[9]W. E. Gardner, J. Penfold, T. F. Smith, and I. R. Harris, J. Phys. F 2, 133 (1972); R. D. Hutchens, V. U. S. Rao, J. E. Greedan, W. E. Wallace, and R. S. Craig, J. Appl. Phys. 42, 1293 (1971).
[10]E. Holland-Moritz, M. Loewenhaupt, W. Schmatz, and D. K. Wohlleben, Phys. Rev. Lett. 38, 983 (1977).
[11]A. C. Gossard, A. J. Heeger, and J. H. Wernick, J. Appl. Phys. 38, 1251 (1967).
[12]P. Urban and D. Seipler, J. Phys. F 7, 1589 (1977).
[13]D. Seipler and B. Elschner, Phys. Lett. 55A, 115 (1975).
[14]L. L. Hirst, in *Valence Instabilities and Related Narrow-Band Phenomena*, edited by R. D. Parks (Plenum, New York, 1977), pp. 3, 113, 259.
[15]P. W. Anderson, Phys. Rev. 124, 41 (1961).
[16]The difference between the relaxation rates of Gd in $CePd_3$ and YPd_3 could result in part from the different conduction-band populations implied by intermediate valency, but it seems unlikely that this could account for a change by a factor of 3.
[17]H. Bjerrum-Møller, S. M. Shapiro, and R. J. Birgeneau, Phys. Rev. Lett. 39, 1021 (1977).
[18]M. Loewenhaupt and E. Holland-Moritz, private communication.

Dispersion of the Volume Plasmon of Silicon (16.7 eV) at Large Wave Vectors

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The dispersion of the volume plasmon of silicon at 16.7 eV has been measured with 50-keV electrons in the directions ⟨100⟩ and ⟨111⟩ up to the critical wave vector $q_c \simeq 1.1$ Å^{-1}. It shows a strong anisotropy. Along the ⟨100⟩ direction the q dependence could be measured up to large q vectors of ~ 2.4 Å^{-1}. At $q \gtrsim q_c$ the slope of the dispersion curve decreases strongly in a manner similar to what has been found earlier for Al and Be.

As is well known from different experiments, the position of the volume plasmon $\hbar\omega_p$ is displaced to higher energy values with increasing wave vector q approximately proportional to q^2 [see, e.g., Kloos[1] for details and further references]. This is in qualitative agreement with the approximation for $q < q_F$ (q_F Fermi wave vector),

$$\hbar\omega_p(q) = \hbar\omega_p(0) + \alpha(\hbar^2/m)q^2, \quad (1)$$

obtained from the Lindhard function with $\alpha = \frac{3}{5}E_F/\hbar\omega_p(0)$. However, agreement is poor when one compares theoretical and experimental α values: e.g., α(obs) for Li, Na, and K are 0.22, 0.22, and 0.12, whereas α(calc) come out as 0.36, 0.31, and 0.28, respectively. The exchange correction[2] reduces the calculated values by about 10% which does not improve the agreement essentially. Recent measurements on monocrystalline materials, e.g., Al,[3] and PbS, PbTe, and PbSe,[4] showed that the dispersion coefficient α is a function of crystal direction ⟨hkl⟩. This indicates that the influence of the lattice potential on the dispersion of the volume plasmon has to be taken into account. Formula (1) is therefore only a rough approximation.

Concerning collective oscillations the valence electrons of silicon behave like those in Al: Although in Si the four valence electrons are bound (energy gap of ~1 eV), the volume plasmon energy of $\hbar\omega_p(0) \simeq 17$ eV is large enough to treat these electrons as nearly free; thus a large loss peak due to this volume oscillation is seen in the loss spectrum. It was therefore of interest to look at the dispersion behavior of this loss which had not yet been measured.

The measurements were performed with 50-keV electrons in transmission. The Si films, about 1000 Å thick, are monocyrstalline as demonstrated by electron diffraction patterns; they were made from thicker plates of Si monocrystals, thinned mechanically,[5] and then reduced to a thickness of $\sim 10^3$ Å by sputtering.[6] The results of our measurements are reproduced in Fig. 1 for the two crystal directions ⟨100⟩ and ⟨111⟩. Above $q \sim 0.6$ Å^{-1} the losses in the different directions are well separated so that two α's can be derived. The values of the dispersion coefficients in the ⟨100⟩ and ⟨111⟩ directions are $\alpha_{\langle 100\rangle} = 0.41 \pm 0.01$ and $\alpha_{\langle 111\rangle} = 0.32 \pm 0.02$ α of the nearly free electron gas has the value of $\alpha_{fr} = 0.4$ [calculated with the electron density 2×10^{23} cm^{-3}, $E_F = 12.4$ eV, $\hbar\omega_p(0) = 16.6$ eV, and exchange correction]. This anisotropy is similar to that found for the substances mentioned above. However, one finds that the α value in Si has the highest value in the ⟨100⟩ direction whereas in Al this occurs for the ⟨110⟩ direction (Al: $\alpha_{\langle 110\rangle} = 0.46$, $\alpha_{\langle 100\rangle} = 0.40$). Thus Si behaves like PbS, PbSe, and PbTe, the

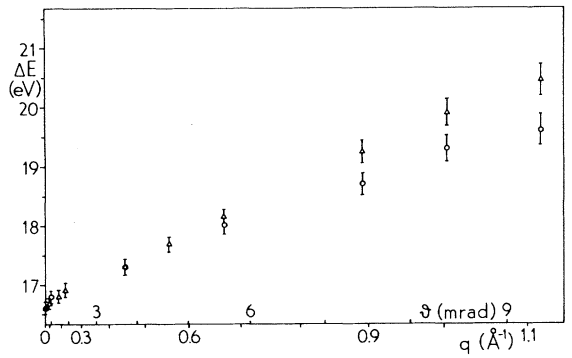

FIG. 1. Measured dispersion curve $\hbar\omega_p(q)$ up to q_c (quadratic scale of the wave vector q). The upper points (triangles) represent values in the ⟨100⟩ direction, the lower ones (circles) those in the ⟨111⟩ direction.

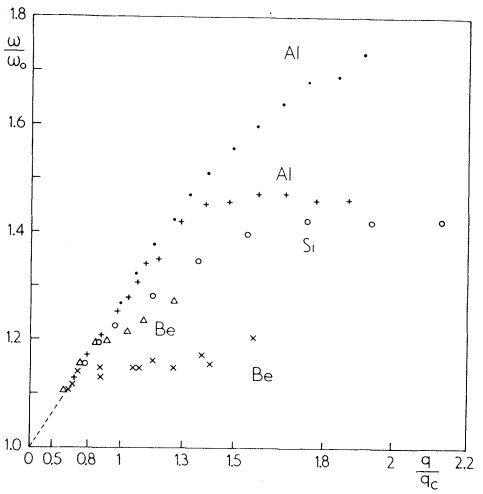

FIG. 2. Normalized experimental dispersion curve ω/ω_0 [$\omega_0=\omega_p(0)$] of several substances up to large q vectors. Solid circles, Al (measured with fast electrons) (Ref. 12); plusses, Al (measured with fast electrons) (Ref. 10); open circles, Si (present work); triangles, Be (measured with x rays) (Ref. 9); crosses, Be (measured with x-rays) (Refs. 7 and 8).

α values of which decrease in the same order.

These results stimulated measurements of the position of this Si loss at high q values, $q>q_c$ (q_c: cutoff vector). Experiments with x rays[7-9] on beryllium and with fast electrons[10-12] on Al demonstrated that the inelastic peak which is regarded as the plasmon loss for $q<q_c$ persists for $q>q_c$. It was found in Refs. 10 and 11 that in both these solids the slope of the plasmon energy $\hbar\omega_p$ as function of q^2 decreases rapidly in the q region $q_c \lesssim q \lesssim 1.5q_c$ and becomes approximately zero for larger q values. More recent measurements[12] on Al with fast electrons had a different result insofar as the slope of $\hbar\omega_p(q)$ for $q>q_c$ ~ 1.2 Å^{-1} turned out to be much steeper than that reported in Refs. 10 and 11 as Fig. 2 demonstrates. The discrepancy is rather large. Batson, Chen, and Silcox have obtained the higher energy positions of the plasmon by a procedure which separates multiple from single scattering effects. In this way energy values appear which are up to 30% larger than those obtained by Zacharias.[10]

Such a procedure may be perhaps justified for Al since the dispersive plasmon is rather weak and, in addition, a rather strong surface loss (7.2 eV) is observed in the loss spectrum. However, in order to recognize the dispersive plasmon in Si this procedure is not necessary for the following reasons: (a) If the 24-eV loss in Si at high q values is actually produced by a triple process (elastic–volume plasmon-surface plasmon), as suggested in Ref. 12, one would expect a loss at about 6 eV (elastic–surface plasmon) with an intensity higher than that at 24 eV. Such a surface loss is not visible in most of the spectra and certainly does not have the intensity one would expect. (Notice: The surface loss of 10 eV in Si has a width of 6 eV without oxide[13]; with oxide it is shifted to about 6 eV and is reduced in height and broadened.) (b) A triple process should be visible at q values smaller than 1.6 Å^{-1}; this is not the case.

For these reasons experiments on Si with the following results were performed: Figure 3 displays the change in the spectrum with the value of the wave vector q in the ⟨100⟩ direction. There is a continuous displacement of the volume loss to higher values with increasing q, then at $q\sim 0.7$ Å^{-1} it splits into the dispersive loss $\hbar\omega_p(q)$ and a loss which remains at $\hbar\omega_p(0)\sim 17$ eV due to the double process of elastic scattering into the angle ϑ and inelastic scattering without deflection. The double loss $2\hbar\omega_p(0)$ is also observed, but it is not reproduced in Fig. 3. In Fig. 4 the observed values of the loss position are shown as function of q^2. The q dependence of this Si loss shows agreement with the shape of the curves found for Be and Al discussed above; see Fig. 2. With regard to the volume loss of SiO_2 at ~ 23 eV,[14] we can say that we do not observe an oxide loss, neither at small nor at large q values, because of the small thickness of this oxide film (some 10 Å) compared to the approximately 1200-Å-thick Si film. The registered loss is regarded as the dispersive volume loss of silicon.

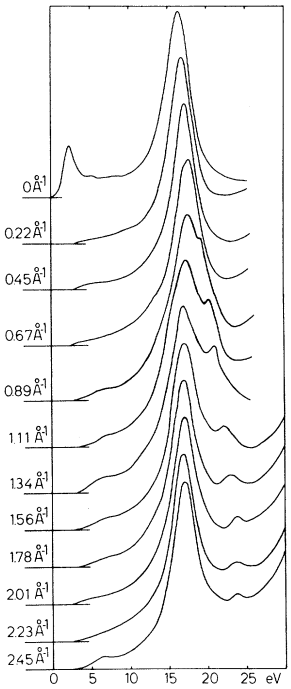

FIG. 3. Intensity versus lost energy for Si (in arbitrary units) demonstrating the displacement of the volume loss of Si with increasing wave vector up to $q \sim 2.5$ Å^{-1}.

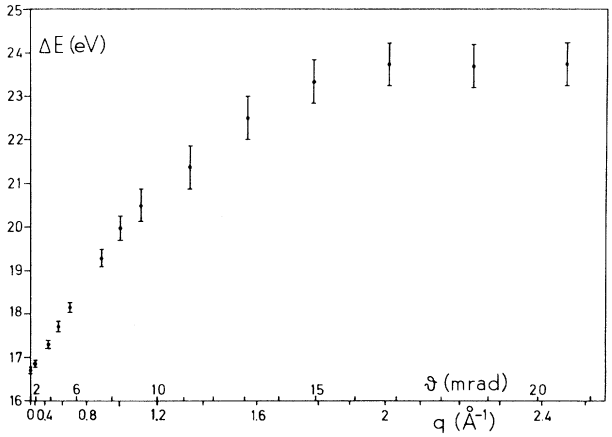

FIG. 4. Experimental values of $\hbar\omega_p(q)$ as function of q^2; $q_c \simeq 1.15$ Å^{-1}.

Theoretical considerations using the Lindhard function and taking into account damping[15] lead to a dispersion curve $\hbar\omega_p(q)$ with a small break of slope at $q \sim q_c$ in qualitative agreement with observations. However, the slopes do not agree quantitatively, especially at large q values.[16,10] The dielectric function $\epsilon(\omega, q)$ given by Vashishta and Singwi[17] leads to better agreement with observed values, especially for $q > q_c$, but quantitative agreement cannot be achieved either. There exists better agreement between Ref. 12 and random-phase–approximation theory.

The discussion can be summarized as follows: There exists a region around q_c, visible by the break of the slope in the dependence of $\hbar\omega_p(q)$ as function of q^2, which can be interpreted as the transition from the collective excitations to single-particle excitation. This interpretation is supported by measurements of the linewidth. The electron energy-loss experiments on Al demonstrated that for $q > q_c$ the width of the plasma loss line increases strongly[10,18] indicating a new channel of damping, viz. the decay of the plasmon into an electron-hole pair (single-particle excitation) which becomes possible for $q \gtrsim q_c$. Quantitative agreement of the observed and calculated slopes, however, has not yet been reached; better agreement could probably be achieved by considering the effect of the lattice potential along with an improvement of the random-phase approximation including exchange and correlation.

[1]T. Kloos, Z. Phys. 265, 225 (1973).
[2]R. A. Ferrell, Phys. Rev. 107, 450 (1957); K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjölander, Phys. Rev. 176, 589 (1968).
[3]M. Urner-Wille and H. Raether, Phys. Lett. 58A, 265 (1976).
[4]U. Büchner, Phys. Status Solidi (b) 83, 493 (1977).
[5]H. Kiendl, Z. Naturforsch. 31a, 2093 (1966).
[6]I. Grambow, Z. Phys. 187, 197 (1965).
[7]D. M. Miliotis, Phys. Rev. B 3, 701 (1971).
[8]D. Marinos and D. M. Miliotis, Phys. Status Solidi (b) 68, K133 (1975).
[9]P. Eisenberger, P. M. Platzman, and K. C. Pandey, Phys. Rev. Lett. 31, 311 (1973).
[10]P. Zacharias, J. Phys. C 7, L26 (1974), and J. Phys. F 5, 645 (1975).
[11]H. J. Höhberger, A. Otto, and E. Petri, Solid State Commun. 16, 175 (1975).
[12]P. E. Batson, C. H. Chen, and J. Silcox, Phys. Rev. Lett. 57, 937 (1976).
[13]J. Schilling, Z. Phys. B25, 61 (1976).
[14]U. Büchner, J. Phys. C 8, 2781 (1975).
[15]D. Mermin, Phys. Rev. B 1, 2362 (1970).
[16]K. Kliewer and H. Raether, Phys. Rev. Lett. 30, 971 (1973).
[17]P. Vashishta and K. S. Singwi, Phys. Rev. B 6, 875 (1972).
[18]P. C. Gibbons, S. E. Schnatterly, J. J. Ritsko, and J. R. Fields, Phys. Rev. B 13, 2451 (1976).