these conditions.

Li⁷ AND F¹⁹ NUCLEAR MAGNETIC RESONANCES IN NEUTRON-IRRADIATED LiF[†]

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Nuclear magnetic resonance examinations of LiF samples subjected to neutron dosages of the order of 10^{18} nvt have revealed the presence of constituent nuclei in environments other than those of the normal lattice sites. These nuclei produce narrow lines which are superimposed on the normal broad lines.

The fluorine line, Fig. 1, was observed in a single crystal¹ of LiF which had received a neutron dose of 1×10^{19} nvt. The resonance was observed at a frequency of 28.5 Mc/sec and the separation of the centers of the two derivative traces was 18.5 kc/sec. This is a shift of about 0.07% to a higher frequency for the more narrow

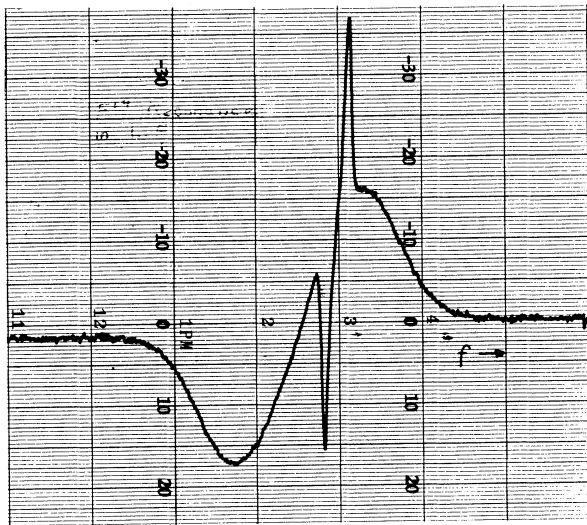


FIG. 1. F¹⁹ resonances in a neutron-irradiated single crystal of LiF.

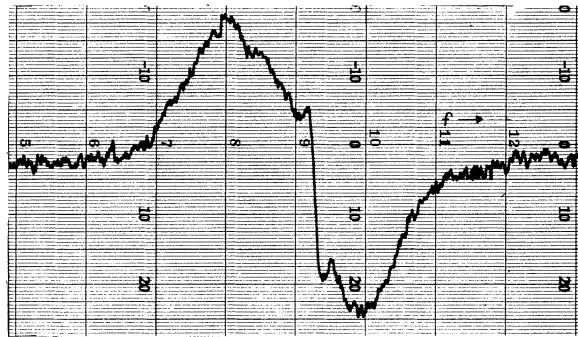


FIG. 2. Li⁷ resonances in a polycrystalline sample of neutron-irradiated LiF.

line. This same combination of narrow and broad lines has been observed in another single-crystal sample of LiF that had received a dose of about 10^{18} nvt.

Comparison of the areas under the two F¹⁹ derivative curves, each of which was obtained with a modulation amplitude appropriate to the particular line, gives a value of 0.07 for the ratio of the area of the more narrow line to the total area. Thus about 7% of the fluorine nuclei are contributing to the narrow line. The frequency shift of the narrow line with respect to the wide line is comparable with the value 0.063% between HF and F₂ given by Gutowsky and Hoffman.² Thus the narrow line may be due to molecular fluorine. The frequency shift expected if the nuclei were ionic fluorine is much smaller than that measured.

The line width, that is the separation of maximum derivatives, of the broad line is approximately 47.4 kc/sec which is, within experimental error, in agreement with the value of 46.6 kc/sec calculated from the equation of Van Vleck.³ The narrow line has a width of about 4 kc/sec.

The lithium line, Fig. 2, has been observed in a polycrystalline LiF sample which received a neutron dose of 1.6×10^{18} nvt. The sample was originally a single crystal¹ but after irradiation was found to be completely fractured.

The intensity of the narrow Li⁷ line in the polycrystalline sample is not sufficient to allow a determination of the percentage of Li⁷ nuclei contributing to it. Measurement of the frequency of this line and comparison of this value with that of Li⁷ in a LiCl solution gives a value of $\Delta f/f = 0.028$ for the shift of the narrow line. This value compares favorably with the value⁴ $\Delta H/H = 0.0249$ for the Knight shift in metallic lithium. The fluorine resonance in this polycrystalline sample exhibits a narrow line similar to that of