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Abstract. – We review results of Raman and Brillouin scattering in metallic intermediate-valence rare-earth compounds and in heavy-fermion actinide compounds. The charge relaxation rate in valence fluctuating coumpounds is identified experimentally by phonon spectroscopy, whereas spin and electron density fluctuations in heavy fermion compounds are revealed by quasielastic scattering.

Introduction

During the past decade light scattering has increasingly been applied to spectroscopic investigations of metallic compounds of the rare earths (RE) and actinides [1, 2], which exhibit valence fluctuations and heavy fermion (HF) behavior. The $q \approx 0$ investigations have provided informations complementary to neutron scattering. Among the highlights are the study of crystalline-electric-field excitations and their interaction with optical phonons in Kondo-like compounds [3], the observation of intraionic and interconfigurational excitations in intermediate valence (IV) compounds as well as the direct spectroscopic identification of the temperature dependence of the fluctuation temperature and the interconfigurational excitation energy [4, 5]. Most recent achievements concern the experimental identification of the charge relaxation rates (Γ_c) in IV compounds by phonon spectroscopy [6], the measurement of the spin relaxation rate Γ_s in UPt_3 [7] and UBe_{13} [8, 9], and the finding [10] of the theoretically predicted diffusive mode due to electron density fluctuations in heavy fermion systems [11, 12]. Besides the diffusive excitations Raman scattering has also been used to study crystalline-electric-field excitations and localized electronic excitations in $CeCu_2Si_2$ [13] and UPt_3 [14-16].

Light scattering in solids (see Fig. 1) can show quasielastic contributions about the central laser frequency ($\Delta\omega = 0$ in Fig. 1) due to nonpropagating fluctuations and/or inelastic excitations due to propagating modes. The latter can be acoustic phonons, i.e. sound waves of wave vector q and velocity v, or optical phonons. On the other hand, quasielastic scattering intensities of full width at half maximum Γ may be due to single particle excitations of spin, charge or energy densities.

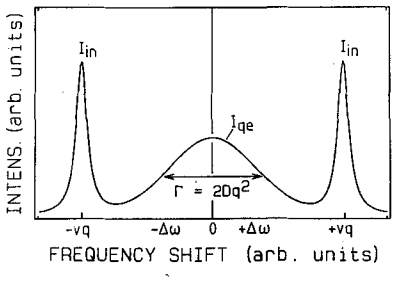

Fig. 1. – Schematic light scattering spectrum showing quasielastic scattering intensity (I_{qe}) due to diffusive or relaxational modes and inelastic Stokes ($+\Delta\omega$) and anti-Stokes ($-\Delta\omega$) scattering intensity (I_{in}) due to propagating modes of frequency $\omega = v.q$, where v is the velocity and q the wave vector.

Charge fluctuations

In IV rare-earth compounds the interaction of localized 4f electrons with conduction electrons leads to an instability of the 4f occupation number, i.e. to valence fluctuations, which consist of charge and spin fluctuations. The charge fluctuations at a rate Γ_c couple to the lattice because of the large volume changes of the RE ion associated with the valence transition $4f^n \leftrightarrow 4f^{n-1} + e^- (E_F)$, where the last term denotes the energy of an electron at the Fermi energy. Charge fluctuations in IV compounds could so far not be observed by quasielastic light scattering. Therefore we have chosen the simple model approach in which we compare the phonon frequencies $\hbar\omega$ with Γ_c. For $\hbar\omega \gg \Gamma_c$ the phonons "see" as a "snapshot" a static mixture of large and small RE ions of valence n^+ and $(n+1)^+$, respectively, because of the slow rate Γ_c. This situation is illustrated in the left-hand side of figure 2a. (n^+ and $(n+1)^+$ denote 2^+ and 3^+, respectively, in all IV compounds,except Ce-compounds where they denote 3^+ and 4^+). Hence $\hbar\omega$ of the IV compound will be intermediate (according to the RE valence) be-

tween the corresponding phonon frequencies of the n^+ and $(n+1)^+$ reference compounds (right-hand side of Fig. 2a). Such a behavior is also found for a static mixture of stable valence RE^{2+} and Re^{3+} ions in a compound. On the other hand, for $\hbar\omega \lesssim \Gamma_c$ (Fig. 2b) the charge relaxations can follow the movement of the lattice, i.e. can adjust to the atom displacements. The ionic radius adjusts to a value intermediate between those of the n^+ and $(n+1)^+$ valence RE ions, leading to a softening of the interatomic force constants and hence to a softening of the phonon frequencies which exceeds the intermediate value of the above case in figure 2a.

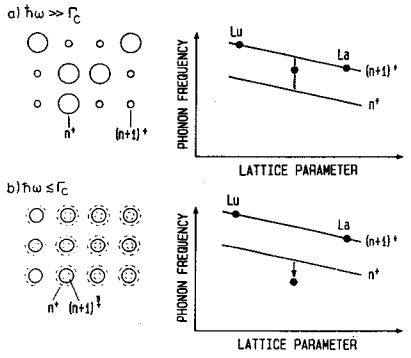

Fig. 2. – Comparison of phonon frequencies $\hbar\omega$ with charge relaxation rates Γ_c in IV compounds with n^+ and $(n+1)^+$ valent rare-earth ions. The phonon frequencies of stable valence n^+ and $(n+1)^+$ reference compounds are shown schematically in the right-hand side as a function of lattice parameter over the RE series. For explanations see the text.

This model has been applied successfully to over 15 IV-type compounds, which so far have been investigated by phonon spectroscopy [6, 17]. Moreover, the model analysis could clarify the absence of phonon anomalies of IV compounds, such as $CeSn_3$ and $CePd_3$, because of Γ_c being much larger than the highest optical phonon frequencies. Good agreement has been achieved between the experimentally identified values of Γ_c and the theoretically predicted ones [18, 19].

Another major goal in comparing experiment and theory has recently been achieved concerning the temperature dependence of Γ_c. The latter could be deduced for the IV compound $Sm_{0.75}Y_{0.25}S$ [6] from the anomalous temperature dependence of the longitudinal acoustic phonon frequencies in [111] direction and of the bulk modulus, which serves as a measure of the $q \approx 0$ acoustic phonon frequencies. As another example we present the case of SmB_6 in figure 3, where we show in the upper part the Γ_4^- optical phonon frequencies of $RE - B_6$ as a function of the lattice parameter across the RE series for three different temperatures [20]. The 2^+ and 3^+ reference lines fall on top of each other. The frequency of SmB_6 is indicated by the open circle. In the middle part of figure 3 we show the bulk modulus c_B of SmB_6 as a function of temperature [21]. At 300 K the phonon frequency $\hbar\omega\left(\Gamma_4^-\right)$ of SmB_6 is soft with respect to the reference lines, i.e. $\Gamma_c > \hbar\omega$. The position of $\hbar\omega$ on the reference lines for $T = 77$ K and 4 K can be explained by $\Gamma_c < \hbar\omega$. The decrease of Γ_c with decreasing temperature is also reflected in the softening of c_B upon cooling. As shown in the bottom part of figure 3, very good agreement is found between the experimentally deduced values of $\Gamma_c(T)$ (open circles) and the calculated $\Gamma_c(T\ \ )$ [19] (solid line).

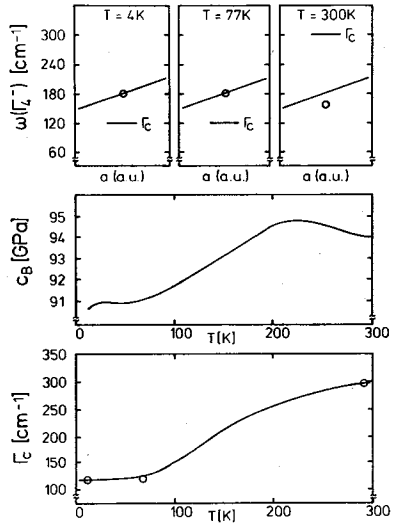

Fig. 3. – Upper part: optical $\left(\Gamma_4^-\right)$ optical phonon frequency of $RE - B_6$ as a function of lattice parameter for three different temperatures, with that of SmB_6 denoted by the open circle [20]. The $RE^{2+}-$ and $RE^{3+}-B_6$ reference lines are coinciding. Middle part: temperature dependence of the bulk modulus [21]. Bottom part: $\Gamma_c(T)$ from experiment (open circle) and theory [19] (solid line).

Spin fluctuations

Quasielastic Raman scattering due to spin fluctuations has recently been observed in UBe_{13} [8, 9] and UPt_3 [7]. Figure 4 shows quasielastic Raman scattering of polycrystalline UPt_3 at 300 K, 77 K and 5 K which is of magnetic origin because of the polarization selection rules. The pronounced asymmetry at 5 K between the Stokes (energy loss) and the anti-Stokes (energy gain) side of the spectrum is due to the Bose factor. The scattering cross section has been fitted by

a Lorentzian line shape, which is the Fourier transform of the spin-spin correlation function proportional to $e^{-\Gamma_s t}$ of uncorrelated fluctuating U 5f-spins with a spin relaxation rate Γ_s. The hatched areas in figure 4 represent the magnetic scattering contributions of half width at half maximum $\Gamma_s / 2 = 13.6$ meV at 300 K and 10.5 meV at 5 K.

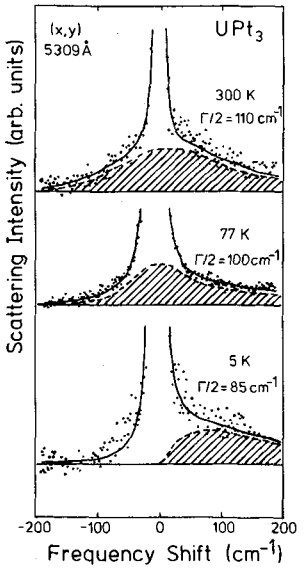

Fig. 4. – Temperature dependence of the quasielastic Raman spectra of UPt_3 for perpendicular polarizations of incident (5309 Å) and scattered light. The hatched areas mark the Lorentzian lineshape fit (half width at half maximum $\Gamma_s / 2$) of the magnetic scattering contributions due to spin fluctuations of relaxation rate Γ_s.

In figure 5 we show the spin relaxation rate $\Gamma_s / 2$ as a function of momentum transfer q for UPt_3. The Raman data for different temperatures are shown at $q \approx 0$. Neutron scattering data of polycrystalline UPt_3 for $q \geq 1$ Å^{-1} at 1.2 K are shown by the solid squares [22]. In addition we show also neutron measurements of single crystals at 4.2 K and 1.2 K [23] by the crossed circles and the cross, respectively. The Raman results together with the neutron data establish the q independence of Γ_s, which proves the localized nature of the spin fluctuations. However, this result contradicts the expectations from non-interacting Fermi liquid theory that $\Gamma_s \sim v_F.q$ for $q \to 0$, where v_F is the Fermi velocity. It has been noted before that the heavy-fermion system $CeCu_6$ exhibits spin correlations of a kind not anticipated by simple Fermi-liquid theory [24]. The reason that we observe a finite-frequency zone-center contribution to the dynamical susceptibility reflects the fact that the spin or the magnetization is not conserved due to the strong spin-orbit coupling [25]. The calculated mean-field zone-center dynamical susceptibility at $T = 0$ K is found to exhibit a maximum at $\omega \approx 4\, T_K$ [25], where T_K or the characteristic temperature T^* characterizes the energy scale of the excitations involved. From the maximum of the magnetic scattering at 5 K in figure 5 we deduce $T^* \approx 20$ cm^{-1} (2.5 meV = 30 K) in good agreement with other experimental evidence [26].

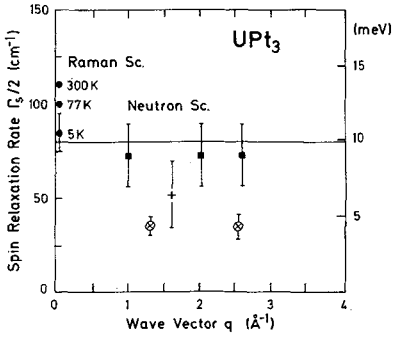

Fig. 5. – Spin relaxation rate $\Gamma_s / 2$ as a function of momentum transfer q for UPt_3. Polycrystalline samples: full circles (Raman data), full squares (neutron data at 1.2 K [22]). Single crystalline samples: cross (1.2 K) and crossed circles (4.2 K) (neutron data [23]).

Electron density fluctuations

An unusually strong quasielastic nonmagnetic scattering intensity of width (see Fig. 1) $\Gamma = 417$ GHz (1.7 meV) has been found in UPt_3 by means of Brillouin scattering using a tandem Fabry-Perot interferometer [10]. Quasielastic scattering due to single-particle excitations or due to thermal energy density fluctuations (heat diffusion) [11] could not account for the experimental value of Γ. The experimentally observed Γ for $T < T^*$ agrees within a factor of two with the diffusive mode of width $\Gamma_2 = 2.\, D.q^2$ due to electron density fluctuations (heavy quasiparticle diffusion) as calculated within a model of hydrodynamic fluctuations in HF systems [12]. This unusually strong nonmagnetic quasielastic scattering intensity I_{qe}, which has no analogue in ordinary metals, is due to an enhanced Landau-Placzek ratio $R^* = I_{qe} / 2.I_{in}$ (see Fig. 1). The enhancement is due to the large electronic Grüneisen parameter and the large effective mass of the heavy fermions [11, 12].

Conclusions

In conclusion, we would like to stress that Raman and Brillouin scattering in rare-earth and actinide

intermetallics have proven to yield significant information to the understanding of valence fluctuations and heavy fermion phenomena. These two spectroscopic techniques have established themselves as valuable tools, which complement neutron scattering investigations as well as other spectroscopic methods.

Acknowledgments

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