

Referring to Fig. 2, we see that these values are roughly twice those obtained from extrapolation to T_m . Considering the previously mentioned uncertainties in the calculated values of α_m and in the extrapolation of the measured α to the melting temperature, the qualitative comparison is good.

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¹E. M. Saunders, Phys. Rev. **126**, 1724 (1962).

²N. Bernardes, Phys. Rev. **120**, 1927 (1960).

³L. Goldstein, Ann. Phys. (N.Y.) **8**, 390 (1959).

⁴R. L. Mills, E. R. Grilly, and S. G. Sydorik, Ann. Phys. (N.Y.) **12**, 41 (1961).

⁵E. C. Heltemes and C. A. Swenson, Phys. Rev. **128**, 1512 (1962).

⁶E. D. Adams and G. C. Straty, to be published.

REFLECTION STUDIES OF EXCITONS IN LIQUID AND SOLID XENON*

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In a number of insulating crystals, there exist, in addition to the well-known hydrogenic excitons lying below the threshold energies for direct interband transitions, extra excitons which lie in the continuum above the threshold. For instance, the solid-xenon absorption data taken by Baldini¹ show a strong broad line at 10.3 eV lying in the region of continuous absorption. Several models have been proposed to explain these extra excitons. Overhauser² suggested that just as the conventional excitons may be pictured in an atomic model as formed by the binding of atomic *s* electrons around the *p* hole, so might the extra excitons correspond to the binding of atomic *d* electrons. Phillips approached the problem from the band model. Here the conventional exciton is pictured as a conduction electron bound to the valence-band hole. The localized electron's wave packet is made up from conduction states near Γ in the Brillouin zone, where the high density of states allows the electron to take advantage of the potential energy of the hole with little gain of kinetic energy. Phillips³ therefore suggested that the extra excitons may arise kinematically from the binding of conduction electrons whose wave packets are formed from other regions of *k* space having high density of states—in fact, in the case of xenon, from the saddle points at *L* and *X* in the Brillouin zone. This approach appears to be successful for shallow extra excitons in semiconductors.⁴

At least from the simplest viewpoint it seems essential for the formation of this second type of exciton that the medium have long-range

order, for it is the periodic structure of the crystal which produces the high density of states at the Brillouin zone boundary. Phillips therefore suggested that a study of the exciton spectrum of liquid xenon would serve to show just how critically these states depend upon crystalline properties.

A comparison between the liquid- and solid-xenon spectra is reported here. The liquid exciton spectrum in fact is found to be very similar to that of the solid just below the melting point. The lower lying exciton states are broadened by the increased disorder, and, of special interest, the extra exciton at 10.3 eV is still present in the liquid.

Liquid-xenon's high vapor pressure makes it essential for the sample to be contained in a windowed cell. The light reflected from a lithium-fluoride window has been measured when the cell is first empty, and then filled, the back surface of the window (with a reflectivity R_b) now forming an interface between lithium fluoride and xenon. The ratio of the total light reflected from both surfaces of the window of the filled cell $R(2)$ to that reflected from the empty cell $R(1)$ may be shown to be approximately

$$\frac{R(2)}{R(1)} \cong \frac{1 + T^2 R_b(2)}{1 + T^2 R_b(1)}, \quad (1)$$

where T is the fraction of the light transmitted by the window. $R_b(2)$ may be found from Eq. (1) if the known properties of the window material⁵ are used. If $n + ik$ is the complex

refractive index of xenon and n_0 that of lithium fluoride, then $R_b(2)$ and $R_b(1)$ are given by

$$R_b(2) = \frac{(n-n_0)^2 + k^2}{(n+n_0)^2 + k^2}, \quad R_b(1) = \frac{(1-n_0)^2}{(1+n_0)^2}. \quad (2)$$

In our case n_0 is about 1.5, increasing slowly as the limit of transmission is approached, so that $R_b(1)$ is around 0.04. Changes in $R_b(2)$ are, therefore, mainly associated with changes of n in weakly absorbing regions, and with changes of k in strongly absorbing regions.

The cell design posed certain problems. The temperature difference between liquid and solid phases at 1 atm vapor pressure is only 3.5°K (bp of liquid xenon is 165°K, mp of solid xenon is 161.5°K), so the temperatures of the walls and window had to be uniform to within 0.5°K or so, to prevent the existence of mixed phases. The cell was designed to have walls and window cooled independently by heat leaks from a liquid-nitrogen bath, and the temperatures, measured by thermocouples, were maintained constant by electrical heaters in feedback circuits. In this way the temperatures everywhere could be set to better than 0.2°K. A check on the window temperature was made in a dummy experiment by means of an additional thermocouple glued to its center, and it agreed to within 0.2°K with that of the walls.

Measurements were made in the region 7.8 to 11 eV. This region covers the hydrogenic exciton lines and just includes the lower of the extra excitons. Absorption by the window itself prevents measurements at higher energies. In Fig. 1, $R_b(2)$ derived from Eq. (1) is shown for liquid xenon at 165°K and for solid xenon at 155 and 130°K. The measured curves varied a little with different fillings of the cell, and with different windows, but they could be brought into coincidence by either small over-all shifts of less than 10% in the reflectivity, or by similarly small changes in $R_b(1)$ in Eq. (1). The liquid-xenon curve shown here is the average of three separate measurements using different windows. The other two curves, where the structure is not in doubt, were taken with only one window. Under the curves has been drawn the absorption data of Baldini for an annealed solid film at 21°K. The interface reflectivity R_b could in principle provide the optical constants of xenon, n and k , if the Kronig-Kramers relation connecting R_b and the phase change at the boundary were used. For such a procedure the measurements must

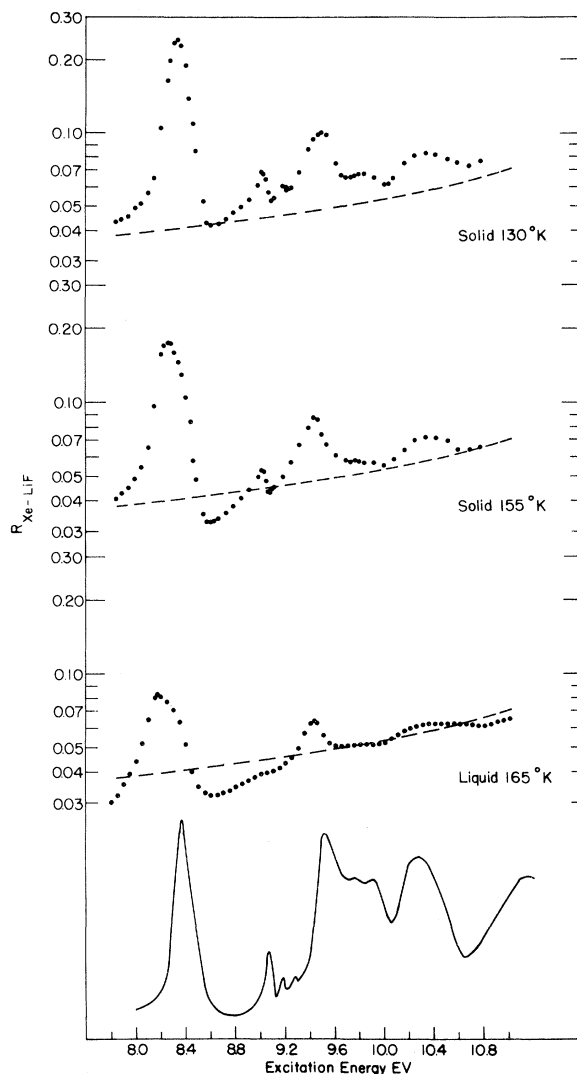


FIG. 1. Curves showing the reflectivity of a Xe-LiF interface. The reflectivity was found from measured values of $R(2)/R(1)$ using Eq. (1) and optical constants of LiF reported by Schneider.⁵ The reflectivity of the front surface of the window is shown by the dotted line. The lower curve is the absorption data of Baldini¹ for an annealed solid-xenon film at 21°K. The ordinate here is proportional to k .

be extended over a much wider energy range. Comparison with Baldini's data, however, enables us to interpret all the reflectivity structure.

The main exciton line of the solid at 8.4 eV, formed by excitation of a $6p_{3/2}$ valence electron to a $1s$ -like bound state near Γ in the Brillouin zone, can be seen to shift to lower energy and broaden as the temperature is raised, becoming quite markedly wider in the liquid

phase. The subsidiary lines of its hydrogenic series become smeared by the increased lattice disorder, but do exist, in a much broadened form, in the liquid phase. Thus a hydrogenic series of exciton lines can be formed in a pure disordered medium. The second 1s exciton at 9.5 eV and its associated series, formed by excitation of a $6p_{1/2}$ valence electron to states at Γ , exhibit similar broadening behavior.

The puzzling line at 10.3 eV, the extra exciton, is found also in the liquid state, with its amplitude only partially reduced by the disorder. It appears then that the deep extra excitons must have rather more of an atomic than kinematic band origin.

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¹G. Baldini, Phys. Rev. 128, 1562 (1962).

²A. W. Overhauser, Phys. Rev. 101, 1702 (1956).

³J. C. Phillips, Phys. Rev. 136, A1714 (1964).

⁴J. C. Phillips, Phys. Rev. Letters 10, 329 (1963).

⁵E. G. Schneider, Phys. Rev. 49, 341 (1936).

TEMPERATURE DEPENDENCE OF CONDUCTIVITY EFFECTIVE MASS OF HOLES IN Ge

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In a recent Letter,¹ Champlin *et al.* report that they have found, using a modification of the Benedict-Shockley microwave technique,² that the conductivity effective mass of holes in germanium increases with temperature as $T^{0.7}$ in the range 125 to 300°K, reaching a value of $0.78m_0$ at the upper end of this range. They reason from this that the $T^{-2.33}$ dependence of the mobility found for relatively pure p -Ge samples in this temperature range can be explained as the combined effect of acoustic-mode scattering and mass variation. As a consequence, they conclude, the strong coupling to optical modes that had been invoked to explain the $T^{-2.33}$ dependence does not in fact exist. It is the purpose of the present note to point out that these conclusions are, to say the least, questionable.

Measurements of the conductivity effective mass of holes in Ge by microwave techniques have been reported by many workers.³⁻⁶ Benedict (B) claimed a value of $0.3m_0$,³ although, according to Goldey and Brown,⁵ a correct interpretation of his measurements would lead to $0.45m_0$. D'Altroy and Fan⁴ (DF) obtained $(0.34 \pm 0.06)m_0$ for the range 20 to 300°. Goldey and Brown⁵ (GB) obtained $(0.29 \pm 0.05)m_0$ for the range 200 to 300°. Gibson, Granville, and Paige⁶ (GGP) obtained $(0.59 \pm 0.12)m_0$ at 300°.

Champlin *et al.* in their Letter do not mention the results of DF and dismiss the results of B and GB by saying they believe their experimental technique to be significantly more accurate. They quote the result of GGP as being in fair agreement with their own (extrapolated) value of $0.78m_0$ at 300°. It is noteworthy as an indication of the accuracy of some of the measurements that GGP obtained a value of 13.62 for the room-temperature dielectric constant of intrinsic Ge, while GB obtained 16.6 ± 0.3 , the latter in good agreement with the accepted value. Champlin *et al.* do not quote the value they obtain for the lattice dielectric constant and, in fact, do not give sufficient detail to make it possible to judge the accuracy of their measurements.

As Champlin *et al.* were undoubtedly aware, in early work⁷ use of the optical-mode coupling constant obtained from the $T^{-2.33}$ dependence of μ led to poor agreement of theory with the observed field variation of hot-carrier mobility in p -Ge. In particular, the theory appeared to predict much less carrier heating, i.e., a greater rate of energy loss, at a given field than was actually observed. Since the energy losses of the holes are to optical modes (which would be true even if the coupling constant were much smaller), this made it appear that the