London, Sect. A 65, 368 (1952).
[13]As a result of the fluctuating Pr fields, the usual nuclear modulation of the echo decay was absent [L. G. Rowan *et al.*, Phys. Rev. 137, A61 (1965)].
[14]J. E. Gulley, D. Hone, D. J. Scalapino, and B. G. Silbernagel, Phys. Rev. B 1, 1020 (1970).
[15]S. Katsura, T. Horiguchi, and M. Suzucki, Physica 46, 67 (1970).
[16]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).
[17]D. L. Huber and J. S. Semura, Phys. Rev. 182, 602 (1969).

Sum Rules and Inelastic Neutron Scattering in Paramagnetic Intermediate-Valence Compounds

C. E. T. Gonçalves da Silva[a]
Institut de Physique Théorique, Université de Lausanne, CH-1015 Lausanne, Switzerland
(Received 27 November 1978)

Exact evaluation of low-order moments of the imaginary part of the dynamic susceptibility is used to analyze inelastic neutron scattering in a paramagnetic intermediate-valence system. It is shown that (i) the second moment of $\chi''(\vec{q},\omega)/\omega$ measures the mixing energy, (ii) only a weak $\vec{q}$ dependence of $\chi''(\vec{q},\omega)$ is expected even in "coherent" systems, and (iii) there are no diffusive modes in the hydrodynamic regime.

Intermediate-valence compounds, in which rare-earth ions have a $4f$ shell with nonintegral occupancy, have been the object of many experimental and theoretical investigations in the past few years.[1] The latter have thus far emphasized detailed microscopic models and calculations. In this paper, we discuss an application of the method of moments expansion to a model Hamiltonian which, at least qualitatively, is expected to describe paramagnetic intermediate valence compounds. Such a general approach is of limited usefulness from a practical point of view, although it may shed light on a variety of questions. Hence our purpose is more one of pointing out a possible path along which some progress may be made in the understanding of these systems than that of offering a practical solution to the problem. The quantity of interest for the analysis of inelastic-neutron-scattering data is the imaginary part $\chi''(q,\omega)$ of the dynamic susceptibility. The few calculations of $\chi''(q,\omega)$ that have been performed[2,3] adopt a perturbative approach of limited validity. To our knowledge, the present work is the first to discuss sum rules for $\chi''(q,\omega)$ in intermediate valence systems. Using such an approach we may address ourselves to some questions of interest. First, that of "incoherent," purely local, impuritylike, versus "coherent," extended, latticelike, intermediate valences. Second, that of the mixing energy, i.e., the contribution of the hybridization to the internal energy, of importance in the analysis of cohesive properties. Third, the existence of diffusive modes in the paramagnetic phase. Our results apply to paramagnetic compounds, such as Ce and Yb intermetallics, SmS-based systems, and the paramagnetic phase of TmSe.

Let us start with a brief review of the inelastic-neutron-scattering results. They have been obtained for the pure intermetallic $CePd_3$,[4] the alloy $Ce_{1-x}Th_x$,[5] and TmSe.[6,7] The salient feature of the data in $CePd_3$ (Ref. 4) is the presence of a quasielastic peak, the width of which is temperature independent below room temperature and of the order of 19 meV. The situation in $Ce_{1-x}Th_x$ (Ref. 5) is slightly more complicated because of the presence of a phase transition (essentially the α-γ transition of Ce modified by the alloying). This is traditionally interpreted as reflecting a temperature dependence of the valence of Ce ions,[8] although an alternative view has been proposed.[9] If we adhere to the traditional viewpoint, the difference between $CePd_3$ and $Ce_{1-x}Th_x$ is due solely to the fact that, in the former compound, the Ce valence changes less drastically between 0 K and room temperature. A wide quasielastic peak is also observed in $Ce_{1-x}Th_x$, with a width that increases from about 20 meV at 300 K to about 24 meV just before the transition ($T_c \sim 150$ K). Below T_c a quasielastic peak can still be detected but with a smaller intensity and much larger width. The important new fact which has emerged in the analysis of these results is that the $\vec{q}$ dependence of the scattering cross section

follows that of the ionic form factor. This led Shapiro *et al.*[5] to propose that the phenomenon of intermediate valence may be purely local. Because it orders magnetically at low temperatures, TmSe differs qualitatively from the Ce compounds discussed above. For our purposes it suffices to know that the width of the quasielastic peak stays roughly constant in the interval 100 K $< T <$ 300 K and of the order of 6 meV. Below 100 K the inelastic-neutron-scattering spectrum begins to change in a complex way.

The starting point for our theoretical discussion is the well-known Hamiltonian

$$H = H_c + H_f + H_m = \sum_{k\sigma} \epsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{i\sigma} (E f_{i\sigma}^{\dagger} f_{i\sigma} + \tfrac{1}{2} U n_{i\sigma} n_{i\bar{\sigma}}) + (N)^{-1/2} \sum_{ik\sigma} (V_{ik} f_{i\sigma}^{\dagger} c_{k\sigma} + \text{H.c.}). \quad (1)$$

In (1), $c_{k\sigma}^{\dagger}$ ($c_{k\sigma}$) and $f_{i\sigma}^{\dagger}$ ($f_{i\sigma}$) create (destroy), respectively, itinerant and localized electrons. The mixing term is coherent, being given by

$$V_{ik} = \exp(-i\vec{k} \cdot \vec{R}_i) V(\vec{k}). \quad (2)$$

This Hamiltonian neglects many important aspects of the real problem: the itinerant-localized electron Coulomb interaction,[8] the electron-phonon interaction,[10] and crystalline electric field effects. As will become clear, these additional terms do not affect our main results.

The imaginary part of the dynamic susceptibility is defined by

$$\chi''(\vec{R}_i, t) \equiv \tfrac{1}{2} \langle [\sigma^z(\vec{R}_i, t), \sigma^z(\vec{0}, 0)] \rangle, \quad (3)$$

where the angular brackets denote equilibrium thermal averaging. Since we are interested in cubic paramagnetic compounds, it is sufficient to consider the z component of the spin operator, given by

$$\sigma^z(\vec{R}_i) = \sum_{\sigma} \sigma f_{i\sigma}^{\dagger} f_{i\sigma}. \quad (4)$$

(In our units $\hbar = 1$ and $\mu_B = 1$.) The Fourier transform of (3) is related to the Fourier transform of the Kubo relaxation function[11]:

$$C(\vec{q}, t) \equiv \langle \sigma^z(\vec{q}, t) \mid \sigma^z(\vec{q}) \rangle \equiv \beta^{-1} \int_0^{\beta} d\lambda \langle \sigma^z(-\vec{q}, t) \sigma^z(\vec{q}, i\lambda) \rangle, \quad (5)$$

through

$$\chi''(\vec{q}, \omega) = \tfrac{1}{2} \beta \omega C(\vec{q}, \omega), \quad (6)$$

where $\beta = (k_B T)^{-1}$.

Sum rules for $\chi''(\vec{q}, \omega)$ are obtained by the usual procedure of generating equal-time commutators. We define

$$\langle \omega^n(\vec{q}) \rangle \equiv \pi^{-1} \int d\omega\, \omega^{n-1} \chi''(\vec{q}, \omega) = \langle [[[[\cdots [\sigma^z(-\vec{q}), H], H], \ldots], H], \sigma^z(\vec{q})] \rangle, \quad n > 0, \quad (7)$$

where on the last expression we have $n-1$ successive commutators of $\sigma^z(-\vec{q})$ with H. These can be tediously, but straightforwardly, evaluated for small n. We find, for the first nonvanishing moment,

$$\langle \omega^2(\vec{q}) \rangle = \beta \langle \dot{\sigma}^z(\vec{q}) \mid \dot{\sigma}^z(\vec{q}) \rangle = -(N)^{-1} \langle H_m \rangle, \quad (8)$$

with the dot indicating time derivative.

The remarkable feature of Eq. (8) is that $\langle \omega^2(\vec{q}) \rangle$ turns out to be $\vec{q}$ *independent*. In isotropic paramagnets,[11] the second moment is proportional to q^2 for small wave vectors as a direct consequence of the conservation of magnetization. In an intermediate valence paramagnet, on the other hand, $\sigma^z(\vec{q} = 0)$ is not a conserved quantity, and $\langle \omega^2 \rangle$ does not tend to zero as does not tend to zero as $\vec{q} \to 0$. The complete $\vec{q}$ independence of (8) is a consequence of assuming no dispersion for the localized levels in the absence of hybridization. This result is not affected by the inclusion of the neglected interaction terms and crystal field level structure in Eq. (1). The strict equality between the second moment of $\chi''(\vec{q}, \omega)/\omega$ and the average mixing energy is altered by the consideration of the orbital degeneracy of localized orbitals (see below).

In obtaining Eq. (8) above, only terms in (1) which change the number of localized electrons need be taken into account. If we include, for instance, a localized electron-conduction electron-phonon interaction then V_{ik} becomes an operator involving explicitly phonon terms, as discussed in Ref. 10. It is obvious, however, that Eq. (8) remains unchanged, if we interpret H_m as including all terms in the physical Hamiltonian which change the number of localized electrons by one.

The next nonvanishing moment is the fourth moment. It is a sum of a q-independent term, which to lowest order in perturbation theory is of order H_m^2, and of a q-dependent term, similar-

ly of order H_m^4. The latter are given by

$$\langle\omega^2(q)\rangle \sim N^{-1}\sum_{ik\sigma}|V_k|^2\{\exp[-i(\vec{k}+\vec{q})\cdot\vec{R}_i]\langle(\epsilon_k - E - Un_{i\bar{\sigma}})f_{i\sigma}{}^{\dagger}f_{0\sigma}\rangle - 3(N)^{-1/2}\langle V_{k+q}f_{0\sigma}{}^{\dagger}c_{k+q\sigma}\rangle + \text{c.c.}\}. \quad (9)$$

This result is exact, but model dependent. Inclusion of further interactions in Eq. (1) modifies it slightly. That any q dependence appears only in terms of the order of at least H_m^4 follows from the fact that H_m couples different sites only in fourth or higher order.[12]

It is worthwhile remarking that Eq. (8) indicates the inadequacy, in principle, of Lorentzian fittings to the data, because these yield infinite second moments. It must be kept in mind that such fittings are the simplest possible phenomenological approach to the analysis of the data, even though the experimental uncertainties may be large enough to render an unambiguous fit impossible—Holland-Moritz *et al.*[4] found, for instance, that the data for $CePd_3$ could be fitted by either one or three Lorentzians. What is important, however, is that such fittings are possible at all, since there is no *a priori* reason to expect a Lorentzian line shape.

To explore this point further, we recall that the Laplace transform of $C(q, t)$ may be written[11]

$$C(\vec{q}, z) = i[z + i\,\Sigma(\vec{q}, z)]^{-1}C(\vec{q}, t=0), \quad (10)$$

where $\Sigma(\vec{q}, z)$ is the Laplace transform of

$$\Sigma(\vec{q}, t) = \langle\dot{\sigma}^z(\vec{q}, t)\,|\,\dot{\sigma}^z(\vec{q})\rangle C^{-1}(\vec{q}, t=0). \quad (11)$$

The operator governing the time evolution of $\dot{\sigma}^z(\vec{q})$ in (11) is not the same as the one given by (1). This point is discussed in detail, for instance, in Ref. 11. The success of the phenomenological approach indicates that the generalized torques $\dot{\sigma}^z$ must become uncorrelated in times faster than the time scale probed by the neutrons ($\tau \sim 10^{-15}$ s). In such a case $\Sigma(\vec{q}, t)$ may be approximated by a δ function in time, the strength of which gives the width of the quasielastic peak. Unfortunately, experimental investigation of the high-frequency tail of $\chi''(\vec{q}, \omega)$, where the Lorentzian *Ansatz* must break down, is hampered by resolution and statistic problems.

The nonexistence of diffusive modes in intermediate-valence paramagnets follows from the nonconservation of $\sigma^z(\vec{q}=0)$. To prove this formally, if suffices to show that $\Sigma(\vec{q}\to 0, z) \neq 0$. Since the zeroth moment of $\Sigma(\vec{q}, \omega)$ is equal to the second moment of $C(\vec{q}, \omega)$, and this is q independent, it follows immediately that $\Sigma(\vec{q}\to 0, z)$ cannot vanish, for a nonvanishing $\langle\omega^2(\vec{q}\to 0)\rangle$.

We now return to Eq. (8). It may be easily generalized to the case of orbitally degenerate localized levels. Inserting the necessary dimensional factors, we find

$$E_m = 3g^2\hbar^2(p\mu_B)^{-2}\langle\omega^2\rangle, \quad (12)$$

where E_m is an average of the mixing energy over the various orbitals [weighted by the expectation value of $(J^z)^2$], and g and p are averaged gyromagnetic ratio and effective number of Bohr magnetons, respectively, for the configurations of importance. The second moment may be estimated from the experiments if we introduce a cutoff factor in the Lorentzians. Then

$$\langle\omega^2\rangle \sim 2\pi^{-1}h^{-2}R\,\Gamma^2\chi, \quad (13)$$

where R is a number of the order of unity for a cutoff of a few half widths and χ is the susceptibility.

In $CePd_3$ the susceptibility[13] and the width[4] are temperature independent for $T \lesssim 300$ K. We use $\chi \sim 4$ μemu/g[13] and obtain

$$E_m \sim 20 \text{ meV/cell}. \quad (14)$$

In paramagnetic TmSe the situation is very different. The susceptibility is well fitted by a Curie-Weiss expression with $p_{\text{eff}} = 6.32$ and $\theta_p = -33$ K.[14] On the other hand, the width Γ varies by, at most, 20% from $T = 100$ K to room temperature. Equations (12) and (13) then yield a mixing energy which follows the temperature behavior of χ. For $T = 100$ K we find

$$E_m \sim 3 \text{ meV/cell}. \quad (15)$$

The results above confirm the different character of Ce intermediate-valence compounds and TmSe; in particular, the temperature dependence of E_m for the latter is typical of temperature fluctuations. It would be of great interest to identify the behavior of E_m for SmS-based compounds through measurements of Γ for isotopically pure samples.

In conclusion, we emphasize that the present "hydrodynamic" approach does not supersede microscopic calculations. It cannot, for instance, say anything about the numerical values of the various thermal averages of importance and, *a fortiori*, about the functional form of $\chi''(\vec{q}, \omega)$.

However, within its limitations it is quite illuminating. We have been able to show that (i) the second moment of $\chi''(\vec{q}, \omega)/\omega$ gives a measure of the mixing energy, allowing us, in principle, to establish a connection between inelastic neutron scattering and cohesive-property data; (ii) the $\vec{q}$ dependence of $\chi''(\vec{q}, \omega)$ is weak, even for a fully "coherent" intermediate valence paramagnet; (iii) the success of Lorentzian fittings implies very fast ($\tau < 10^{-15}$ s) correlation times for the torques $\vec{\sigma}^{z}$; and (iv) there can be no diffusive modes in the paramagnetic phase. It seems, in addition, that only very precise measurements, from which the fourth moment of $\chi''(\vec{q}, \omega)/\omega$ could be reliably determined, would allow us to distinguish incoherent ($\vec{q}$-independent) from coherent ($\vec{q}$-dependent) intermediate valence. We suggest that both TmSe and $Ce_{1-x}Th_x$ fall into the former category, but for different reasons: thermal disorder in the case of TmSe and static potential disorder in the case of $Ce_{1-x}Th_x$.

The author would like to acknowledge useful discussions with Professor Erdös, Dr. G. Solt, and Mr. H. Razafimandimby.

[a]On leave of absence from Instituto de Fisica, UNICAMP, Campinas, Brazil.

[1]See, for instance, in *Valence Instabilities and Related Narrow Band Phenomena*, edited by R. D. Parks (Plenum, New York, 1977).

[2]C. A. Balseiro and A. Lopez, Solid State Commun. 17, 1241 (1975).

[3]M. E. Foglio, J. Phys. C 11, 4171 (1978).

[4]E. Holland-Moritz, M. Loewenhaupt, W. Schmatz, and D. K. Wohlleben, Phys. Rev. Lett. 38, 983 (1977).

[5]S. M. Shapiro, J. D. Axe, R. J. Birgeneau, J. M. Lawrence, and R. D. Parks, Phys. Rev. B 16, 2225 (1977).

[6]M. Loewenhaupt and E. Holland-Moritz, to be published.

[7]E. Holland-Moritz and M. Loewenhaupt, to be published.

[8]B. Coqblin and A. Blandin, Adv. Phys. 17, 281 (1968); R. Ramirez, L. M. Falicov, and J. C. Kimball, Phys. Rev. B 2, 3383 (1970).

[9]B. Johansson, Philos. Mag. 30, 469 (1974).

[10]D. Sherrington and S. von Molnar, Solid State Commun. 16, 1347 (1975); S. K. Ghatak and K. H. Bennemann, J. Phys. F 8, 571 (1978); P. Entel, H. J. Leder, and N. Grewe, Z. Phys. B30, 277 (1978).

[11]D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (Benjamin, New York, 1975).

[12]C. E. T. Gonçalves da Silva and L. M. Falicov, J. Phys. C 5, 63 (1972).

[13]W. E. Gardner, J. Penfold, T. F. Smith, and I. R. Harris, J. Phys. F 2, 133 (1972).

[14]E. Bucher, K. Andres, F. J. di Salvo, J. P. Maita, A. C. Gossard, A. S. Cooper, and G. W. Hull, Jr., Phys. Rev. B 11, 500 (1975).

Inelastic Light Scattering from a Quasi-Two-Dimensional Electron System in GaAs-$Al_xGa_{1-x}As$ Heterojunctions

Gerhard Abstreiter

Max-Planck-Institut für Festkörperforschung, Hochfeld-Magnetlabor, 38042 Grenoble Cédex, France

and

Klaus Ploog

Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Federal Republic of Germany

(Received 21 December 1978; revised manuscript received 28 March 1979)

Resonance enhanced inelastic light scattering from a quasi-two-dimensional electron gas confined at the interface of abruptly doped GaAs/n-$Al_xGa_{1-x}As$ heterojunctions has been measured. The samples were fabricated using molecular-beam epitaxy with a high-contrast doping technique. The results show strong evidence for intersubband excitations in a two-dimensional electron system.

We report the observation of resonant Raman scattering from a quasi-two-dimensional electron system which is confined at the interface of GaAs/n-$Al_xGa_{1-x}As$ heterojunctions. The experiments were performed in backscattering geometry using an exciting laser frequency at resonance with the $E_0+\Delta_0$ energy gap of GaAs. Recently it has been shown that at this resonance one can observe free-carrier excitations with electron densities as low as about 1×10^{11} cm^{-2}.[1] It has also been suggested that the resonance enhancement of the carrier-density light-scattering mechanism

