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Inelastic neutron scattering from intermediate-valence compounds in the quasiparticle approximation

D. L. Huber
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706
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We investigate the dynamic structure factor characterizing inelastic neutron scattering from intermediate-valence compounds. Starting with the ionic model of Jefferson and Stevens, we formulate a quasiparticle theory for the high-frequency scattering. At low temperatures the scattering at the center of the zone arises from three processes: excitation across the hybridization gap, excitation from gap modes, which do not hybridize with the conduction electrons to the upper hybrid mode, and excitation from the lower hybrid mode to the gap modes. We calculate the structure factor at $q=0$, neglecting crystal-field splittings. The qualitative features of the temperature and wave-vector dependence of the scattering are discussed. An alternative approach based on a decoupled-mode approximation is proposed for the high-temperature regime. We comment on the relation of the theory to recent theoretical and experimental studies.

I. INTRODUCTION

In recent years the existence of rare-earth and actinide compounds showing intermediate-valence (IV) behavior has stimulated a great number of experimental and theoretical studies which have led to a qualitative and in some instances quantitative understanding of their properties.[1,2] At the risk of some oversimplification we can identify an IV system as one where the rare-earth or actinide ions fluctuate between f^n and f^{n-1} configurations by transferring electrons to a conduction band. Even at high temperatures this transfer takes place sufficiently "infrequently" that the ionic character of the f-electron state is largely preserved.

Although the model of a weakly coupled mixture of f^n and f^{n-1} ions and conduction electrons in thermal equilibrium is often an adequate first approximation for interpreting various thermodynamic measurements,[3] there are dynamic properties which cannot be explained on this basis. For example, the inelastic neutron scattering does not resemble the scattering from an array of ions in static configurations with characteristic sharp crystal-field levels and weak interionic interactions. Rather, the dynamic structure factor usually displays a quasielastic central peak which in some instances has a long tail with structure at frequencies which can be much greater than the crystal-field splittings of the f^n and f^{n-1} manifolds.[4-7]

In this paper we will focus on the aforementioned high-frequency tail. We calculate the dynamic structure factor in an independent-quasiparticle approximation. By neglecting the crystal-field splittings of the f manifolds and limiting the analysis to the center of the Brillouin zone ($q=0$) we are able to obtain an algebraic expression for the structure factor. The restriction to $q=0$ can be circumvented at the expense of numerical calculations. However, the omission of crystal-field effects is a fundamental approximation which is loosely equivalent to having an "instrumental width" which is much greater than the Stark splittings of the relevant manifolds. Since we are investigating only part of the scattering, we cannot make use of the fluctuation-dissipation theorem to obtain the static susceptibility. Furthermore, although the chemical potential can be calculated within our approximation we choose to regard it as part of the input to the analysis. We adopt this position because we believe that while the quasiparticle model is a reasonable approach for characterizing inelastic neutron scattering at low temperatures there is no certainty that it will work equally well for thermodynamic parameters, such as the chemical potential, which are expressed as integrals over the Brillouin zone of various functions of the quasiparticle energies.

The remainder of this paper is divided into five sections. In Sec. II we introduce the model Hamiltonian and present a formal expression for the structure factor. The quasiparticle approximation is outlined in Secs. III and IV. In Sec. V we calculate the structure factor utilizing the quasiparticle model. We also introduce an alternative approximation which is appropriate at high temperatures. We discuss our findings in Sec. VI where we make contact with other theoretical treatments of the problem. We also comment briefly on the experimental situation. The emphasis in this paper is on the development of the formal theory of inelastic neutron scattering from IV compounds; applications to specific systems will be presented elsewhere.

II. HAMILTONIAN AND DYNAMIC STRUCTURE FACTOR

In our analysis of the dynamic structure factor we adopt the microscopic model of Jefferson and Stevens.[8] In their approach one considers only the Hund's-rule ground states of the f^n and f^{n-1} configurations whose levels we designate by λ and μ, respectively. As formulated by Hewson[9] the model Hamiltonian takes the form

$$\mathscr{H}=\sum_i\sum_\lambda \epsilon_\lambda X_{\lambda\lambda}(i)+\sum_i\sum_\mu \epsilon_\mu X_{\mu\mu}(i)+\sum_{k,\sigma}\epsilon_k c^\dagger_{k\sigma}c_{k\sigma} + \frac{1}{\sqrt{N}}\sum_i\sum_{k,\sigma}\sum_{\mu,\lambda}[V^{k\sigma}_{\mu\lambda}e^{ikr_i}X_{\mu\lambda}(i)c^\dagger_{k\sigma}+\text{H.c.}] \ , \tag{2.1}$$

where the sum on i is over the N ions located at $r_i, i=1,\ldots,N$ and H.c. designates the Hermitian conjugate. The symbols ϵ_λ and ϵ_μ denote the energies of the various levels of the f^n and f^{n-1} configurations, respectively, while ϵ_k is the energy of a state in the conduction band. The symbol $V^{k\sigma}_{\mu\lambda}$ represents a matrix element characterizing the strength of the interaction between the conduction electrons and the ions. The former are described by fermion operators $c_{k\sigma}$ and $c^\dagger_{k\sigma}$ for modes with wave vector k and spin σ. The operators $X_{\mu\lambda}(i)$, $X_{\lambda\lambda'}(i)$, and $X_{\mu\mu'}(i)$ refer to the ionic levels; the latter obey the commutation relations

$$[X_{\lambda\lambda'}(i),X_{\mu\mu'}(j)]=0 \tag{2.2}$$

and

$$[X_{\lambda\lambda'}(i),X_{\lambda''\lambda'''}(j)]=\delta_{ij}[\delta_{\lambda'\lambda''}X_{\lambda\lambda'''}(i) - \delta_{\lambda\lambda'''}X_{\lambda''\lambda'}(i)] \ , \tag{2.3}$$

with a similar result for $[X_{\mu\mu'}(i),\ X_{\mu''\mu'''}(j)]$. In the case of $X_{\mu\lambda}(i)$ one has fermionlike behavior, i.e.,

$$\{X_{\mu\lambda}(i),X_{\mu'\lambda'}(j)\}=0 \ , \tag{2.4}$$

$$\{X_{\mu\lambda}(i),X_{\lambda'\mu'}(j)\}=\delta_{ij}[\delta_{\lambda\lambda'}X_{\mu\mu'}(i)+\delta_{\mu\mu'}X_{\lambda'\lambda}(i)] \ , \tag{2.5}$$

where the brackets denote the anticommutator, $\{A,B\}=AB+BA$. We also have

$$[X_{\mu\lambda}(i),X_{\lambda'\lambda''}(j)]=\delta_{ij}\delta_{\lambda\lambda'}X_{\mu\lambda''}(i) \ , \tag{2.6}$$

with a similar result for $[X_{\lambda\mu}(i),X_{\mu'\mu''}(j)]$. In addition the operators $X_{\mu\mu'}(i)$ and $X_{\lambda\lambda'}(i)$ commute with the $c_{k\sigma}$ and $c^\dagger_{k\sigma}$ in contrast to the $X_{\mu\lambda}(i)$ which anticommute with the conduction-electron operators.

The dynamic structure factor, $S_{\alpha\beta}(q,\omega)$, characterizing the inelastic neutron scattering is obtained from the Fourier transform of the correlation function of the spatial transforms of the magnetic-moment operators of the ionic system. We write the structure factor as

$$S_{\alpha\beta}(q,\omega)=\int_{-\infty}^{\infty}dt\,e^{i\omega t}\langle M_\alpha(q,t)M_\beta(-q,0)\rangle \ . \tag{2.7}$$

In (2.7) we have $\alpha,\beta=x,y,z$ while the angular brackets denote a thermal average. The magnetic-moment operator is given by[5]

$$M(q)=\sum_i e^{iqr_i}\left[\sum_{\lambda,\lambda'}M_{\lambda\lambda'}X_{\lambda\lambda'}(i)+\sum_{\mu,\mu'}M_{\mu\mu'}X_{\mu\mu'}(i)\right] , \tag{2.8}$$

where $M_{\lambda\lambda'}$ and $M_{\mu\mu'}$ are matrix elements of $-g_J\mu_B J_{\text{op}}$ within the appropriate Hund's-rule ground states, g_J being the Lande g factor, μ_B the Bohr magneton, and J_{op} the total angular momentum operator.

In our analysis we will find it useful to rewrite (2.7) in the form ($\omega\neq 0$)

$$S_{\alpha\beta}(q,\omega) =\omega^{-2}\int_{-\infty}^{\infty}dt\,e^{i\omega t}\left\langle\frac{dM_\alpha(q,t)}{dt}\frac{dM_\beta(-q,t)}{dt}\right\rangle_{t=0} . \tag{2.9}$$

Equation (2.9) is obtained from (2.7) by integrating twice by parts and then making use of the fact that the correlation function is a function of the separation in time of the two operators. In arriving at (2.9) we have neglected contributions coming from evaluating the correlation functions at $t=\pm\infty$. In general, these contributions are zero in the absence of long-range order, which we assume to be the case. When there is long-range order associated with the wave vector q_0 the magnetic-moment correlation function is proportional to $\langle M_z(q_0)\rangle^2$ at large time separations. This property leads to an elastic scattering term in $S_{zz}(q_0,\omega)$ which is proportional to $\langle M_z(q_0)\rangle^2\delta(\omega)$.

Using the Heisenberg equation of motion ($\hbar=1$),

$$\frac{dM(q,t)}{dt}=-i[M(q,t),\mathscr{H}] \ , \tag{2.10}$$

the time derivatives appearing in (2.9) can be expressed in terms of the X and c operators in the Hamiltonian. Before proceeding we will make the approximation of neglecting the crystal-field splittings of the spin-orbit manifolds. This amounts to taking all of the ϵ_λ (and all of the ϵ_μ) to be equal. Under these conditions we can label the eigenstates of the λ and μ manifolds by the quantum numbers M_J and $M_{J'}$, respectively, where J and J' are the corresponding angular momenta.

Focusing attention on the longitudinal component we have

$$\frac{dM_z}{dt}=\sum_i e^{iqr_i}\left[\sum_\lambda m_\lambda\frac{dX_{\lambda\lambda}(i)}{dt}+\sum_\mu m_\mu\frac{dX_{\mu\mu}(i)}{dt}\right] , \tag{2.11}$$

where m_λ ($\equiv m_{\lambda\lambda}$) is identified with $-g_J\mu_B M_J$ and m_μ ($\equiv M_{\mu\mu}$) with $-g_{J'}\mu_B M_{J'}$. Utilizing the commutation relations we can write the time derivatives in (2.11) in the form

$$\frac{dX_{\lambda\lambda}(i)}{dt}=\frac{-i}{\sqrt{N}}\sum_{k,\sigma}\sum_{\mu'}[e^{-ikr_i}(V^{k\sigma}_{\mu'\lambda})^*c_{k\sigma}X_{\lambda\mu'}(i)-e^{ikr_i}V^{k\sigma}_{\mu'\lambda}X_{\mu'\lambda}(i)c^\dagger_{k\sigma}] , \tag{2.12}$$

$$\frac{dX_{\mu\mu}(i)}{dt}=\frac{-i}{\sqrt{N}}\sum_{k,\sigma}\sum_{\lambda'}[e^{ikr_i}V^{k\sigma}_{\mu\lambda'}X_{\mu\lambda'}(i)c^\dagger_{k\sigma}-e^{-ikr_i}(V^{k\sigma}_{\mu\lambda'})^*c_{k\sigma}X_{\lambda'\mu}(i)] , \tag{2.13}$$

where the asterisk denotes complex conjugate.

Equation (2.11) can be simplified by introducing the operators $X_{k\mu\lambda}$ and $X^\dagger_{k\mu\lambda}$ defined by

$$X_{k\mu\lambda}=\frac{1}{\sqrt{N}}\sum_i e^{ikr_i}X_{\mu\lambda}(i)\ , \tag{2.14}$$

$$X^\dagger_{k\mu\lambda}=\frac{1}{\sqrt{N}}\sum_i e^{-ikr_i}X_{\lambda\mu}(i)\ , \tag{2.15}$$

which obey the anticommutation relations

$$\{X_{k\mu\lambda},X^\dagger_{k'\mu'\lambda'}\}=\frac{1}{N}\sum_i e^{i(k-k')r_i}[\delta_{\lambda\lambda'}X_{\mu\mu'}(i)+\delta_{\mu\mu'}X_{\lambda'\lambda}(i)]\ . \tag{2.16}$$

Utilizing (2.14) and (2.15) we can rewrite (2.11) as

$$\frac{dM_z}{dt}=-i\sum_\lambda m_\lambda\sum_{k,\sigma}\sum_{\mu'}[(V^{k\sigma}_{\mu'\lambda})^*c_{k\sigma}X^\dagger_{k-q\mu'\lambda}-V^{k\sigma}_{\mu'\lambda}X_{k+q\mu'\lambda}c^\dagger_{k\sigma}]$$
$$-i\sum_\mu m_\mu\sum_{k,\sigma}\sum_{\lambda'}[V^{k\sigma}_{\mu\lambda'}X_{k+q\mu\lambda'}c^\dagger_{k\sigma}-(V^{k\sigma}_{\mu\lambda'})^*c_{k\sigma}X^\dagger_{k-q\mu\lambda'}]\ . \tag{2.17}$$

Equations (2.9) and (2.17) are the principal results of this section. It should be noted that were we to take into account the crystal-field splittings there would be additional terms in (2.17) involving $\epsilon_\lambda-\epsilon_{\lambda'}$ and $\epsilon_\mu-\epsilon_{\mu'}$. When the interaction with the conduction electrons is set equal to zero these give rise to δ functions in the structure factor at $\omega=\epsilon_\lambda-\epsilon_{\lambda'}$, etc., which collapse to a term proportional to $\delta(\omega)$ in the absence of crystal-field splittings. Because of this result Eq. (2.9), as written, is only applicable to systems with crystal-field splittings when the frequency is large in comparison with the widths of the λ and μ manifolds. For this reason we will refer to the right-hand side of (2.9) as ${}^{\rm HF}S_{\alpha\beta}(q,\omega)$, the high-frequency (HF) part of the structure factor.

III. QUASIPARTICLE APPROXIMATION

In this section we introduce an independent quasiparticle approximation which will be used in the evaluation of the high-frequency part of the dynamic structure factor. The central feature of the approximation is the representation of $X_{k\mu\lambda}$ and $c_{k\sigma}$ in (2.17) as a linear combination of quasiparticle annihilation operators. In order to develop the approximation we utilize the retarded Green's function,

$$\langle\langle A(t);B(0)\rangle\rangle=-i\Theta(t)\langle\{A(t),B(0)\}\rangle\ , \tag{3.1}$$

where $\Theta(t)$ is the unit step function. We write the transform of $\langle\langle A(t);B(0)\rangle\rangle$ as

$$\langle\langle A;B\rangle\rangle_\omega=\int_{-\infty}^{\infty}dte^{i\omega t}\langle\langle A(t);B(0)\rangle\rangle\ . \tag{3.2}$$

Using the Hamiltonian and the commutation relations given in Sec. II we obtain an equation for $\langle\langle c_{k\sigma};c^\dagger_{k\sigma}\rangle\rangle_\omega$ of the form

$$\omega\langle\langle c_{k\sigma};c^\dagger_{k\sigma}\rangle\rangle_\omega=1+\epsilon_k\langle\langle c_{k\sigma};c^\dagger_{k\sigma}\rangle\rangle_\omega-\sum_{\mu,\lambda}V^{k\sigma}_{\mu\lambda}\langle\langle X_{k\mu\lambda};c^\dagger_{k\sigma}\rangle\rangle_\omega\ . \tag{3.3}$$

Repeating the procedure for $\langle\langle X_{k\mu\lambda};c^\dagger_{k\sigma}\rangle\rangle_\omega$ we obtain

$$\omega\langle\langle X_{k\mu\lambda};c^\dagger_{k\sigma}\rangle\rangle_\omega=\epsilon_0\langle\langle X_{k\mu\lambda};c^\dagger_{k\sigma}\rangle\rangle_\omega-\sum_{\mu',\lambda}\sum_{k',\sigma'}(V^{k'\sigma'}_{\mu'\lambda'})^*\langle\langle c_{k'\sigma'}\{X_{k\mu\lambda},X^\dagger_{k'\mu'\lambda'}\};c^\dagger_{k\sigma}\rangle\rangle_\omega\ , \tag{3.4}$$

where $\epsilon_0=\epsilon_\lambda-\epsilon_\mu$ is the difference in energy between the Hund's-rule ground states of the f^n and f^{n-1} configurations.

At this point the equations of motion are decoupled by replacing the anticommutator on the right-hand side of (3.4) by its thermal average which according to (2.16) is equal to $\delta_{kk'}\delta_{\mu\mu'}\delta_{\lambda\lambda'}(\langle X_{\mu\mu}\rangle+\langle X_{\lambda\lambda}\rangle)$, all sites being equivalent.[10] Thus in place of (3.4) we have

$$\omega\langle\langle X_{k\mu\lambda};c^\dagger_{k\sigma}\rangle\rangle_\omega=\epsilon_0\langle\langle X_{k\mu\lambda};c^\dagger_{k\sigma}\rangle\rangle_\omega-\sum_{\sigma'}(V^{k\sigma'}_{\mu\lambda})^*A_{\mu\lambda}\langle\langle c_{k\sigma'};c^\dagger_{k\sigma}\rangle\rangle_\omega\ , \tag{3.5}$$

where

$$A_{\mu\lambda}=\langle X_{\mu\mu}\rangle+\langle X_{\lambda\lambda}\rangle\ . \tag{3.6}$$

Further discussion of this approximation is left to Appendix A where it is shown that the leading correction is of order V/W, where W is the width of the conduction band, and vanishes identically when there is full rotational symmetry about the rare-earth site. Generally speaking the approximation is appropriate only at low temperatures, $k_BT\ll V^2/W$, where thermal fluctuations have only a small effect on the phase coherence of the hybrid modes.

We note that if we make the identification

$$X_{k\mu\lambda}\to A^{1/2}_{\mu\lambda}c_{k\mu\lambda}\ , \tag{3.7}$$

then Eqs. (3.3) and (3.5) are formally equivalent to the equations for the Green's functions associated with the fermion operators $c_{k\sigma}$ and $c_{k\mu\lambda}$ which are obtained from the effective Hamiltonian,

$$\mathcal{H}_{\rm eff}=\sum_{k,\mu,\lambda}\epsilon_0c^\dagger_{k\mu\lambda}c_{k\mu\lambda}+\sum_{k,\sigma}\epsilon_kc^\dagger_{k\sigma}c_{k\sigma}+\sum_k\sum_{\mu,\lambda,\sigma}(\tilde{V}^{k\sigma}_{\mu\lambda}c_{k\mu\lambda}c^\dagger_{k\sigma}+\text{H.c.})\ , \tag{3.8}$$

where $\tilde{V}^{k\sigma}_{\mu\lambda}$ denotes the temperature-dependent interaction

$$\tilde{V}^{k\sigma}_{\mu\lambda}=V^{k\sigma}_{\mu\lambda}A^{1/2}_{\mu\lambda} . \tag{3.9}$$

The essence of the quasiparticle approximation is contained in (3.7) and (3.8). That is to say, in the evaluation of ${}^{\mathrm{HF}}S(q,\omega)$ we make the replacement (3.7) and then use the effective Hamiltonian to evaluate the resulting fermion correlation function. Although $A_{\mu\lambda}$, like the chemical potential, can be evaluated within the quasiparticle model we choose to regard it, too, as input to the calculation. However, we note in passing that to zero order in V, $A_{\mu\lambda}$ is given by[9]

$$A_{\mu\lambda}=\frac{e^{\beta(\epsilon_0-\mu)}+1}{(2J+1)+(2J'+1)e^{\beta(\epsilon_0-\mu)}} , \tag{3.10}$$

where μ is the chemical potential and $\beta=(k_BT)^{-1}$. Equation (3.10) shows that in the limit $k_BT\ll|\epsilon_0-\mu|$, $A_{\mu\lambda}\to(2J+1)^{-1}$ or $(2J'+1)^{-1}$ depending on the sign of $\epsilon_0-\mu$. Thus at low temperatures $A_{\mu\lambda}$ is dominated by the contribution from a single configuration ($\epsilon_0\neq\mu$).

It must be stressed that the replacement (3.7) is intended only for correlation functions which are either linear or bilinear in operators of the type $X_{k\mu\lambda}$. When applied to more general functions, e.g.,

$$\langle X^\dagger_1(t)X_2(t)X^\dagger_3(0)X_4(0)\rangle ,$$

it leads to incorrect results even in the limit $V\to0$.[9] For this reason we cannot use it to evaluate $S(q,\omega)$ directly from Eq. (2.7). However, starting from (2.9) we obtain correlation functions of the type

$$\langle c_1(t)X^\dagger_2(t)c^\dagger_3(0)X_4(0)\rangle$$

involving only pairs of the $X_{k\mu\lambda}$ in which case our replacement is exact for $V=0$. For $V\neq0$ we evaluate the correlation functions in an approach which is equivalent to (implicitly) factorizing them into expressions which are either linear or bilinear in the $X_{k\mu\lambda}$ and then making the replacement. Thus we have

$$\begin{aligned}\langle c_\sigma(t)X^\dagger_{\mu\lambda}(t)X_{\mu'\lambda'}(0)c^\dagger_\sigma(0)\rangle&\to(A_{\mu\lambda}A_{\mu'\lambda'})^{1/2}\langle c_\sigma(t)c^\dagger_{\mu\lambda}(t)c_{\mu'\lambda'}(0)c^\dagger_\sigma(0)\rangle\\&\to(A_{\mu\lambda}A_{\mu'\lambda'})^{1/2}\langle c_\sigma(t)c^\dagger_\sigma(0)\rangle\langle c^\dagger_{\mu\lambda}(t)c_{\mu'\lambda'}(0)\rangle ,\end{aligned} \tag{3.11}$$

which is equivalent to

$$\begin{aligned}\langle c_\sigma(t)X^\dagger_{\mu\lambda}(t)X_{\mu'\lambda'}(0)c^\dagger_\sigma(0)\rangle&\to\langle c_\sigma(t)c^\dagger_\sigma(0)\rangle\langle X^\dagger_{\mu\lambda}(t)X_{\mu'\lambda'}(0)\rangle\\&\to(A_{\mu\lambda}A_{\mu'\lambda'})^{1/2}\langle c_\sigma(t)c^\dagger_\sigma(0)\rangle\langle c^\dagger_{\mu\lambda}(t)c_{\mu'\lambda'}(0)\rangle .\end{aligned} \tag{3.12}$$

IV. QUASIPARTICLE SPECTRUM

In this section we analyze the quasiparticle Hamiltonian (3.8). Since the effective Hamiltonian is bilinear in the fermion operators it is convenient to use equation-of-motion techniques instead of Green's functions. The annihilation operators for the normal modes, α_k, are written as follows:

$$\alpha_k=\sum_\mu u_{k\sigma}c_{k\sigma}+\sum_{\mu,\lambda}u_{k\mu\lambda}c_{k\mu\lambda} . \tag{4.1}$$

From the requirement $\{\alpha_k,\alpha^\dagger_k\}=1$ we obtain the normalization condition for the expansion coefficients,

$$\sum_\sigma|u_{k\sigma}|^2+\sum_{\mu,\lambda}|u_{k\mu\lambda}|^2=1 . \tag{4.2}$$

The stipulation that α_k be a normal-mode operator is equivalent to the equation,

$$\begin{aligned}\omega\left[\sum_\sigma u_{k\sigma}c_{k\sigma}+\sum_{\mu,\lambda}u_{k\mu\lambda}c_{k\mu\lambda}\right]&\\=\sum_\sigma u_{k\sigma}[c_{k\sigma},\mathscr{H}_{\mathrm{eff}}]+\sum_{\mu,\lambda}u_{k\mu\lambda}[c_{k\mu\lambda},\mathscr{H}_{\mathrm{eff}}] .&\end{aligned} \tag{4.3}$$

Evaluating the commutators in (4.3) we find

$$\begin{aligned}\omega\left[\sum_\sigma u_{k\sigma}c_{k\sigma}+\sum_{\mu,\lambda}u_{k\mu\lambda}c_{k\mu\lambda}\right]&\\=\sum_\sigma u_{k\sigma}\left[\epsilon_kc_{k\sigma}-\sum_{\mu,\lambda}\tilde{V}^{k\sigma}_{\mu\lambda}c_{k\mu\lambda}\right]&\\+\sum_{\mu,\lambda}u_{k\mu\lambda}\left[\epsilon_0c_{k\mu\lambda}-\sum_\sigma(\tilde{V}^{k\sigma}_{\mu\lambda})^*c_{k\sigma}\right] ,&\end{aligned} \tag{4.4}$$

which is equivalent to the algebraic equations,

$$(\omega-\epsilon_k)u_{k\sigma}=-\sum_{\mu,\lambda}(\tilde{V}^{k\sigma}_{\mu\lambda})^*u_{k\mu\lambda} , \tag{4.5a}$$

$$(\omega-\epsilon_0)u_{k\mu\lambda}=-\sum_\sigma\tilde{V}^k_{\mu\lambda}u_{k\sigma} . \tag{4.5b}$$

Equations (4.5a) and (4.5b) are a set of $(2J+1)(2J'+1)+2$ linear equations. Four of the eigenmodes are hybrid in character, being linear combinations of $c_{k\sigma}$ and $c_{k\mu\lambda}$. The remaining $(2J+1)(2J'+1)-2$ modes have energy ϵ_0 and involve only the $c_{k\mu\lambda}$. They are orthogonal to the hybrid modes and can be made orthogonal to each other. We refer to these modes as gap excitations since their energy lies in the hybridization gap.

In order to evaluate the energies of the hybrid modes we use (4.5b) in (4.5a) obtaining the two equations ($\sigma=\pm$):

$$\begin{aligned}(\omega-\epsilon_0)(\omega-\epsilon_k)u_{k+}=&\left[\sum_{\mu,\lambda}|\tilde{V}^{k+}_{\mu\lambda}|^2\right]u_{k+}\\&+\left[\sum_{\mu,\lambda}(\tilde{V}^{k+}_{\mu\lambda})^*\tilde{V}^{k-}_{\mu\lambda}\right]u_{k-} ,\end{aligned} \tag{4.6a}$$

$$\begin{aligned}(\omega-\epsilon_0)(\omega-\epsilon_k)u_{k-}=&\left[\sum_{\mu,\lambda}|\tilde{V}^{k-}_{\mu\lambda}|^2\right]u_{k-}\\&+\left[\sum_{\mu,\lambda}(\tilde{V}^{k-}_{\mu\lambda})^*\tilde{V}^{k+}_{\mu\lambda}\right]u_{k+} .\end{aligned} \tag{4.6b}$$

From inversion and time-reversal symmetries it follows

that

$$\sum_{\mu,\lambda} |\tilde{V}^{k+}_{\mu\lambda}|^2=\sum_{\mu,\lambda} |\tilde{V}^{k-}_{\mu\lambda}|^2\equiv |\tilde{V}_k|^2 . \tag{4.7}$$

Equations (4.6a) and (4.6b) can be diagonalized with the resulting eigenvalues

$$\omega_k=\tfrac{1}{2}(\epsilon_k+\epsilon_0)\pm\tfrac{1}{2}[(\epsilon_k-\epsilon_0)^2+4A_k^2]^{1/2} , \tag{4.8a}$$

$$\omega_k=\tfrac{1}{2}(\epsilon_k+\epsilon_0)\pm\tfrac{1}{2}[(\epsilon_k-\epsilon_0)^2+4B_k^2]^{1/2} , \tag{4.8b}$$

where

$$A_k^2=|\tilde{V}_k|^2+\left|\sum_{\mu,\lambda}(\tilde{V}^{k+}_{\mu\lambda})^*\tilde{V}^{k-}_{\mu\lambda}\right| , \tag{4.9}$$

and

$$B_k^2=|\tilde{V}_k|^2-\left|\sum_{\mu,\lambda}(\tilde{V}^{k+}_{\mu\lambda})^*V^{k-}_{\mu\lambda}\right| . \tag{4.10}$$

The corresponding eigenvectors are linear combinations of u_{k+}, u_{k-}, and $u_{k\mu\lambda}$.

In the analysis of the structure factor we will make the simplifying approximation of neglecting the second term on the right-hand side of (4.9) and (4.10). When this is done u_{k+} is decoupled from u_{k-}, and the hybrid modes become two-fold degenerate with energies

$$\omega_k^\nu=\tfrac{1}{2}(\epsilon_k+\epsilon_0)\pm\tfrac{1}{2}[(\epsilon_k-\epsilon_0)^2+4|\tilde{V}_k|^2] \quad (\nu=1-4) . \tag{4.11}$$

In this limit the coefficients $u_{k\mu\lambda}$ in Eq. (4.1) are given by

$$u^\nu_{k\mu\lambda}=-\tilde{V}^{k\sigma}_{\mu\lambda}u^\nu_{k\sigma}/(\omega_k^\nu-\epsilon_0) . \tag{4.12}$$

Using (4.12) in (4.2) we obtain

$$u^\nu_{k\sigma}=[1+|\tilde{V}_k|^2/(\omega_k^\nu-\epsilon_0)^2]^{-1/2} , \tag{4.13}$$

where it is understood that $\nu=1,2$ are the two hybrid modes associated with $\sigma=+$ and $\nu=3,4$ are the two modes associated with $\sigma=-$ (i.e., $u^1_{k-}=u^2_{k-}=u^3_{k+}=u^4_{k+}=0$, $\omega^1_k=\omega^3_k,\omega^2_k=\omega^4_k$) .

Since our diagonalization is equivalent to performing a unitary transformation on $\mathscr{H}_{\rm eff}$ we can express $c_{k\sigma}$ and $c_{k\mu\lambda}$ as a linear combination of the α_k, $\nu=1,\ldots,(2J+1)(2J'+1)+2$, by means of the equations,

$$c_{k\sigma}=\sum_\nu (u^\nu_{k\sigma})^*\alpha^\nu_k , \tag{4.14a}$$

$$c^\nu_{k\mu\lambda}=\sum_\nu (u^\nu_{k\mu\lambda})^*\alpha^\nu_k , \tag{4.14b}$$

where $u^\nu_{k\lambda}$ and $u^\nu_{k\sigma}$, are given by (4.12) and (4.13), respectively, for the hybrid modes (in an approximation where $A_k^2=B_k^2=|\tilde{V}_k|^2$), while in the case of the gap modes $u^\nu_{k\sigma}=0$.

It was mentioned above that we can calculate the chemical potential in the quasiparticle approximation. It is determined by the condition that there be a total of nN electrons in the conduction and f states,[9] i.e.,

$$\sum_{k,\sigma}\langle c^\dagger_{k\sigma}c_{k\sigma}\rangle+nN\sum_\lambda\langle X_{\lambda\lambda}\rangle +(n-1)N\sum_\mu\langle X_{\mu\mu}\rangle=nN . \tag{4.15}$$

The details of the calculation, which utilizes the spectral representation of the Green's function, are developed in Appendix B.

V. CORRELATION FUNCTIONS AND DYNAMIC STRUCTURE FACTOR

In this section we use the results of Secs. II—IV to calculate the high-frequency part of the structure factor [Eq. (2.9)]. As noted we will limit the quantitative analysis to $q=0$ where we can obtain algebraic expressions for ${}^{\rm HF}S(0,\omega)$. In order to minimize the algebra we will consider only the case where the ground state of the f^{n-1} configuration is a singlet (e.g., Eu). Under these conditions we have

$$\left\langle\frac{dM_z(0,t)}{dt}\left[\frac{dM_z(0,t)}{dt}\right]_{t=0}\right\rangle=-\sum_{\lambda,\lambda'}m_\lambda m_{\lambda'}\sum_{k,\sigma}\sum_{k',\sigma'}\langle[(\tilde{V}^{k\sigma}_{\mu\lambda})^*c_{k\sigma}(t)c^\dagger_{k\mu\lambda}(t)-\tilde{V}^{k\sigma}_{\mu\lambda}c_{k\mu\lambda}(t)c^\dagger_{k\sigma}(t)] \times[(\tilde{V}^{k'\sigma'}_{\mu\lambda'})^*c_{k'\sigma'}(0)c^\dagger_{k'\mu\lambda'}(0)-\tilde{V}^{k'\sigma'}_{\mu\lambda'}c_{k'\mu\lambda'}(0)c^\dagger_{k'\sigma'}(0)]\rangle , \tag{5.1}$$

where we have made the replacement indicated by (3.7) and (3.9) (cf. the discussion at the end of Sec. III).

We proceed by expanding $c_{k\sigma}$ and $c_{k\mu\lambda}$ in terms of normal-mode operators using (4.14a) and (4.14b). The resulting expression involves fermion functions of the form

$$\langle\alpha^\nu_k(t)\alpha^{\nu'\dagger}_k(t)\alpha^{\nu''}_{k''}(0)\alpha^{\nu'''\dagger}_{k'''}(0)\rangle ,$$

which reduces to

$$\delta_{kk'}\delta_{\nu\nu'}\delta_{\nu''\nu'''}\langle\alpha^{\nu'\dagger}_k(t)\alpha^{\nu'}_k(0)\rangle\langle\alpha^\nu_k(t)\alpha^{\nu''\dagger}_k(0)\rangle . \tag{5.2}$$

[We omit the term involving the pairing of $\alpha^\nu_k\alpha^{\nu'\dagger}_k$ as it vanishes if we first calculate ${}^{\rm HF}S(q,\omega)$ and then take the limit $q\to 0$.]

From (5.2) it follows that the quasiparticle contribution to ${}^{\rm HF}S(0,\omega)$ is a sum of terms of the type

$$\langle\alpha^{\nu'\dagger}_k\alpha^{\nu'}_k\rangle\langle\alpha^\nu_k\alpha^{\nu\dagger}_k\rangle\delta(\omega+\omega^{\nu'}_k-\omega^\nu_k) .$$

The high-frequency scattering describes the destruction of a quasiparticle in mode $\nu' k'$ with energy $\omega_{k'}^{\nu'}$ and the creation of a quasiparticle in mode νk with energy $\omega_k^\nu = \omega + \omega_{k'}^{\nu'}$. The equilibrium averages are given by Fermi distributions

$$\langle \alpha_k^{\nu\dagger} \alpha_k^\nu \rangle = n_k^\nu = (e^{\beta(\omega_k^\nu - \mu)} + 1)^{-1} , \tag{5.3}$$

$$\langle \alpha_k^\nu \alpha_k^{\nu\dagger} \rangle = 1 - n_k^\nu = (e^{-\beta(\omega_k^\nu - \mu)} + 1)^{-1} . \tag{5.4}$$

When $q = 0$ there will be three types of transitions contributing to the scattering at high frequencies; one of these involves two hybrid modes, the other two a hybrid mode and a gap mode. We first consider the former. Using (4.14a) and (4.14b) we can write the (lower) hybrid to (upper) hybrid contribution to the structure factor in the form

$$\begin{aligned} {}^{\mathrm{HF}}S^{hh}(0,\omega) = (2\pi/\omega^2) \sum_{\lambda,\lambda'} m_\lambda m_{\lambda'} \sum_{k,\sigma} [& (\tilde{V}_{\mu\lambda}^{k\sigma})^* \tilde{V}_{\mu\lambda'}^{k\sigma} u_{k\mu\lambda}^2 (u_{k\mu\lambda'}^2)^* \mid u_{k\sigma}^1 \mid^2 + \tilde{V}_{\mu\lambda}^{k\sigma} (\tilde{V}_{\mu\lambda'}^{k\sigma})^* \mid u_{k\sigma}^2 \mid^2 (u_{k\mu\lambda}^1)^* u_{k\mu\lambda'}^1 \\ & - (\tilde{V}_{\mu\lambda}^{k\sigma})^* (\tilde{V}_{\mu\lambda'}^{k\sigma})^* u_{k\mu\lambda}^2 (u_{k\sigma}^2)^* u_{k\mu\lambda'}^1 (u_{k\sigma}^1)^* - \tilde{V}_{\mu\lambda}^{k\sigma} \tilde{V}_{\mu\lambda'}^{k\sigma} u_{k\sigma}^2 (u_{k\mu\lambda'}^2)^* (u_{k\mu\lambda}^1)^* u_{k\sigma}^1] \\ & \times n_k^2 (1 - n_k^1) \delta(\omega + \omega_k^2 - \omega_k^1) , \end{aligned} \tag{5.5}$$

where $\nu = 1$ refers to the upper hybrid mode with energy $\frac{1}{2}(\epsilon_k + \epsilon_0) + \frac{1}{2}[(\epsilon_k - \epsilon_0)^2 + 4 \mid \tilde{V}_k \mid^2]^{1/2}$ while $\nu = 2$ specifies the lower mode with energy $\frac{1}{2}(\epsilon_k + \epsilon_0) - \frac{1}{2}[(\epsilon_k - \epsilon_0)^2 + 4 \mid \tilde{V}_k \mid^2]^{1/2}$. Using (4.12) and (4.13) we can reduce (5.5) to

$${}^{\mathrm{HF}}S^{hh}(0,\omega) = (2\pi/\omega^2) \sum_{\lambda,\lambda'} m_\lambda m_{\lambda'} \sum_{k,\sigma} \mid \tilde{V}_{\mu\lambda}^{k\sigma} \mid^2 \mid \tilde{V}_{\mu\lambda'}^{k\sigma} \mid^2 \mid \tilde{V}_k \mid^{-2} n_k^2 (1 - n_k^1) \delta(\omega + \omega_k^2 - \omega_k^1) . \tag{5.6}$$

If we overlook the k dependence of the matrix elements of the ion-conduction electron interaction in the energy region of interest we can convert the sum over k in (5.6) to an integral over the density of states of the unperturbed conduction band, $\rho_0(\epsilon)$, viz.,

$$\sum_k h(\epsilon_k) \rightarrow \int \rho_0(\epsilon) h(\epsilon) d\epsilon . \tag{5.7}$$

We finally obtain ($\omega^2 \geq 4 \mid \tilde{V} \mid^2$)

$${}^{\mathrm{HF}}S^{hh}(0,\omega) = C_{hh} [\omega E(\omega)]^{-1} [\rho_0(\epsilon_0 + E(\omega)) f_a (1 - f_b) + \rho_0(\epsilon_0 - E(\omega)) f_c (1 - f_d)] , \tag{5.8}$$

where

$$E(\omega) = (\omega^2 - 4 \mid \tilde{V}_k \mid^2)^{1/2} , \tag{5.9}$$

and

$$f_a = \{\exp \beta[\epsilon_0 + \tfrac{1}{2}E(\omega) - \tfrac{1}{2}\omega - \mu] + 1\}^{-1} , \tag{5.10}$$

$$f_b = \{\exp \beta[\epsilon_0 + \tfrac{1}{2}E(\omega) + \tfrac{1}{2}\omega - \mu] + 1\}^{-1} . \tag{5.11}$$

$$f_c = \{\exp \beta[\epsilon_0 - \tfrac{1}{2}E(\omega) - \tfrac{1}{2}\omega - \mu] + 1\}^{-1} , \tag{5.12}$$

$$f_d = \{\exp \beta[\epsilon_0 - \tfrac{1}{2}E(\omega) + \tfrac{1}{2}\omega - \mu] + 1\}^{-1} , \tag{5.13}$$

with C_{hh} a frequency-independent parameter proportional to $\tilde{V}^2$.

The contribution to the scattering from the destruction of a gap mode and the creation of an upper hybrid mode takes the form

$$\begin{aligned} {}^{\mathrm{HF}}S^{hg}(0,\omega) = (2\pi/\omega^2) \sum_{\lambda,\lambda'} m_\lambda m_{\lambda'} \sum_{k,\sigma} \sum_{\nu} & (\tilde{V}_{\mu\lambda}^{k\sigma})^* \tilde{V}_{\mu\lambda'}^{k\sigma} u_{k\mu\lambda}^\nu (u_{k\mu\lambda'}^\nu)^* \mid u_{k\sigma}^1 \mid^2 (e^{\beta(\epsilon_0 - \mu)} + 1)^{-1} \\ & \times (e^{-\beta(\omega_k^1 - \mu)} + 1)^{-1} \delta(\omega + \epsilon_0 - \omega_k^1) , \end{aligned} \tag{5.14}$$

where the sum on ν is over the $2J - 2$ gap modes. As in (5.8) we can convert the sum to an integral obtaining

$${}^{\mathrm{HF}}S^{hg}(0,\omega) = C_{hg} \omega^{-2} \rho_0(\epsilon_0 - (\mid \tilde{V} \mid^2 - \omega^2)/\omega) (e^{-\beta(\epsilon_0 - \mu)} + 1)^{-1} (e^{-\beta(\epsilon_0 + \omega - \mu)} + 1)^{-1} , \tag{5.15}$$

where C_{hg} is independent of frequency.

A similar analysis for the lower hybrid to gap scattering leads to

$$\begin{aligned} {}^{\mathrm{HF}}S^{gh}(0,\omega) = (2\pi/\omega^2) \sum_{\lambda,\lambda'} m_\lambda m_{\lambda'} \sum_{k,\sigma} \sum_{\nu} & \tilde{V}_{\mu\lambda}^{k\sigma} (\tilde{V}_{\mu\lambda'}^{k\sigma})^* \mid u_{k\sigma}^2 \mid (u_{k\mu\lambda}^\nu)^* u_{k\mu\lambda'}^\nu (e^{\beta(\omega_k^2 - \mu)} + 1)^{-1} \\ & \times (e^{-\beta(\epsilon_0 - \mu)} + 1)^{-1} \delta(\omega + \omega_k^2 - \epsilon_0) , \end{aligned} \tag{5.16}$$

which becomes

$$^{HF}S^{gh}(0,\omega)=C_{gh}\omega^{-2}\rho_0(\epsilon_0+(|\tilde{V}|^2-\omega^2)/\omega)(e^{\beta(\epsilon_0-\omega-\mu)}+1)^{-1}(e^{-\beta(\epsilon_0-\mu)}+1)^{-1}\,, \tag{5.17}$$

where $C_{gh}\approx C_{hg}$.

The quasiparticle contribution to the inelastic scattering is given by the sum $^{HF}S^{hh}+{}^{HF}S^{hg}+{}^{HF}S^{gh}$. Since the frequencies of the gap modes are independent of wave vector the hybrid-to-gap and gap-to-hybrid scattering at fixed ω is only weakly dependent on wave vector. In contrast, the hybrid-to-hybrid scattering is predicted to have a stronger q dependence. Moreover, when $q\neq 0$ inelastic *intraband* transitions, $\omega_k^\nu\rightarrow\omega_{k+q}^\nu$, involving the hybrid modes will also contribute to scattering at finite ω.

As mentioned, the quasiparticle model is appropriate at low temperatures. At high temperatures, $k_BT\gg|\tilde{V}|^2\rho_0(\epsilon_0)$, the thermal fluctuations will destroy the phase coherence between the electronic and ionic contributions to the wave functions of the hybrid modes. Under these conditions a more reasonable approach is to evaluate ^{HF}S in a decoupled-mode approximation where correlation functions of the form

$$\langle c_{k\sigma}(t)X_{k\lambda\mu}(t)X^\dagger_{k'\mu\lambda'}(0)c_{k'\sigma}(0)\rangle$$

are evaluated treating c and X as independent operators. This leads to the expression

$$\begin{aligned}^{HF}S^0(0,\omega)=(2\pi/\omega^2)\sum_\lambda m_\lambda^2\sum_{k,\sigma}|\tilde{V}^{k\sigma}_{\mu\lambda}|^2[&(e^{\beta(\epsilon_0-\mu)}+1)^{-1}(e^{-\beta(\epsilon_k-\mu)}+1)^{-1}\delta(\omega+\epsilon_0-\epsilon_k)\\&+(e^{-\beta(\epsilon_0-\mu)}+1)^{-1}(e^{\beta(\epsilon_k-\mu)}+1)^{-1}\delta(\omega+\epsilon_k-\epsilon_0)]\,,\end{aligned} \tag{5.18}$$

which reduces to

$$\begin{aligned}^{HF}S^0(0,\omega)=C_0\omega^{-2}[&\rho_0(\epsilon_0+\omega)(e^{\beta(\epsilon_0-\mu)}+1)^{-1}(e^{-\beta(\epsilon_0+\omega-\mu)}+1)^{-1}\\&+\rho_0(\epsilon_0-\omega)(e^{-\beta(\epsilon_0-\mu)}+1)^{-1}(e^{\beta(\epsilon_0-\omega-\mu)}+1)^{-1}]\,,\end{aligned} \tag{5.19}$$

where C_0 is a frequency-independent parameter $\approx C_{gh}+C_{hh}\approx C_{hq}+C_{hh}$.

A comparison of (5.19) with (5.8), (5.15), and (5.17) shows that when $\omega\gg|\tilde{V}|$ the quasiparticle and decoupled-mode results become the same. Only when $\omega\lesssim|\tilde{V}|$ do the particular coherence effects associated with hybridization become significant. Moreover, apart from the k dependence of the matrix elements implicit in C_0, $^{HF}S^0(q,\omega)$ is independent of wave vector. Finally, we note that although the expressions obtained for $^{HF}S(0,\omega)$ pertain to a system where $J'=0$ they hold equally well for the general case provided appropriate C_{hh}, C_{hg}, C_{gh}, and C_0 are used.

VI. DISCUSSION

The goal of this paper has been to outline a theory for the high-frequency component of the inelastic neutron scattering from IV compounds. It must be emphasized that the theory applies only to the regime $\omega\gg\Delta_J,\Delta_{J'}$ where Δ_J and $\Delta_{J'}$ are measures of the crystal-field splittings of the J and J' manifolds, respectively. The theory focuses on the evaluation of correlation functions of the type

$$\langle X_{k\mu\lambda}(t)c^\dagger_{k\sigma}(t)X_{k'\lambda'\mu'}(0)c^\dagger_{k'\sigma'}(0)\rangle\,.$$

To describe the scattering at low temperatures we introduce a quasiparticle model. The quasiparticle Hamiltonian (3.8) should not be confused with the true Hamiltonian (2.1). The former is defined so as to have the property that it leads to the same set of equations for the Green's functions $\langle\langle X_{\mu\lambda};c^\dagger_\sigma\rangle\rangle$, $\langle\langle c_\sigma;c^\dagger_\sigma\rangle\rangle$, and $\langle\langle X_{\mu\lambda};X^\dagger_{\mu\lambda}\rangle\rangle$ as are obtained from (2.1) with our approximate decoupling scheme. The distinction between (2.1) and (3.8) is further illustrated by the fact that the equation for the chemical potential, (4.15), is not equivalent to the requirement that there be nN quasiparticle in the system. Rather, the chemical potential of the quasiparticles is equated to that of the IV system.

Our low-temperature results are summarized in Eqs. (5.8), (5.15), and (5.17) which display $^{HF}S(0,\omega)$ as a sum of terms associated with the hybrid-to-hybrid, gap-to-hybrid, and hybrid-to-gap transitions. In all cases the scattering depends on $\epsilon_0-\mu$ and the density of states of the conduction band. The hybrid-to-hybrid scattering is characterized by a threshold singularity at the hybridization gap $2|\tilde{V}|$. In the gap-to-hybrid and hybrid-to-gap scattering the threshold is determined by the lower and upper limits of the conduction band, respectively.

At higher temperatures, $k_BT\gg|\tilde{V}|^2\rho_0(\epsilon_0)$, the effects of hybridization disappear. The scattering is then predicted to follow the decoupled-mode result, Eq. (5.19), as a first approximation. Of the various expressions characterizing the scattering in different regimes only the hybrid-to-hybrid and intraband-to-hybrid scattering will show a significant dependence on wave vector.

The theory we have outlined is not intended to apply to the central peak regime where intramanifold transitions contribute to the scattering. However, we note that $^{HF}S(q,\omega)$ is proportional to ω^{-2} so that aside from threshold effects it will tend to peak at low frequencies. This is evident in (5.19) which reduces to

$$^{HF}S^0(0,\omega)\approx(C_0/2\omega^2)\rho_0(\epsilon_0)\cosh^{-2}[\beta(\epsilon_0-\mu)/2]\,, \tag{6.1}$$

as $\omega \to 0$. As a consequence at high temperatures ${}^{\mathrm{HF}}S$ will appear as a tail to the Lorentzian peak characterizing the quasielastic scattering.

As mentioned, there have been a number of recent theories of the dynamic susceptibility of IV compounds.[11–18] These can be divided into two categories. In Refs. 11–15 the analysis is based on the periodic Anderson model whereas in Refs. 16–18 the calculations are carried out with a Hamiltonian similar to (2.1). Although there are points of correspondence between the hybrid-to-hybrid scattering and the results obtained with the periodic Anderson model (cf. the threshold at the hybridization gap shown in Fig. 12 of Ref. 15) the Anderson model does not provide a very satisfactory starting point for realistic calculations of the properties of IV compounds.[19] As emphasized by Anderson[20] the orbital degeneracy of the f states plays an important role. In our analysis this degeneracy is reflected in the appearance of the $(2J+1)(2J'+1)-2$ gap modes which do not hybridize with the conduction electrons.

The work reported in Refs. 16 and 17 is complementary to our own in that it focuses on the width of the central peak. The calculation is carried using an approach equivalent to our decoupled-mode approximation. The resulting expression for the width is proportional to $\cosh^{-2}(\beta(\epsilon_0-\mu)/2)$ and thus vanishes exponentially in the integer-valence limit. It should be noted that were one to carry out a similar analysis in the quasiparticle approximation one would find that the width of the central peak was zero. This happens because in the approach of Ref. 16 the width of the central peak is approximately equal to

$$\lim_{\omega\to 0} \omega^{2\,{}^{\mathrm{HF}}}S(0,\omega)(2T\chi_T)^{-1} , \tag{6.2}$$

where X_T is the static susceptibility. According to (5.8), (5.15), and (5.17) the limit in (6.2) vanishes for the quasiparticle model. Thus in this approximation the central peak is a δ function. The difference in the results of the two calculations emphasizes the point made earlier about the regions of applicability of the quasiparticle and decoupled-mode approximations. In an operational sense we expect the latter to be appropriate at high temperatures where the homogeneous width of the central peak is weakly temperature dependent, the former in a regime where the width has decreased to a value which is much less than its high-temperature limit (e.g., TmSe below 50 K[6]).

The Foglio calculation[18] is based on a model appropriate to $CePd_3$ ($n=1$). The dynamic structure factor is obtained from a Green's function analysis with a local decoupling approximation. Because the decoupling is local, hybridization effects are not taken into account. Thus the theory may be more appropriate for characterizing scattering in dilute IV systems.

Concerning the relevance of this work to experimental studies we have noted that in addition to measurements of the width of the central peak there have been a number of studies reporting structure in the high-frequency scattering.[4–7,21] In particular, in Refs. 6 and 7 evidence is presented suggesting a hybridization gap in TmSe. (See *Note added in proof.)*

Taken together with Refs. 16 and 17 the theory developed in this paper leads to a subdivision of the inelastic neutron scattering spectra of IV compounds into two categories. Type A behavior is characterized by a Lorentzian central peak with a (nearly) temperature-independent width. The behavior of the structure factor is indicated schematically by the following sequence, the arrows denoting increasing values of ω,

$$\frac{2T\chi_T\Gamma}{\omega^2+\Gamma^2} \to \frac{2T\chi_T\Gamma}{\omega^2} \approx \frac{1}{\omega^2}\lim_{\omega\to 0}\omega^{2\,{}^{\mathrm{HF}}}S^0(0,\omega)$$

$$\to {}^{\mathrm{HF}}S^0(0,\omega) . \tag{6.3}$$

Type B behavior is characterized by a relatively narrow central peak having a temperature-dependent width. In addition there may be resolved or partially resolved structure associated with intramanifold transitions. The corresponding sequence takes the forms temperature-dependent, central peak, and/or intramanifold structure, which, at high frequency, goes over to

$${}^{\mathrm{HF}}S^{hh}(0,\omega)+{}^{\mathrm{HF}}S^{hg}(0,\omega)+{}^{\mathrm{HF}}S^{gh}(0,\omega) . \tag{6.4}$$

Since only the hybrid-to-hybrid (inter- and intraband) scattering is expected to show significant dispersion it may be possible to identify the contribution from ${}^{\mathrm{HF}}S^{hh}(q,\omega)$ by comparing data taken at different wave vectors.

We have commented above on the appearance of the density of states of the conduction band in the expression for ${}^{\mathrm{HF}}S(q,\omega)$. Because of this it may be possible to relate features in the high-frequency scattering to fine structure in $\rho_0(\epsilon)$, which might be observed, for example, in photoemission experiments.[22] The existence of such a connection would be strong evidence in support of the theory.

Finally, we emphasize that there are still many theoretical problems relating to the neutron scattering from IV compounds. In the context of this paper perhaps the most important is to understand the crossover from type A to type B behavior with decreasing temperature and why it is seen in some systems [e.g., TmSe (Ref. 6)] and not in others [e.g., $CeSn_3$ (Ref. 7)].[23]

Note added in proof. The inelastic line reported for TmSe in Ref. 7 has also been found in dilute systems (0.05 at. % Tm). This suggests the transition is a single-ion effect and thus is not associated with excitation across a hybridization gap [E. Holland-Moritz and M. Prager, J. Magn. Magn. Mater. 31–34, 395 (1983)].

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APPENDIX A

In this appendix we discuss the decoupling approximation introduced in Sec. III. In Eq. (3.4) we made the replacement

$$\langle\langle c_{k'\sigma'}\{X_{k\mu\lambda},X^{\dagger}_{k'\mu'\lambda'}\};c^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\rightarrow\delta_{kk'}\delta_{\lambda\lambda'}\delta_{\mu\mu'}(\langle X_{\mu\mu}\rangle\langle X_{\lambda\lambda}\rangle)\langle\langle c_{k\sigma};c^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\ . \tag{A1}$$

Here we examine the approximation in greater detail focusing on the equation of motion for the higher-order function. In light of (2.16) we write the Green's function in the form

$$G\equiv\langle\langle c_{k'\sigma'}\{X_{k\mu\lambda},X^{\dagger}_{k'\mu'\lambda'}\};c^{\dagger}_{k\sigma}\rangle\rangle_{\omega}=N^{-1/2}\langle\langle c_{k'\sigma'}(\delta_{\lambda\lambda'}X_{k-k'\mu\mu'}+\delta_{\mu\mu'}X_{k-k'\lambda'\lambda});c^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\ , \tag{A2}$$

where $X_{k\mu\mu'}$ and $X_{k\lambda\lambda'}$ are defined by equations similar to (2.14).

The function G satisfies the equation

$$\begin{aligned}(\omega-\epsilon_{k'})G=&\delta_{kk'}\delta_{\mu\mu'}\delta_{\lambda\lambda'}\delta_{\sigma\sigma'}(\langle X_{\mu\mu}\rangle+\langle X_{\lambda\lambda}\rangle)\\&+N^{-1/2}\sum_{k'',\sigma''}\sum_{\mu'',\lambda''}V^{k''\sigma''}_{\mu''\lambda''}\langle\langle[c_{k'\sigma'}(\delta_{\lambda\lambda'}X_{k-k'\mu\mu'}+\delta_{\mu\mu'}X_{k-k'\lambda'\lambda})\\&\times X_{k''\mu''\lambda''}c^{\dagger}_{k''\sigma''}-X_{k''\mu''\lambda''}c^{\dagger}_{k''\sigma''}c_{k'\sigma'}\\&\times(\delta_{\lambda\lambda'}X_{k-k'\mu\mu'}+\delta_{\mu\mu'}X_{k-k'\lambda'\lambda})];c^{\dagger}_{k\sigma}\rangle\rangle_{\omega}+\cdots\ ,\end{aligned} \tag{A3}$$

where the ellipsis signifies terms involving $(V^{k''\sigma''}_{\mu''\lambda''})^*$ which drop out after making the approximations discussed below.

We approximate the higher order Green's function on the right-hand side of (A3) by replacing the products $c_{k'\sigma'}c^{\dagger}_{k''\sigma''}$ and $c^{\dagger}_{k''\sigma''}c_{k'\sigma'}$ by their thermal averages $\delta_{k'k''}\delta_{\sigma'\sigma''}(1-n_{k'\sigma'})$ and $\delta_{k'k''}\delta_{\sigma'\sigma''}n_{k'\sigma'}$, respectively, where $n_{k\sigma}=[\exp\beta(\epsilon_k-\mu)+1]^{-1}$. Since $c_{k''\sigma''}$ and $X_{k''\mu''\lambda''}$ anticommute we obtain an expression of the type,

$$\begin{aligned}&N^{-1/2}\sum_{\mu'',\lambda''}V^{k'\sigma'}_{\mu''\lambda''}n_{k'\sigma'}\langle\langle[(\delta_{\lambda\lambda'}X_{k-k'\mu\mu'}+\delta_{\mu\mu'}X_{k-k'\lambda'\lambda}),X_{k'\mu''\lambda''}];c^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\\&-N^{-1/2}\sum_{\mu'',\lambda''}V^{k'\sigma'}_{\mu''\lambda''}\langle\langle(\delta_{\lambda\lambda'}X_{k-k'\mu\mu'}+\delta_{\mu\mu'}X_{k-k'\lambda'\lambda})X_{k'\mu''\lambda''};c^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\ .\end{aligned} \tag{A4}$$

The commutator in (A4) can be evaluated using (2.6). We approximate the second term by repeating (A1). The combined effect of these operations is to reduce (A3) to

$$\begin{aligned}(\omega-\epsilon_{k'})G=&\delta_{kk'}\delta_{\mu\mu'}\delta_{\lambda\lambda'}\delta_{\sigma\sigma'}(\langle X_{\mu\mu}\rangle+\langle X_{\lambda\lambda}\rangle)\\&+\frac{1}{N}\sum_{\mu'',\lambda''}V^{k'\sigma'}_{\mu''\lambda''}n_{k'\sigma'}(\delta_{\lambda\lambda'}\delta_{\mu'\mu''}\langle\langle X_{k\mu\lambda''};c^{\dagger}_{k\sigma}\rangle\rangle_{\omega}-\delta_{\mu\mu'}\delta_{\lambda'\lambda''}\langle\langle X_{k\mu''\lambda};c^{\dagger}_{k\sigma}\rangle\rangle_{\omega})\\&-\delta_{kk'}\delta_{\mu\mu'}\delta_{\lambda\lambda'}\delta_{\sigma\sigma'}(\langle X_{\mu\mu}\rangle+\langle X_{\lambda\lambda}\rangle)\sum_{\mu'',\lambda''}V^{k\sigma}_{\mu''\lambda''}\langle\langle X_{k\mu''\lambda''};c^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\ .\end{aligned} \tag{A5}$$

The first and third terms on the right-hand side of (A5) are the ones obtained when G is approximated by

$$(\langle X_{\mu\mu}\rangle+\langle X_{\lambda\lambda}\rangle)\delta_{kk'}\delta_{\mu\mu'}\delta_{\lambda\lambda'}\delta_{\sigma\sigma'}\langle\langle c_{k\sigma};c^{\dagger}_{k\sigma}\rangle\rangle_{\omega}\ .$$

The second term is the leading correction to this approximation. When (A5) is introduced into (3.4) the correction term appears in the form

$$-\sum_{\mu'',\lambda''}\sum_{\mu',\lambda'}\left[\frac{1}{N}\sum_{k',\sigma'}V^{k'\sigma'}_{\mu''\lambda''}(V^{k'\sigma'}_{\mu'\lambda'})^*n_{k'\sigma'}(\omega-\epsilon_{k'})^{-1}\right](\delta_{\lambda\lambda'}\delta_{\mu'\mu''}\langle\langle X_{k\mu\lambda''};c^{\dagger}_{k\sigma}\rangle\rangle_{\omega}-\delta_{\mu\mu'}\delta_{\lambda'\lambda''}\langle\langle X_{k\mu''\lambda};c^{\dagger}_{k\sigma}\rangle\rangle_{\omega})\ . \tag{A6}$$

The term in large parentheses in the above expression is of order V^2/W, where W is a measure of the width of the conduction band. Moreover, the expression vanishes identically if one assumes complete rotational symmetry about the ionic site. In order to see this we expand $V^{k\sigma}_{\mu\lambda}$ in terms of the matrix elements of the annihilation and creation operators for the f electrons[17]

$$V^{k\sigma}_{\mu\lambda}=\sum_{m=-3}^{3}V_{km}\langle\mu\,|\,f_{m\sigma}\,|\,\lambda\rangle\ . \tag{A7}$$

Thus we can write

$$\sum_{k'}V^{k'\sigma'}_{\mu''\lambda''}(V^{k'\sigma'}_{\mu'\lambda'})^*n_{k'\sigma'}(\omega-\epsilon_{k'})^{-1}=\sum_{m,m'}\sum_{k'}V_{k'm}(V_{k'm'})^*\langle\mu''\,|\,f_{m\sigma'}\,|\,\lambda''\rangle\langle\lambda'\,|\,f^{\dagger}_{m'\sigma'}\,|\,\mu'\rangle n_{k'\sigma'}(\omega-\epsilon_{k'})^{-1}\ . \tag{A8}$$

If we postulate rotational symmetry then the angular average over the direction of k' reduces to[17]

$$(4\pi)^{-1}\int d\Omega_{k'} V_{k'm}(V_{k'm'})^*(\omega-\epsilon_{k'})^{-1}\propto\delta_{mm'}\ , \quad \text{(A9)}$$

which vanishes unless $m=m'$. In the evaluation of (A6) one encounters terms of the form

$$\sum_{\mu'}\sum_{k',\sigma'} V^{k'\sigma'}_{\mu'\lambda''}(V^{k'\sigma'}_{\mu'\lambda})^* n_{k'\sigma'}(\omega-\epsilon_{k'})^{-1}\ ,$$

which are proportional to

$$\sum_{\mu'}\sum_{m}\langle\lambda\,|\,f^\dagger_{m\sigma'}\,|\,\mu'\rangle\langle\mu'\,|\,f_{m\sigma'}\,|\,\lambda''\rangle\ , \quad \text{(A10)}$$

and

$$\sum_{\lambda'}\sum_{k',\sigma'} V^{k'\sigma'}_{\mu''\lambda'}(V^{k'\sigma'}_{\mu\lambda})^* n_{k'\sigma'}(\omega-\epsilon_{k'})^{-1}\ ,$$

which are proportional to

$$\sum_{\lambda'}\sum_{m}\langle\mu''\,|\,f_{m\sigma'}\,|\,\lambda'\rangle\langle\lambda'\,|\,f^\dagger_{m\sigma'}\,|\,\mu\rangle\ , \quad \text{(A11)}$$

where in both cases we have made use of (A9). Because of the spherical symmetry assumed for the ionic states (A10) vanishes after summing over m unless $\lambda=\lambda''$; likewise (A11) vanishes unless $\mu''=\mu$. As a consequence (A6) is identically zero.

From this analysis we conclude that the decoupling approximation leading to (3.5) is justified in the sense that the leading correction is small when $V/W\ll 1$ and vanishes identically when (A9) is satisfied.[24] Finally, we note that in the (unphysical) situation where both the λ and μ manifolds are nondegenerate the decoupling approximation becomes exact since in this case $X_{\mu\mu}(i)+X_{\lambda\lambda}(i)=1$.[9] Moreover, our treatment of ${}^{\rm HF}S(0,\omega)$ is also exact. However, there is only hybrid-to-hybrid scattering since there are no gap modes (cf. Sec. V).

APPENDIX B

In this appendix we outline the calculation of the chemical potential, $\langle X_{\lambda\lambda}\rangle$ and $\langle X_{\mu\mu}\rangle$. The calculation begins with Eq. (4.15). The first term on the left-hand side can be evaluated by expanding the $c_{k\sigma}$ in terms of the α^ν_k using (4.14a). We have

$$\frac{1}{N}\sum_{k,\sigma}\langle c^\dagger_{k\sigma}c_{k\sigma}\rangle=\frac{1}{N}\sum_{k,\nu}|\,u^\nu_{k\sigma}\,|^2(e^{\beta(\omega^\nu_k-\mu)}+1)^{-1}\ , \quad \text{(B1)}$$

where as before μ denotes the chemical potential.

The $\langle X_{\lambda\lambda}\rangle$ and $\langle X_{\mu\mu}\rangle$ can be calculated from the Green's function $\langle\langle X_{\mu\lambda}(i);X_{\lambda\mu}(i)\rangle\rangle_\omega$. We obtain

$$\langle X_{\mu\mu}\rangle=\frac{1}{\pi}\int_{-\infty}^{\infty}d\omega(e^{-\beta(\omega-\mu)}+1)^{-1}\times\mathrm{Im}\langle\langle X_{\mu\lambda}(i);X_{\lambda\mu}(i)\rangle\rangle_\omega\ , \quad \text{(B2)}$$

$$\langle X_{\lambda\lambda}\rangle=\frac{1}{\pi}\int_{-\infty}^{\infty}d\omega(e^{\beta(\omega-\mu)}+1)^{-1}\times\mathrm{Im}\langle\langle X_{\mu\lambda}(i);X_{\lambda\mu}(i)\rangle\rangle_\omega\ , \quad \text{(B3)}$$

where

$$\mathrm{Im}\langle\langle A;B\rangle\rangle_\omega=(i/2)(\langle\langle A;B\rangle\rangle_{\omega+i\epsilon}-\langle\langle A;B\rangle\rangle_{\omega-i\epsilon})\ , \quad \text{(B4)}$$

in the limit $\epsilon\to 0+$, taking ω to be real. Note that in (B1)—(B3) we have introduced the chemical potential through the correlation function. The results are identical to what we would have found were we to have worked in the grand canonical formalism with a number operator whose expectation value is equal to nN [cf. (4.15)].

In the quasiparticle approximation $\langle\langle X_{\mu\lambda}(i);X_{\lambda\mu}(i)\rangle\rangle_\omega$ is obtained by making use of (2.14), (2.15), and (3.7) and then expanding $c_{k\mu\lambda}$ in terms of the α^ν_k. We find

$$\langle\langle X_{\mu\lambda}(i);X_{\lambda\mu}(i)\rangle\rangle_\omega=\frac{A_{\mu\lambda}}{N}\sum_k\langle\langle c_{k\mu\lambda};c^\dagger_{k\mu\lambda}\rangle\rangle_\omega=\frac{A_{\mu\lambda}}{N}\sum_k\sum_\nu|\,u^\nu_{k\mu\lambda}\,|^2(\omega-\omega^\nu_k)^{-1}\ . \quad \text{(B5)}$$

Thus we have

$$\langle X_{\mu\mu}\rangle=(\langle X_{\mu\mu}\rangle+\langle X_{\lambda\lambda}\rangle)f_{\mu\lambda}\ , \quad \text{(B6)}$$

$$\langle X_{\lambda\lambda}\rangle=(\langle X_{\mu\mu}\rangle+\langle X_{\lambda\lambda}\rangle)(1-f_{\mu\lambda})\ , \quad \text{(B7)}$$

where

$$f_{\mu\lambda}=\frac{1}{N}\sum_{k,\nu}(e^{-\beta(\omega^\nu_k-\mu)}+1)^{-1}|\,u^\nu_{k\mu\lambda}\,|^2\ , \quad \text{(B8)}$$

having made use of the unitarity property,

$$\sum_\nu|\,u^\nu_{k\mu\lambda}\,|^2=1\ . \quad \text{(B9)}$$

Equations (4.21) and (4.22) can be solved for $\langle X_{\mu\mu}\rangle$ and $\langle X_{\lambda\lambda}\rangle$ by making use of the identity[9]

$$\sum_\mu X_{\mu\mu}(i)+\sum_\lambda X_{\lambda\lambda}(i)=1\ . \quad \text{(B10)}$$

This is done by identifying arbitrary reference levels $\bar\mu$ and $\bar\lambda$. Then from (B6) and (B7) we have ($\mu\neq\bar\mu,\lambda\neq\bar\lambda$)

$$\langle X_{\mu\mu}\rangle=\langle X_{\bar\lambda\bar\lambda}\rangle f_{\mu\bar\lambda}(1-f_{\mu\bar\lambda})^{-1}\ , \quad \text{(B11)}$$

$$\langle X_{\lambda\lambda}\rangle=\langle X_{\bar\mu\bar\mu}\rangle(1-f_{\bar\mu\lambda})f^{-1}_{\bar\mu\lambda}\ , \quad \text{(B12)}$$

whereas $\langle X_{\bar\mu\bar\mu}\rangle$ and $\langle X_{\bar\lambda\bar\lambda}\rangle$ are related by

$$\langle X_{\bar\mu\bar\mu}\rangle/\langle X_{\bar\lambda\bar\lambda}\rangle=f_{\bar\mu\bar\lambda}/(1-f_{\bar\mu\bar\lambda})\ . \quad \text{(B13)}$$

Using (B11)—(B13) in (B10) we have

$$\sum_\mu f_{\mu\bar\lambda}(1-f_{\mu\bar\lambda})^{-1}+f_{\bar\mu\bar\lambda}(1-f_{\bar\mu\bar\lambda})^{-1}\sum_\lambda(1-f_{\bar\mu\lambda})f^{-1}_{\bar\mu\lambda}=\langle X_{\bar\lambda\bar\lambda}\rangle^{-1}\ . \quad \text{(B14)}$$

Equations (4.15), (B8), and (B11)—(B14) thus form a set of coupled nonlinear equations for the chemical potential, the $\langle X_{\lambda\lambda}\rangle$, and the $\langle X_{\mu\mu}\rangle$. In the limit $V\to 0$ we obtain

$$\langle X_{\lambda\lambda}\rangle=[(2J+1)+(2J'+1)e^{\beta(\epsilon_0-\mu)}]^{-1}\ , \quad \text{(B15)}$$

$$\langle X_{\mu\mu}\rangle=e^{\beta(\epsilon_0-\mu)}\langle X_{\lambda\lambda}\rangle\ , \quad \text{(B16)}$$

in agreement with earlier calculations.[9]

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