been found in the ion concentrations across the stream even with seeding flow rates ten times greater than those used with SF_6.

These results seem to indicate that when the argon plasma is seeded by very small amounts of SF_6 not only the electron density (as shown by the microwave measurements) but also the positive-ion density is markedly reduced. This conclusion is based on the fact that the double-probe saturation current is a measure of the ion density in the plasma and a simple replacement of electrons by negative ions should not radically change the probe saturation current. Even including the effect of the low mobility of heavy negative ions in the plasma, the very large changes in probe current that have been observed can only by explained by a reduction in the ion density. This suggests that the capture of electrons in the plasma by SF_6 to form negative ions is quickly followed by a charge exchange process between the argon positive ions and the SF_6 negative ions. In addition, the efficiency of both these processes appears to be very high since the SF_6/A ratio is of the same order of magnitude as the ratio of electron to argon concentration in the unseeded plasma.

The authors wish to express their appreciation to Dr. M. P. Bachynski, for the many useful discussions concerning this investigation.

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EXCITON-INDUCED IMAGES OF PHONON SPECTRA IN ULTRAVIOLET REFLECTANCE EDGES

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Ultraprecise measurements of the ultraviolet reflectance of a number of semiconductors have been reported by Lukeš and Schmidt.[1,2] The relative accuracy of the reflectance is apparently 0.03% and of the spectral resolution 0.003 eV. Their results for Si at 359°K (Fig. 1) show a hyperfine splitting of the M_1 absorption edge at 3.350 eV into subsidiary edges at 3.310, 3.333, 3.367, 3.387, 3.404, 3.419, and 3.436 eV. Similar splittings which are seen in various absorption edges of other semiconductors are collected in Table I.

Here we observe that this structure is exactly what one expects when multiphonon transitions are taken into account. Consider first the direct transitions between conduction band i and valence band j. If we have an M_0 threshold at energy E_0, the form of the imaginary part of the dielectric constant ϵ_2 is[3]

$$\epsilon_2(\nu) = C(h\nu - E_0)^{1/2}, \tag{1}$$

while that of an M_1 edge[4] at E_1 is

$$\epsilon_2(\nu) = C_1 - C_2(E_1 - h\nu)^{1/2} \quad h\nu \lesssim E_1, \tag{2}$$

$$= C_1 + C_3(h\nu - E_1) \quad h\nu \lesssim E_1. \tag{3}$$

The M_0 direct edge (1) is associated with a sphe-

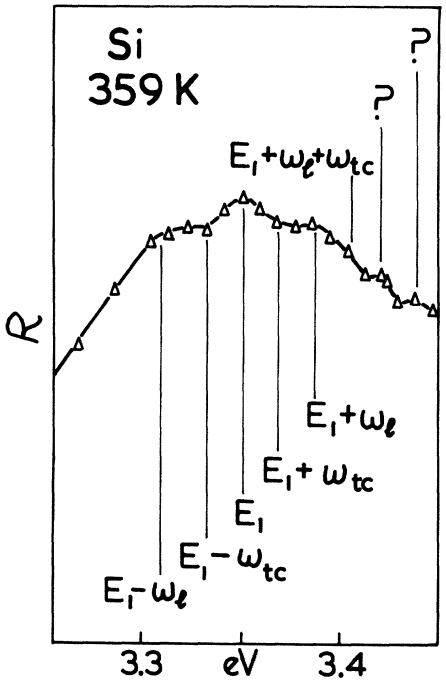

FIG. 1. Ultraviolet reflectance of Si near 3.35 eV at 359°K. The longitudinal acoustic phonon frequency is ω_l, the transverse acoustic ω_{tc}, and E_1 is the no-phonon intrinsic M_1 reflectance edge energy.

roidal neighborhood of k space defined by $(\hbar\delta k)^2 \lesssim m^* kT$. The M_1 direct edge (2)-(3) transitions occur along a hyperbolic surface[5] in $\vec{k}$ space defined by $E_i(\vec{k}) - E_j(\vec{k}) = E_1$.

Now consider transitions which involve the absorption or emission of n phonons, with $n = 1$ for simplicity. These take place between states $E_i(\vec{k}+\vec{q}) - E_j(\vec{k}) = h\nu \pm \hbar\omega_\alpha(\vec{q})$, where α is an index labeling phonon polarization. For M_0 edges these are called indirect transitions and they take place through virtual intermediate states which do not conserve energy.[6] Usually $\delta k \ll q = |\vec{k}_i - \vec{k}_j|$ which means that $\hbar\omega_\alpha(\vec{q})$ takes on discrete values. Near an M_1 ultraviolet edge transitions may take place through energy-conserving intermediate states. Such transitions alter ϵ_2 by

$$\Delta\epsilon_2 = \sum_n \sum_{\vec{k}_i} \sum_{\vec{q}_l, \alpha_l} \beta(\vec{q}_1, \alpha_1)\cdots\beta(\vec{q}_n, \alpha_n) \times [\epsilon_2(2\pi\nu \pm \omega_1 \cdots \pm \omega_n) - \epsilon_2(2\pi\nu)], \quad (4)$$

where $\sum\vec{q}_l = \vec{k}_j - \vec{k}_i$. In (4) $\beta(\vec{q})$ is an electron-phonon interaction constant proportional to $n(\vec{q}) + \frac{1}{2} \mp \frac{1}{2}$. Here $n(\vec{q})$ is the mean occupation number for phonons of energy $\hbar\omega_\alpha(\vec{q})$.

In the absence of detailed knowledge of the coupling constants β, we may assume that the surface covered by $\vec{q}_l$ effectively samples the Brillouin zone. Then retaining only the terms $n = \pm 1$ for simplicity,

$$\Delta\epsilon_2 = \sum_\alpha B_\alpha \int d\omega_1 N_\alpha(\omega_1)[n(\omega_1) + \tfrac{1}{2} \mp \tfrac{1}{2}][\epsilon_2(2\pi\nu \pm \omega_1) - \epsilon_2(2\pi\nu)], \quad (5)$$

where $N_\alpha(\omega)$ is the αth phonon density of states. At an M_1 edge $(d\epsilon_2/d\omega)_- = -\infty$, so that (5) maps the phonon spectrum $N_\alpha(\omega)$.

The density of phonon states $N_\alpha(\omega)$ in Ge and Si has been computed[7] from neutron scattering measurements.[8,9] The acoustic spectrum in Si is characterized by a large, narrow peak near 0.045 eV for the LA branch and a broad peak between 0.015 and 0.024 eV for the TA branch. In Fig. 2 we show $\epsilon_2(\omega)$ (direct transitions), $\epsilon_2(\omega) + \Delta\epsilon_2(\omega)$ when $N_1(\omega_1) = \delta(\omega_1 - 0.045$ eV), and $\epsilon_2(\omega) + \Delta\epsilon_2(\omega)$ including N_1 and $N_2 = $ const for 0.015 eV $\leq \omega_2 \leq$ 0.024 eV. The latter curve bears a striking resemblance to the experimental curves of Fig. 1. Similar agreement is obtained for the other semiconductors where the phonon energies are half as great.

The structure at 3.404 eV in Fig. 1 may be due either to TO phonons or to the combination mode TA + LA. The edges at 3.419 and 3.436 eV are probably LA + 2TA, LA + 3TA. Multiphonon combination edges are also seen in other cases and are identified in Table I.

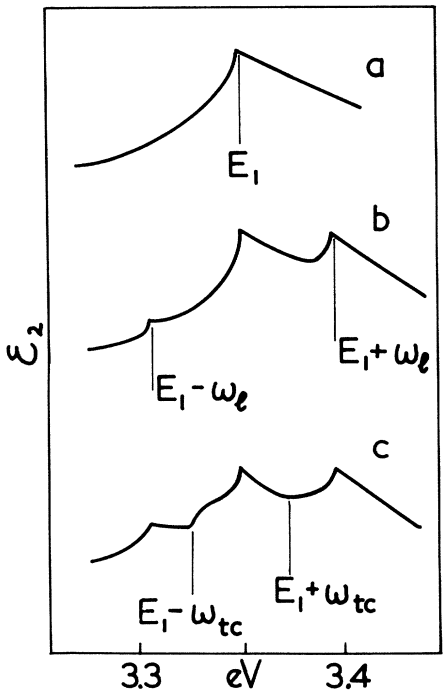

FIG. 2. The imaginary part of the dielectric constant ϵ_2, as a function of energy near an M_1 edge at 3.35 eV. Curve a: no phonons; b: sharp longitudinal acoustic phonons; c: broad transverse acoustic phonons as well.

It is remarkable that the ultraviolet reflectance R displays[10] the phonon spectrum with an accuracy comparable to that of superconductive tunneling.[11,12] The similarity of this structure to theoretical expectations provides decisive confirmation of the ultraprecision claimed by Lukeš and Schmidt.

In ionic crystals energy-conserving electron-phonon absorption is conventionally described as exciton absorption with the electron and hole regarded as polarons.[13] The localization of the electron and hole in the exciton state couples their Coulomb field to the phonon field. Cardona and Harbeke[14] proposed that excitons were found at the M_1 edge in InSb and CdTe. This was criticized by Marple and Ehrenreich[15] on the grounds that similar line shapes could be produced by interference from a nearby M_3 edge. The situation here is complicated by the possibility[4] of additional singularities due to spin-orbit splitting ("pseudoexcitons," e.g., Table I, InAs, 2.45 eV).

It is important to realize that excitons near an

Table I. Hyperfine ultraviolet reflectance edges. The question marks label edges which are uncertain, usually because of sparsity of experimental measurements near that energy. In general, the phonon energies in the fourth column are consistent within 0.003 eV.

Edge	Energy (eV)	Phonon modes (n, α)	Phonon energies (eV)
M_1	3.350	0	...
Si	3.310	-LA	0.040
359°	3.333	-TA	0.017
	3.367	+TA	0.017
	3.387	+LA	0.037
	3.404	+LA+TA	(0.037)+ (0.017)
	3.419	+LA+2TA?	(0.037)+2(0.016)
	3.436	+LA+3TA?	(0.037)+3(0.016)
M_1	3.075	0	...
GaAs	3.052	-LA	0.023
365°	3.019	-2LA?	(0.023)+ (0.033)
	3.099	+LA	0.022
	3.121	+2LA	2(0.022)
	3.143	+3LA?	3(0.022)
M_1	2.865	0?	...
GaAs	2.840	-LA	0.025
365°	2.887	+LA	0.022
	2.909	+2LA	2(0.022)
	2.926	+3LA?	2(0.022)+0.017
M_1	2.734	0	...
InAs	2.712	-LA?	0.022
293°	2.690	-2LA	2(0.022)
	2.678	-3LA?	3(0.022)
	2.656	-4LA	4(0.022)
	2.756	+LA	(0.022)
	2.778	+2LA	2(0.022)
	2.403		
	2.422		0.019
	2.437		0.015
M_3?	2.497		
InAs	2.519		0.022
293°	2.538		0.019
	2.560?		0.022
M_1	2.458	0	...
GaSb	2.436	-LA?	0.022
293°	2.414	-LO	0.044
	2.366	-2LO	2(0.046)
	2.480	LA?	0.022
	2.502	LO	0.044
	2.524	3LA?	3(0.022)
M_1	2.354	0	...
InSb	2.323	-LO	0.031
293°	2.385	+LO	0.031
	2.416	+2LO	2(0.031)
M_1	4.200	0	...
GaSb	4.192	-TA	0.008
297°	4.180	-LA	0.020
	4.172	-LA-TA	0.020+0.008
	4.160	-2LA	2(0.020)
	4.208	+TA	0.008
	4.220	+LA	0.020
M_1	4.415	0	...
Ge	4.400	-TA	0.015
297°	4.391	-LA	0.024
	4.382	-TO	0.033
	4.367	-2LA	2(0.024)
	4.358	-LA-TO	0.024+0.033
	4.334	-2LA-TO	2(0.024)+0.033
	4.430	+TA	0.015
	4.439	+LA	0.024
	4.455	LA+TA	0.024+0.016
	4.475	2LA+TA	2(0.024)+0.012
	4.490	2LA+2TA	2(0.024)+2(0.015)
	4.514	3LA+2TA	3(0.024)+2(0.015)

M_1 edge have a dynamical character qualitatively different from the conventional hydrogenic excitons formed near an M_0 edge. It is convenient to think of the periodic hyperboloidal energy surfaces in k space as undulating cylinders along the z axis. This is similar to a hydrogenic exciton with $m_z = \infty$. Compared to a conventional exciton binding energy $\epsilon_0 \sim 0.01$ eV, hyperboloidal or dynamically unstable exciton binding energies should be of order[16]

$$\epsilon_1 \sim 4\epsilon_0 \lesssim 0.1 \text{ eV}. \quad (6)$$

It has already been noted[17] that at the 3.4-eV M_1 edge in Si, ϵ_2 has a large peak which is not of the expected character. The proposed explanation for this peak required an energy-dependent linewidth $\Gamma = 0.05$ eV for $E > 3.4$ eV and 0.02 eV for $E < 3.4$ eV. The conduction or valence intraband densities of states show no singularities, however. We conclude that this peak is caused by the singularity in the scattering density of states for dynamically unstable excitons.[18] (The spontaneous emission part of β accounts for the asymmetry of Γ.) The fine structure shown in Fig. 1 provides conclusive proof for this interpretation.

For the 3.35-eV edge in Si, the magnitude of Γ or the strength of the $n = \pm 1$ edges compared to the $n = 0$ edge shows intermediate coupling ($\langle n \rangle \sim 1$) of the exciton to the phonon field. The coupling is even stronger ($\langle n \rangle \sim 4$) at the 4.3-eV edge in Si.

Such strong coupling is a consequence of the large volume of k space filled by the undulating cylinder $|E_i(\vec{k}) - E_j(\vec{k}) - E_1| \lesssim \epsilon_1$.

The phonon hyperfine structure appears to be unusually sensitive to changes in thickness of surface film. Lukeš and Schmidt[1] find that increasing the Ge film thickness from 37 Å to 48 Å enhances edges corresponding to $n = 0, \pm 1$, but tends to suppress other edges. The bulk Ge absorption length here is 50 Å. This anomalous sensitivity may be due to spatial dispersion.[19] Because excitons are formed, there are two normal modes of mixed photons and excitons for transverse electromagnetic waves. These are coherent, and their interference after reflection from the uneven bulk surface into the film affects the degree to which exciton-phonon hyperfine structure is observable in the external reflectance.

Dynamically unstable excitons, like hydrogenic excitons, may annihilate and emit photons and phonons. They may also emit photons and phonons by scattering, as hot electrons do. Finally, they may decay directly into free electrons and holes. We believe this to be the first positive identification of excitons which overlap the electron-hole scattering continuum.

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[19]S. I. Pekar, reference 2, p. 419.

SHAPE RESONANCES IN SUPERCONDUCTING THIN FILMS*

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The basic equations for superconductors[1] are usually written for an infinite, homogeneous medium. We have set up the corresponding equations for a slab with thickness a, and solved them numerically for various slab thicknesses. The equations take into account, in a self-consistent fashion, the Coulomb potential generated by the charge density of the electrons plus an assumed uniform background of positive charge. The boundary condition on the electron wave functions is that they vanish at the faces of the slab.

One rather expects resonance effects whenever an energy level $\eta_n(a)$, for motion perpendicular to the slab faces, passes through the Fermi surface as the thickness a is varied. What is surprising, however, is the size of the resonance ef-