Theoretical investigation of neutron scattering cross sections in Si and Ge

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The development of high-flux high-energy pulsed neutron sources makes it possible to study electronic transitions in solids which are in the electron-volt range. A theoretical study has been carried out to determine the feasibility of using such sources to obtain information about the band structure of semiconductors. Calculations of the inelastic neutron scattering cross sections for germanium and silicon based on an empirical pseudopotential description of the energy bands have been completed. This study is an extension of previous work to more realistic (larger) momentum transfers. The calculated cross sections were found to be quite small for realistic experimental conditions. Measurement of these relatively small cross sections could, however, provide important information about the band structure of semiconductors which cannot be obtained from most other experimental techniques.

I. INTRODUCTION

The development of high-flux high-energy spallation neutron sources has opened up a range of energy transfer in neutron scattering experiments which was hitherto inaccessible. This has made it possible to contemplate a new class of experiments which were impossible to perform using conventional neutron sources. One such area of interest is the study of electronic transitions and elementary excitations in metals and semiconductors which have energies in the electron-volt range. In the past, neutron scattering experiments provided invaluable information about such transitions and excitations for energies below ≈ 100 meV. The use of spallation sources could, in principle, raise this limit significantly, perhaps into the few electron-volts range. Some calculations relevant to the spectroscopy of such experiments have been made by Allen *et al.*[1]

If such experiments could be carried out with reasonable resolution and statistics, then one could extend measurements of excitation spectra, crystal-field-like transitions, etc. to provide additional information about quasiparticles and their interactions in solids. This would also provide a check on theoretical predictions from models developed to explain lower-energy phenomena.

In addition, it has been argued that inelastic neutron scattering experiments could prove to be a useful tool in the experimental determination of band structure. This is because neutrons are scattered by electronic transitions between occupied and unoccupied states in the solid. Therefore, measurement of the neutron cross section provides detailed information about unoccupied states which cannot be obtained from most other experimental techniques. In addition, comparison of photoemission and neutron scattering data may provide some insight into the complicated many-body effects which are important in describing the relaxation process that occurs as a result of electronic transitions.

Because of the potential importance of the technique, we have initiated a theoretical study of magnetic scattering of neutrons with energy transfers in the zero to few electron-volts energy range. The purpose of this study is to assess the feasibility of obtaining new information about electronic transitions and elementary excitations in this expanded energy transfer range. In this paper we present some results from an extensive series of calculations of the total magnetic scattering cross section in the semiconductors, silicon and germanium. These results represent an extension of previous calculations[2] to larger neutron momentum transfer ($\sim$tens of nm^{-1}) which are more relevant to realistic experiments. Prior to this work, calculations of the total magnetic inelastic cross section (spin and orbit) for noninteracting electrons concentrated mainly on the free-electron model[3–5] and tight-binding models of d-band transition metals.[6,7]

The remainder of this paper will be divided into three sections. In Sec. II the formulas for calculating the magnetic inelastic cross section will be given along with relevant definitions and approximations which form the basis of the calculation. Numerical results are presented in Sec. III, and Sec. IV provides a summary of results and some general remarks regarding the prospects for experiments.

II. THEORY

The general theory of neutron scattering is reviewed extensively in Ref. 8. The particular expressions for neutron-induced electronic transitions in semiconductors were obtained in Ref. 2. The expressions relevant to the current discussions are summarized here. In the one-electron approximation for a nonmagnetic system where the energy bands are not spin dependent, the total cross section can be written as the sum of spin and orbital terms:

$$\frac{d^2\sigma}{d\Omega\, dE}=\left.\frac{d^2\sigma}{d\Omega\, dE}\right|_{\text{spin}}+\left.\frac{d^2\sigma}{d\Omega\, dE}\right|_{\text{orbital}} . \tag{1}$$

The spin part of the cross section is given by

$$\left.\frac{d^2\sigma}{d\Omega\, dE}\right|_{\text{spin}}=\left[\frac{\gamma e^2}{mc^2}\right]^2\left|\frac{\mathbf{k}_f}{\mathbf{k}_i}\right| \times\sum_{\substack{nm\\ \mathbf{k}}} |F^{(s)}_{nm}(\mathbf{k},\mathbf{Q})|^2(f_{n\mathbf{k}}-f_{m\mathbf{k}+\mathbf{Q}}) \times\delta(E+E(n\mathbf{k})-E(m\mathbf{k}+\mathbf{Q})) . \tag{2}$$

The spin form factor $F^{(s)}$ is

$$F^{(s)}_{nm}(\mathbf{k},\mathbf{Q})=\frac{1}{V_0}\int d^3r\, e^{i\mathbf{Q}\cdot\mathbf{r}}\psi_{n\mathbf{k}}(\mathbf{r})\psi_{m\mathbf{k}+\mathbf{Q}}(\mathbf{r}) , \tag{3}$$

where V_0 is the volume of the unit cell, $E(n\mathbf{k})$ is the energy, $\psi_{n\mathbf{k}}(\mathbf{r})$ is the Bloch wave function, and $f_{n\mathbf{k}}$ is the Fermi occupation number. The corresponding orbital contribution is

$$\left.\frac{d^2\sigma}{d\Omega\, dE}\right|_{\text{orbital}}=\left[\frac{\gamma e^2}{mc^2}\right]^2\frac{|\mathbf{k}_f|}{|\mathbf{k}_i|}\frac{1}{2|\mathbf{Q}|^2} \times\sum_{\substack{nm\\ \mathbf{k}}} |\mathbf{F}^{(o)}_{nm}(\mathbf{k},\mathbf{Q})|^2(f_{n\mathbf{k}}-f_{m\mathbf{k}+\mathbf{Q}}) \times\delta(E+E(n\mathbf{k})-E(m\mathbf{k}+\mathbf{Q})) . \tag{4}$$

The orbital form factor is defined as

$$\mathbf{F}^{(o)}_{nm}(\mathbf{k},\mathbf{Q})=\frac{1}{V_0}\hat{\mathbf{Q}}\times\int d^3r\, e^{i\mathbf{Q}\cdot\mathbf{r}}[\bar{\psi}_{n\mathbf{k}}(\mathbf{r})\nabla\psi_{m\mathbf{k}+\mathbf{Q}}(\mathbf{r}) -\psi_{m\mathbf{k}+\mathbf{Q}}(\mathbf{r})\nabla\bar{\psi}_{n\mathbf{k}}(\mathbf{r})] . \tag{5}$$

The symbols n and $\mathbf{k}$ are the band and wave-vector labels, respectively. We evaluate these expressions for a semiconductor where the Fermi energy lies in the band gap. It is clear from Eqs. (2) and (4) that the inelastic scattering results entirely from interband transitions, i.e., from the valence band to the conduction band.

The calculations are based on the empirical pseudopotential method used by Cohen and Bergstrasser.[9] The pseudopotential method is an extension of the orthogonalized plane-wave method where the electronic wave function has the form

$$\psi_{n\mathbf{k}}(\mathbf{r})=\phi_{n\mathbf{k}}(\mathbf{r})-\sum_{\mathbf{G}}A_{n\mathbf{k}}(\mathbf{G})\sum_j\alpha^j_{\mathbf{k}}(\mathbf{G}) \times\sum_l e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{R}_l}\theta^j(\mathbf{r}-\mathbf{R}_l) , \tag{6}$$

where $\mathbf{G}$ is a reciprocal-lattice vector. The sum on l is over both unit cells and sites within the unit cell, and $\theta^j(\mathbf{r}-\mathbf{R}_l)$ is the jth core wave function associated with site l. The coefficient $\alpha^j_{\mathbf{k}}(\mathbf{G})$ ensures orthogonalization of ψ to the core states and is given by

$$\alpha^j_{\mathbf{k}}(\mathbf{G})=(V_0)^{-1/2}\int d^3r\,\bar{\theta}^j(\mathbf{r})e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} . \tag{7}$$

The "pseudopotential" wave function $\phi_{n\mathbf{k}}(\mathbf{r})$ is given by

$$\phi_{n\mathbf{k}}(\mathbf{r})=(V_0)^{-1/2}\sum_{\mathbf{G}}A_{n\mathbf{k}}(\mathbf{G})e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} , \tag{8}$$

where $G=|\mathbf{G}|$, and a_0 is the lattice parameter. The expansion coefficient $A_{n\mathbf{k}}(\mathbf{G})$ and the electronic energy $E(n\mathbf{k})$ are obtained by solving the Schrödinger-like equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V_p(\mathbf{r})\right]\phi_{n\mathbf{k}}(\mathbf{r})=E(n\mathbf{k})\phi_{n\mathbf{k}}(\mathbf{r}) . \tag{9}$$

$V_p(\mathbf{r})$ is the pseudopotential which, in general, can be expanded in terms of reciprocal-lattice vectors:

$$V_p(\mathbf{r})=\sum_{\mathbf{G}}V_G\cos(\mathbf{G}\cdot\boldsymbol{\tau})e^{-i\mathbf{G}\cdot\mathbf{r}} , \tag{10}$$

where $\boldsymbol{\tau}=a_0(\frac{1}{8},\frac{1}{8},\frac{1}{8})$.

Numerical calculations of the cross section have shown (as discussed in Ref. 2) that the contributions from the core states in Eq. (6) are small and can, in practice, be neglected. With this approximation, the matrix elements in Eqs. (2) and (4) assume the relatively simple form,

$$F^{(s)}_{nm}(\mathbf{k},\mathbf{Q})=\sum_{\mathbf{G}}A_{n\mathbf{k}}(\mathbf{G})A_{m\mathbf{k}+\mathbf{Q}}(\mathbf{G}) , \tag{11}$$

$$\mathbf{F}^{(o)}_{nm}(\mathbf{k},\mathbf{Q})=-2i\hat{\mathbf{Q}}\times\sum_{\mathbf{G}}(\mathbf{k}+\mathbf{G})A_{n\mathbf{k}}(\mathbf{G})A_{m\mathbf{k}+\mathbf{Q}}(\mathbf{G}) . \tag{12}$$

One final simplification which is helpful in carrying out the numerical calculations is to choose a coordinate system so that the two atoms in each unit cell are located at $\mathbf{R}\pm a_0(\frac{1}{8},\frac{1}{8},\frac{1}{8})$, where $\mathbf{R}$ is an fcc lattice vector. This ensures that the $A_{n\mathbf{k}}(\mathbf{G})$, and thus $F^{(s)}$ and $\mathbf{F}^{(o)}$, are real.

III. COMPUTATIONAL RESULTS

The numerical evaluation of the neutron scattering cross section involves the calculation of the band structure (electronic energies and wave functions), the spin and orbital matrix elements, and the band and Brillouin-zone sums indicated in Eqs. (2) and (4). The band structure was calculated by solving Eq. (9) with a three-parameter pseudopotential. The details of the calculation are given in Ref. 2.

The Brillouin-zone sums were carried out by using symmetry arguments to reduce the full zone sum to a sum over the irreducible zone and a corresponding sum over the point-group operations. The irreducible zone was then subdivided into 1536 tetrahedra. The electronic energy, wave-function expansion coefficients, and subsequently the spin and orbital matrix elements were determined at the unique corner points of the tetrahedral mesh. The tetrahedron method[10] was then used to evaluate the Brillouin-zone sums.

An extensive series of calculations have been carried out for Q along the [100], [111], and [110] directions. The results presented in this paper are based on the use of four valence and four conduction bands which should ensure reasonable accuracy for neutron energy transfers of a few electron volts or less. All factors in the cross-section expressions have been included except for the ratio $|\mathbf{k}_f|/|\mathbf{k}_i|$, which can easily be incorporated for particular conditions of an experiment.

As mentioned before, these calculations represent an extension of earlier work to wave vectors outside the first Brillouin zone which are more relevant to experiments carried out in the electron-volt range. In the course of this work an error was detected in the part of the computer program which manipulated the $A_{n\mathbf{k}}(\mathbf{G})$. This resulted in some changes in the overall structure of the cross section. As will be shown, these changes do not affect significantly the conclusions given in Ref. 2. In addition, the intensities given in Ref. 2 were actually integrated intensities over a histogram representation 23 meV wide. This was done to pick up sharp features in the intensity profile. These points should be kept in mind when comparing the results presented here to those given in Ref. 2.

First of all, a comparison of the joint density of states (JDOS) with the total scattering cross section for germanium with $\mathbf{Q}=(0.25,0.25,0.25)$ in units of $2\pi/a_0$ is shown in Fig. 1. The JDOS is given by Eq. (2) if $F^{(s)}$ is set equal to a constant. The JDOS has been scaled to the total scattering intensity to aid in comparison. This example demonstrates that the band and wave-vector dependence of the matrix elements is important. For some Q's the JDOS was found to track the total scattering reasonably well, but, clearly, one cannot always rely on this. Another important aspect of Fig. 1 is that there is no real structure in the total scattering cross section associated with the band gap (≈ 1 eV). This is due primarily to the fact that the density of states for transitions across the band gap (the JDOS) is relatively small and featureless. This is a general feature of the calculations.

Intensity profiles for Si and Ge are shown in Figs. 2(a)–2(e) and 3(a)–3(e) for a range of Q values, all of which are shifted from zero by a reciprocal-lattice vector. Differences between the profiles for a particular material are then entirely due to form-factor effects. The lower of the two peaks near 4 eV is due to the $X_4 \rightarrow X_1$ transition, and the upper peak just above 5 eV arises from the $L_3^1 \rightarrow L_3$ transition. These are, of course, what one would see in an optical experiment. Each figure contains the total and also the spin and orbital parts of the scattering intensity in mb/sr eV. There are several general features of the calculation that are represented by these intensity profiles. One is that the orbital part of the cross section dominates at small Q as was discussed in Ref. 2, but that at high Q it is the spin part that is the major contributor. The crossover occurs for $|\mathbf{Q}|$ in the region 1.5 to 2.0 (in units of $2\pi/a_0$).

The next point to note is the absolute values of the intensities. For these materials $2\pi/a_0$ is roughly 10 nm^{-1}. For momentum transfers of 10 nm^{-1}, the scattering intensities are 50–100 mb/sr eV. At 20 nm^{-1}, the intensities are 10–20 mb/sr eV and, by 40 nm^{-1}, they have fallen to a few tenths of a mb/sr eV. As noted before, there are no special features associated with the band gap. However, it is clear that these intensity profiles do have considerable structure which varies substantially with Q, even between values of Q that are separated only by a reciprocal-lattice vector. If these cross sections could be measured, then the pseudopotential parameters could be determined by using some type of least-squares-fitting procedure. This approach could then be used as an indirect method of determining the "best" set of pseudopotential bands.

Plots of scattering intensities for Q values that are not equivalent to vertical transitions are displayed [Figs. 2(f)–2(h) and 3(f)–3(h)]. Not surprisingly, there is more definite structure for values of Q [diagrams (f) and (g)] that relate to transitions between points of high symmetry than for those that do not [diagrams (h)]. Finally, intensity profiles for silicon for $\mathbf{Q}=(2.5,0.5,0.5)$ are given in Fig. 4, which provides additional evidence, when compared with Fig. 2(g), of the importance of form-factor effects when calculating the relative magnitudes of features in the scattering intensity.

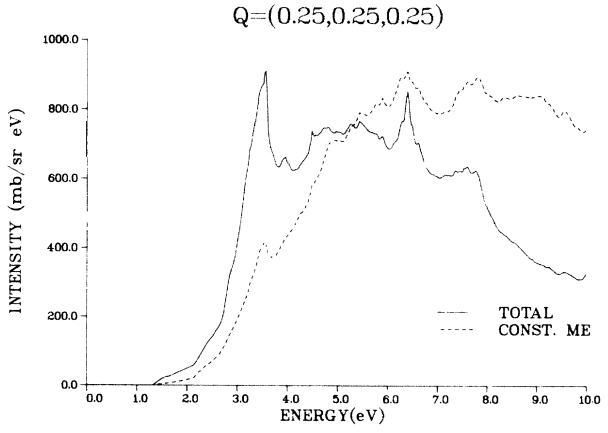

FIG. 1. Comparison of total scattering intensity and joint density of states for germanium with $\mathbf{Q}=(0.25,0.25,0.25)$ in units of $2\pi/a_0$. JDOS results are scaled for comparison.

IV. CONCLUSIONS

The results presented in this paper have helped to resolve some important questions relevant to the feasibility of determining band-structure information from inelastic neutron scattering experiments performed in the electron-volt range. It is clear from the calculations that the band gap in silicon and germanium, and quite possibly all semiconductors, cannot be determined directly from experiment. However, theoretical fits to the structure found in the intensity profiles for different Q's could yield relevant pseudopotential parameters, thereby determining indirectly the band structure and the band gap.

The question of whether experiments can actually detect these relatively small scattering cross sections remains unanswered. Obviously, experiments should be carried out for as small a Q as possible. Conversely, Q

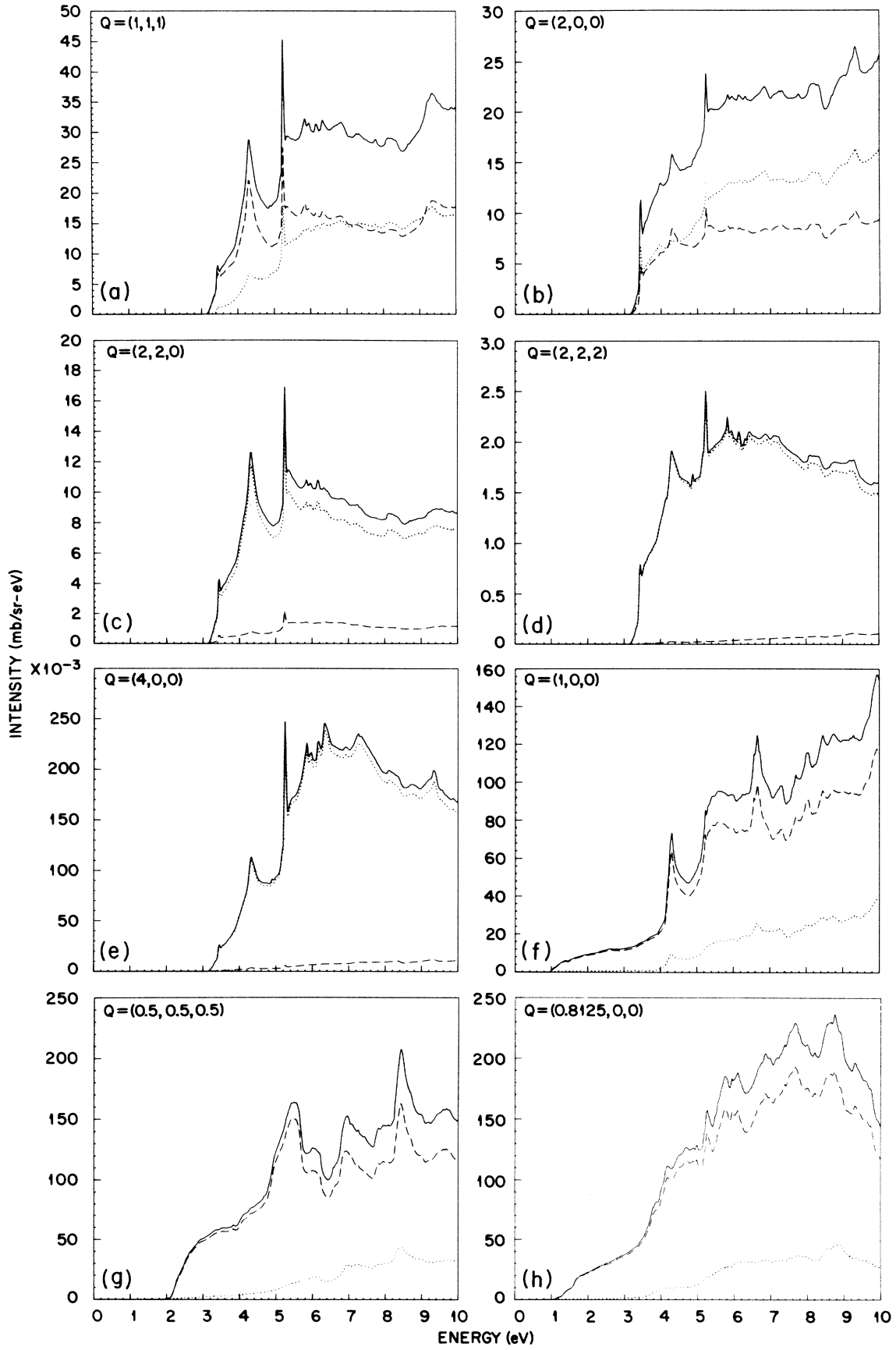

FIG. 2. Results for the total (solid curve), spin (dashed curve), and orbit (dotted curve) scattering for silicon for various values of Q.

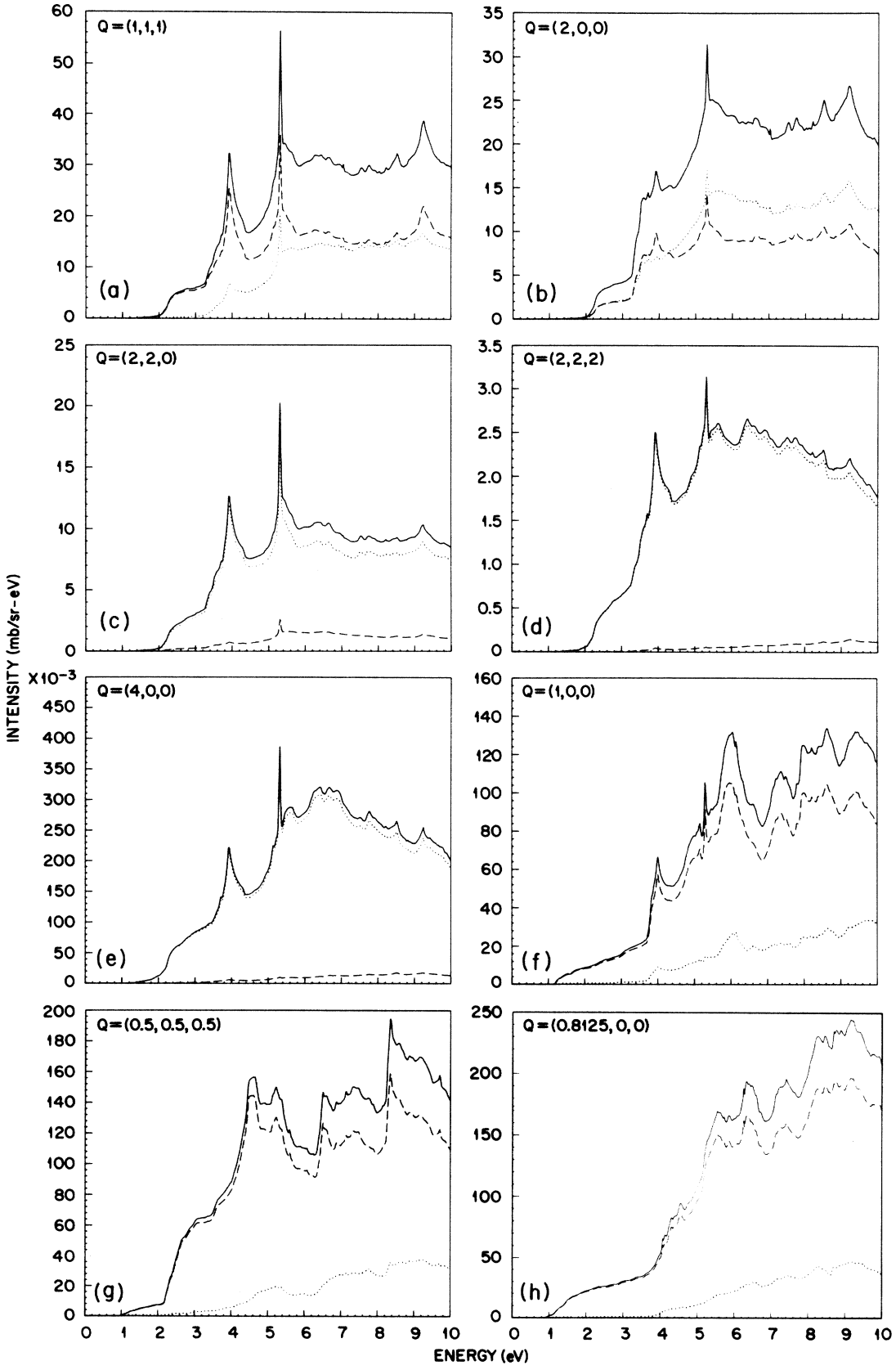

FIG. 3. Results for the total (solid curve), spin (dashed curve), and orbit (dotted curve) scattering for germanium for various values of Q.

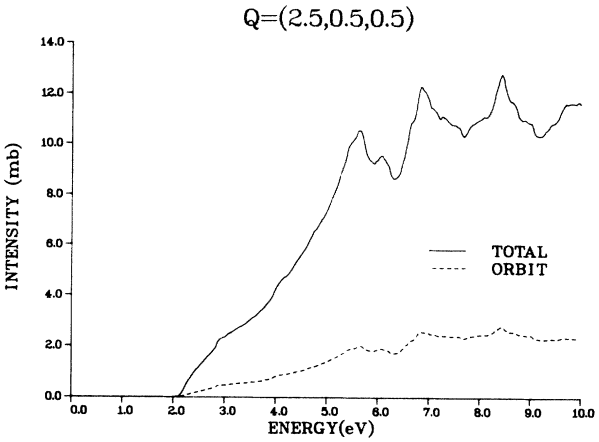

FIG. 4. Results for total scattering and orbital contribution for silicon with $\mathbf{Q}=(2.5,0.5,0.5)$.

must be large enough to satisfy the energy and momentum conservation conditions for experiments where the neutrons have a large energy transfer. The best compromise for silicon and germanium appears to be for Q's in the neighborhood of $2\pi/a_0(2,0,0)$ (≈ 20 nm^{-1}). This, in turn, means that experiments must be able to detect intensities in the range of tens of millibarns.

The real problem lies in the detection of high-energy transfers. From our work it is apparent that energy transfers of about 5 eV are needed in order for experiments to yield useful information. The upper limit with current spectroscopy is anticipated[11] to be about 1 eV.

It appears, therefore, that the proposed experiments for the determination of band-structure information from neutron scattering experiments in the electron-volt range are not going to be possible initially. If the challenge of measuring small cross sections at about 5 eV can be met, neutron scattering could become an important source of information about the band structure of semiconductors.

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