Temperature Dependence of the $4f$ Quadrupole Moment of Yb in $YbCu_2Si_2$

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An explanation is provided for the Mössbauer measurements on $YbCu_2Si_2$ by which the temperature-dependent quadrupole moment $Q(T)$ of Yb is obtained. The quadrupole splitting of the ^{174}Yb Mössbauer line is a direct probe of the noncubic crystalline electric field. We compute $Q(T)$ by using the noncrossing approximation to a Green's-function formulation of the Anderson impurity problem. The observed $Q(T)$ behavior is well reproduced by our theory. The zero-temperature value $Q(0)$ is discussed within the frame of the variational ground state proposed by Varma and Yafet and by Gunnarsson and Schönhammer.

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Recently the temperature dependence of the quadrupole splitting $\Delta E_Q(T)$ of the Yb Mössbauer line in $YbCu_2Si_2$ was measured.[1,2] The existence of the splitting clearly evidenced the importance of crystal electric field (CEF) effects in heavy-fermion compounds. The observed size and temperature dependence, however, cannot be explained within the conventional theory devised for systems where the f shell is decoupled from the conduction band. The essential results of these experiments are (i) a finite value of $\Delta E_Q(T=0)$ (the splitting remains almost constant for $T \leq 20$ K); (ii) a maximum in $\Delta E_Q(T)$ at about $T_{\max} \simeq 100$ K; and (iii) a gradual decrease of $\Delta E_Q(T)$ with increasing $T > T_{\max}$. Attempts have been made[2] to explain on the ground of a phenomenological model[3,4] both the above data and the T dependence of the $4f$ occupancy. But they remain unsatisfactory because no links could be established to either microscopic theories or conventional thermodynamics.

There are two contributions to the quadrupole splitting of the Yb line; one is the electric field gradient set up by the lattice while the other results from the $4f$ shell. The former is practically T independent and cannot explain the large observed temperature variation of ΔE_Q.

The contribution from the $4f$ shell is proportional to

$$Q(T) = \langle 3J_z^2 - \mathbf{J}^2 \rangle, \tag{1}$$

where the angle brackets imply a thermodynamic average and $\mathbf{J}$ and J_z are the total angular momentum of the incomplete $4f$ shell and its z component. The proportionality factor $K = \Delta E_Q(T)/Q(T)$ equals $K = 0.647$ mm/sec for ^{174}Yb and contains, among others, a Sternheimer shielding factor of $R = 0.2$ (for details see Refs. 1 and 2).

The aim of this paper is to show that the T dependence of ΔE_Q for Yb in $YbCu_2Si_2$ follows from an Anderson Hamiltonian for an impurity, which includes the crystalline electric field (CEF) splitting of the $4f$ shell of Yb. The finite value of the $4f$ contribution to $\Delta E_Q(T=0)$ is easily understood from the variational ground state of Varma and Yafet and of Gunnarsson and Schönhammer.[5,6] The T dependence of ΔE_Q is well reproduced by a simplified version of the noncrossing approximation,[7,8] which gives also a small (about 10%) increase of the f electron occupancy $n_f(T)$ as T increases.

In order to evaluate $Q(T)$ one must know the quadrupole moment for the $4f^{13}$ configuration of Yb (the other possible configuration $4f^{14}$ does not have a quadrupole moment). The CEF ground state of the $J = \frac{7}{2}$ multiplet is predominantly of $J_z = |\pm\frac{7}{2}\rangle$ character.[1,2,9] Therefore one may model the CEF by an axial field with one CEF parameter B_2^0 only. There are then four CEF levels consisting of the Kramers doublets $|\pm\frac{7}{2}\rangle, \ldots, |\pm\frac{1}{2}\rangle$. The excitation energies are $18B_2^0$, $30B_2^0$, and $36B_2^0$. The function $Q(T)$ is then given by

$$Q(T) = \sum_{m=1}^{8} \langle m | (3J_z^2 - \mathbf{J}^2) | m \rangle n_{fJm}(T), \tag{2}$$

where $|m\rangle$ denotes the different CEF eigenstates and n_{fJm} is the thermal population of state $|m\rangle$. The matrix elements $\langle m | (3J_z^2 - \mathbf{J}^2) | m \rangle$ equal 21, 3, -9, and -15 for the four Kramers doublets and

$$\sum_{m=1}^{8} \langle m | (3J_z^2 - \mathbf{J}^2) | m \rangle = 0.$$

Therefore $Q(T)$ depends on the *differences* between the thermal populations of different CEF levels and is a sensitive probe of the CEF.

We start out by computing $Q(T=0)$. For that purpose we use the model of an impurity described by the Anderson Hamiltonian. According to Varma and Yafet and Gunnarsson and Schönhammer the following *Ansatz* is made for the ground-state wave function:

$$|\psi_0\rangle = A[\,|0\rangle + \textstyle\sum_{km} a_{kJm} |kJm\rangle]. \tag{3}$$

Here $|0\rangle = |f^{14}\rangle|$ Fermi sea$\rangle$ (i.e., the product state consisting of a filled $4f$ shell of the Yb and a conduction-electron Fermi sea). Furthermore, $|kJm\rangle = c_{kJm}^\dagger f_{J-m}^\dagger |0\rangle$, where $c_{kJm}^\dagger$ creates a conduction electron with quantum numbers $k, l=3$, J, and m and $f_{J-m}^{\dagger}$ creates a hole in the $4f$ shell in the CEF eigenstate $-m$ of the $J=\frac{1}{2}$ multiplet. The partial occupancy of the latter is $n_{fJm}=A^2\sum_k |\alpha_{kJm}|^2$, and equals[6]

$$n_{fJm} \simeq (1-n_f)\frac{\Gamma}{\pi T_0}\frac{1}{1+\Delta_m/T_0}. \tag{4}$$

Here Γ is the well-known resonance width resulting from the hybridization between f and conduction electrons. The Δ_m are the bare CEF excitations measured from the ground-state doublet and T_0 is the Kondo temperature. The latter describes the shift of the ground-state energy (in the presence of the crystal field) due to the hybridization. Furthermore,

$$n_f=\sum_{m=1}^{8} n_{fJm}.$$

For a given set of values Δ_m, Γ, and T_0 one can readily calculate $Q(T=0)$ (and n_f) by using Eqs. (4) and (2). Alternatively one can use as an input Δ_{mv}, T_0, and n_f and determine instead $Q(T=0)$ and Γ. In fact, knowing $Q(T=0)$ from experiment provides for a simple way of our estimating Γ and B_2^0. The low-temperature magnetic susceptibility will fit the value of T_0. This will be described in more detail in an extended paper.

Next we want to determine the T dependence of the quadrupole splitting. For that purpose we must compute the $n_{fJm}(T)$. This is done within the noncrossing approximation (NCA)[7,8] to a Green's-function formulation of the impurity problem. All thermodynamic information is thereby contained in two normalized spectral functions $A_m(\omega,T)$ and $B(\omega,T)$ which refer to pseudofermion and pseudoboson propagators (the fermion propagator refers to the f hole while the boson propagator refers to the filled f shell). In terms of these spectral functions the partial occupancies n_{fJm} are written as

$$n_{fJm}(T)=\frac{\int_{-\infty}^{+\infty}(d\zeta/\pi)A_m(\zeta,T)e^{-\zeta/T}}{\sum_m\int_{-\infty}^{+\infty}(d\zeta/\pi)A_m(\zeta,T)e^{-\zeta/T}+\int_{-\infty}^{+\infty}(d\zeta/\pi)B(\zeta,T)e^{-\zeta/T}}. \tag{5}$$

The spectral densities fulfill a system of coupled integral equations,[7,8] through which $B(\zeta,T)$ is connected with the self-energy $\Sigma_m(\omega)$ of the pseudofermions and $A_m(\zeta,T)$ is connected with the self-energy $\Pi(\omega)$ of the pseudobosons. For details we refer to Cox and co-workers.[10] At finite temperatures the integral equations have to be solved numerically which is usually achieved by iteration with the spectral function of noninteracting pseudofermions as the starting value, i.e., $A_m^{(0)}(\omega)=\Pi(\omega+\epsilon_f-\Delta_m)$. (The energies of the CEF states with respect to the chemical potential are $-\epsilon_f+\Delta_m$ with $\epsilon_f>0$ for Yb.[11]) To calculate the partial occupancies $n_{fJm}(T)$ we approximate the spectral functions $A_m(\omega,T)$ and $B(\omega,T)$ by

$$A_m^{(1)}(\omega,T)=\frac{\Gamma(1-n_f)f(\omega_0-\omega)}{(\omega+\epsilon_f-\Delta_m)^2+[\Gamma(1-n_f)f(\omega_0-\omega)]^2}, \tag{6a}$$

$$B^{(1)}(\omega,T)=\Pi(1-n_f)\delta(\omega_0-\omega), \tag{6b}$$

where $\omega_0=-\epsilon_f-T_0$. The function $f(x)$ is the Fermi distribution function. The expressions (6a) and (6b) are deduced from the iterative solution at low temperatures. The *Ansatz* focuses on self-energy corrections which are associated with the sharp resonant structure in the pseudoboson spectral function. The low-temperature f-valence $n_f(T)$ calculated from Eqs. (5) and (6) for vanishing CEF splitting compare favorably with published NCA data at temperatures $T \le T_0$. The full NCA, however, predicts a less rapid valence saturation in the high-temperature regime which we do not consider in the present paper. We would like to mention that when Eq. (5) is evaluated with $A_m(\omega)$ and $B(\omega)$ given by Eqs. (6a) and (6b), the values $n_{fJm}(T)$ go smoothly over into those of Eq. (4) when $T \to 0$.

We have evaluated $Q(T)$ by using Eqs. (2), (5), (6a), and (6b). Thereby an appropriate choice must be made for the input parameters n_f, T_0, and the crystal field $W=3B_2^0$. Within our approximation the partial occupancies $n_{fJm}(T)$ do *not* depend on the f-level position ϵ_f. The width Γ is calculated from the relation $n_f=\sum n_{fJm}(0)$. If we take the ratio $[Q(T)-Q(0)]/[Q(T_{\max})-Q(0)]$ the factor $K=\Delta E_Q(T)/Q(T)$ drops

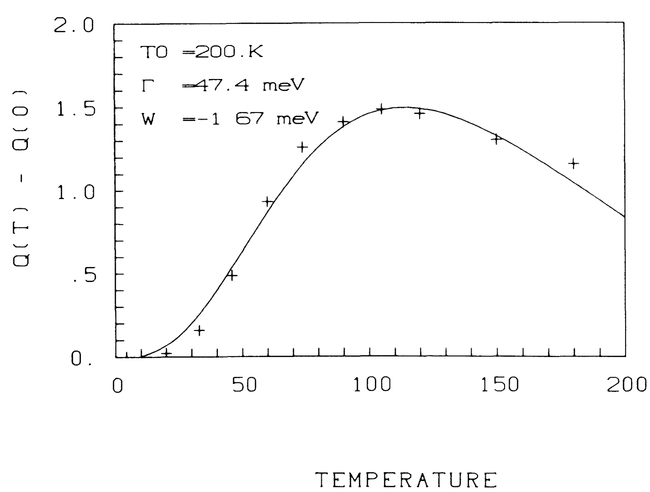

FIG. 1. Temperature-dependent quadrupole moment $Q(T)$ for the $4f$ shell of Yb in $YbCu_2Si_2$. The curves indicate the experimental points (see Ref. 1) while the solid curve is according to our theory as explained in the text. The values of the parameters are shown.

out. The best fit to the experimental data was found for $n_f=0.82$, $T_0=200$ K, and $W=-1.67$ meV. Results are shown in Fig. 1. With these parameters also $Q(T=0)$ was calculated as well as the magnetic susceptibilities $\chi_\parallel(T=0)$ and $\chi_\perp(T=0)$. The corresponding equations for the latter are found, e.g., in Ref. 6. The following values were found: $Q(T=0)=3.6$, $\chi_\parallel(T=0)=12\times10^{-3}$ emu/mol, and $\chi_\perp(T=0)/\chi_\parallel(T=0)=0.43$. ($\chi_\perp$ contained also a Van Vleck contribution.) The numerical results are rather sensitive to the choice of T_0. For example, a value of $T_0=225$ K gave a much poorer value than the optimal value. The value $n_f=0.82$ is in agreement with L_{III} x-ray absorption data.[12] The T dependence of $n_f(T)$ is found to be small (see Fig. 2) and this is again in accordance with experiments.[12,13]

The zero-temperature value of Q, together with the experimental value $\Delta E_Q(T=4\text{ K})=0.946$ mm/sec,[1] implies that the lattice contribution to the quadrupole splitting is $\Delta E_{Q\text{latt}}\simeq-1.4$ mm/sec. This is consistent with a direct estimation of $\Delta E_{Q\text{latt}}$ from the CEF parameter W.[1] Concerning the susceptibility, the most recent measurements give $\chi_\parallel(T\to0)=28\times10^{-3}$ emu/mol, $\chi_\perp^{(0)}/\chi_\parallel^{(0)}=0.3$.[14] Our computed value for the susceptibility anisotropy is not too far from the experimental value, but the calculated $\chi_\parallel(0)$ is too small by a factor of 2. The $\chi_\parallel(0)$ value is mainly dictated by Γ which is fixed by the T dependence of $Q(T)$. Therefore we speculate that the difference between the experimental and the calculated $\chi_\parallel(0)$ is due to quasiparticle interactions (Stoner factor).

The above calculations have employed the Anderson impurity Hamiltonian in the limit of large U and orbital degeneracy N_f (noncrossing approximation) to calculate the temperature-dependent quadrupole moment for $YbCu_2Si_2$. From the experiments it seems that lattice coherence effects are not very important.[15] A satisfying theory to include them is at present missing. For $T=0$ it is possible to extend the above theory and to include

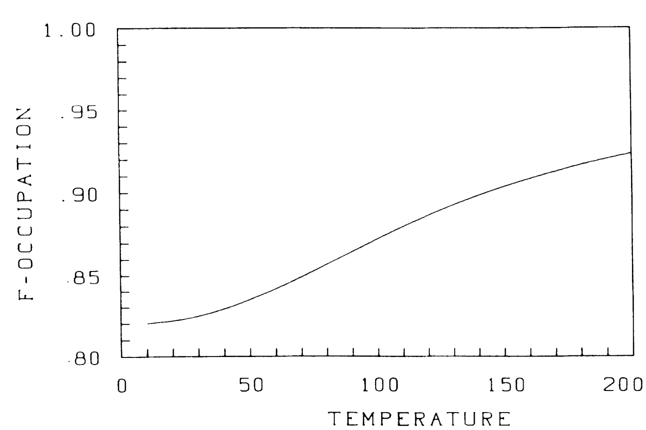

FIG. 2. f-electron occupation n_f as function of T for parameters as used in Fig. 1.

effects resulting from finite value of U. Also, one can go one step further in the $1/N_f$ expansion and include the "$1/N_f$ subspace."[10] Gunnarsson has explicitly checked that for the magnetic susceptibility of $YbCu_2Si_2$ both effects are small.[16]

Neutron-scattering experiments have indicated that the CEF in $YbCu_2Si_2$ deviates from a purely axial one and contains also fourth- and sixth-order terms. However, when we use the CEF parameters suggested in Ref. 9, we obtain a too small temperature variation of $Q(T)$. In principle it would be possible to determine the CEF parameters from a least-squares fit of $Q(T)$ and $\chi(T)$. This requires that the theory is not only qualitatively, but also quantitatively, correct. For that reason we are at present extending the work by including the shifts $\text{Re}\Sigma_m^{(1)}$ and using better expressions for $B(\omega)$. Thereby we want to study how fast the convergence is of the computational scheme shown by relations (6). Also it should be interesting to compare the parameter values obtained for the Anderson Hamiltonian when Mössbauer data and optical data[17] are used. At present there are no optical data available for $YbCu_2Si_2$.

In conclusion, we have demonstrated that the Anderson impurity Hamiltonian can well explain the measured T dependence of the quadrupole moment of the $4f$ shell in Yb.

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