

Electronic heat capacity of the rare-earth metals

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The mass enhancement of the conduction electrons due to their interaction with the ionic magnetic moments is derived. The effect of the mass enhancement on the specific heat is considered as a function of temperature in both the paramagnetic and the spin-polarized ferromagnetic cases. The experimental magnitude and the field dependence of the low-temperature specific heat of Pr metal clearly indicates large mass enhancement. An estimate shows that the theory gives a good account of these observations. A comparison between the result of band-structure calculations and the experimental electronic heat capacity indicates that the electronic masses in the magnetically ordered heavy rare-earth metals are enhanced due to the spin waves. This indication is found to be fairly consistent with a theoretical estimate of the effect.

I. INTRODUCTION

It is known that conduction electrons can acquire an appreciable increase in their effective mass m^* due to interactions with different low-lying excitations of the solid. Well-known examples are the mass enhancements due to the electron-phonon interaction¹ (e.g., in Pb) or the interaction with paramagnons^{2,3} (e.g., in Pd). In the former case the low-lying excitations, i.e., the phonons, refer to a system which is distinct from the electron system, while the paramagnon excitations occur in the conduction-electron system itself. In the latter case we can therefore view the increase in m^* as being due to electron-electron correlations. Recently it was demonstrated⁴ that a large m^* can also result in rare-earth systems due to the interaction of the conduction electrons with the excited levels of the angular momentum of the $4f$ electrons. This explains the experimental findings of Forgan⁵ that the low-temperature specific heat of Pr metal is large and strongly dependent on an applied magnetic field.

In the present investigation we want to extend this earlier work. The effect of the mass enhancement on the specific heat is considered at finite temperatures. An effort is made to demonstrate that the mass enhancements due to phonons, paramagnons, and magnetic excitons can be treated on the same footing. Furthermore, the theory is generalized to the case of ferromagnetically ordered systems. The general theory is developed in Sec. II.

In Sec. III the theory is applied to the rare-earth metals. In the case of Pr the theory is quantitatively

improved without loss of simplicity. In addition, the effects of both the "hexagonal" and the "cubic" sites in Pr are included. The heavy rare-earth metals are magnetically ordered at low temperatures. The increase of the effective masses in these metals is found to be partly canceled by the reduction of the density of states in the exchange split ground state in fair agreement with band-structure calculations. The absolute magnitude of the coupling parameter predicted by the mass-enhancement effects in the rare-earth metals is discussed. It is found to be consistent with other properties depending on the exchange interaction between the conduction and $4f$ electrons. A summary is given in Sec. IV which also contains the conclusion.

II. DERIVATION OF THE EFFECTIVE MASS

The Green's function of an interacting electron system has the general form

$$G(\vec{p}, \omega) = \frac{1}{\omega - \epsilon_{\vec{p}} - \Sigma(\vec{p}, \omega)}, \quad (1)$$

where $\epsilon_{\vec{p}} = (p^2 - p_F^2)/2m$ is the kinetic energy of a noninteracting electron with momentum \vec{p} calculated from the Fermi surface and p_F is the Fermi momentum. $\Sigma(\vec{p}, \omega)$ is the mass operator and contains all irreducible scattering events of the electron with its surroundings. The poles

$$E(\vec{p}) = \epsilon_{\vec{p}} + \Sigma(\vec{p}, E(\vec{p}))$$

of $G(\vec{p}, \omega)$ determine the excitations of the electron-

ic system. The effective mass m^* is defined for the excitations close to the Fermi surface and is given by

$$\frac{1}{m^*} = \frac{1}{p_F} \left. \frac{\partial E(\vec{p})}{\partial \vec{p}} \right|_{p=p_F}. \quad (2)$$

This equation can be rewritten in the form

$$\frac{m^*}{m} = 1 - \left. \frac{\partial \Sigma(p_F, \omega)}{\partial \omega} \right|_{\omega=0} \quad (3)$$

when assuming

$$\left. \frac{m}{p_F} \frac{\partial \Sigma(\vec{p}, \omega)}{\partial \vec{p}} \right|_{p=p_F}$$

to be small compared to 1. m^*/m is a real quantity because the imaginary part of $\Sigma(\vec{p}, \omega)$ vanishes like ω^2 for the quasiparticles close to the Fermi surface. The contribution to m^* becomes appreciable if $\Sigma(p_F, \omega)$ varies rapidly with ω close to $\omega=0$. This will be the case when $\Sigma(p_F, \omega)$ results from interactions of the conduction electrons with excitations of sufficiently low energies.

The effective mass may be determined by cyclotron resonance experiments or by low-temperature heat-capacity measurements. In the zero-temperature limit the electronic part of the specific heat is

$$C = \gamma T = \frac{m^*}{m} \gamma_0 T, \quad \gamma_0 = \frac{2\pi^2}{3} k_B^2 N(0). \quad (4)$$

$$\Sigma(\vec{p}, i\omega_n) = - \frac{g^2}{\beta} \sum_m \int \frac{d\vec{p}'}{(2\pi)^3} G(\vec{p}', i\omega_m) R(\vec{p} - \vec{p}', i(\omega_n - \omega_m)). \quad (5)$$

$\Sigma(\vec{p}, \omega)$ is obtained from $\Sigma(\vec{p}, i\omega_n)$ by analytic continuation. We use the spectral representations¹

$$G(\vec{p}', i\omega_m) = \int_{-\infty}^{\infty} dE \frac{S(\vec{p}', E)}{i\omega_m - E}, \quad (6)$$

$$R(\vec{p} - \vec{p}', i(\omega_n - \omega_m)) = \int_{-\infty}^{\infty} dE' \frac{r(\vec{p} - \vec{p}', E')}{i\omega_n - i\omega_m - E'},$$

and perform the frequency sum over m . This results in (see, for instance, Ref. 6)

$$\Sigma(\vec{p}, i\omega_n) = - \frac{1}{2} g^2 \int \frac{d\vec{p}'}{(2\pi)^3} \int_{-\infty}^{+\infty} dE \int_{-\infty}^{+\infty} dE' S(\vec{p}', E) r(\vec{p} - \vec{p}', E') \frac{1}{E - i\omega_n + E'} \left[\tanh \left[\frac{\beta E}{2} \right] + \coth \left[\frac{\beta E'}{2} \right] \right] \quad (7)$$

In order to simplify the $d\vec{p}'$ integration we use

$$\int \frac{d\vec{p}'}{(2\pi)^3} = N(0) \frac{1}{2p_F^2} \int_0^{2p_F} dq q \int d\epsilon_{\vec{p}'}. \quad (8)$$

The calculation of the average value

$$\Sigma(p, i\omega_n) = \frac{1}{4\pi} \int d\Omega_{\vec{p}} \Sigma(\vec{p}, i\omega_n) \quad (9)$$

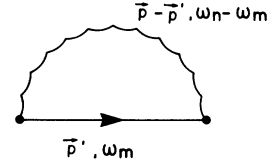


FIG. 1. Lowest-order contribution to the self-energy $\Sigma(\vec{p}, i\omega_n)$. The solid line represents the electron Green's function $G(\vec{p}', i\omega_m)$. The wavy line represents the boson propagator $R(\vec{p} - \vec{p}', i(\omega_n - \omega_m))$ and the dots stand for the coupling constant g .

$N(0)$ is the density of states per spin state at the Fermi surface in the noninteracting case.

Owing to Migdal's theorem,¹ which holds in all cases that will be considered, it suffices to consider the lowest-order diagram shown in Fig. 1 when calculating $\Sigma(\vec{p}, \omega)$. In it the propagator of the boson excitation (phonon, paramagnon, or magnetic excitation) appears just once. We shall denote this propagator by $R(\vec{q}, \omega)$ and specify it only in the end. The coupling constant of the electron to the boson excitations is denoted by g . Since we are interested in calculating m^* at finite temperatures $T = 1/k_B\beta$ we must perform the calculations with finite-temperature Green's functions. This implies working with discrete Matsubara frequencies $\omega_n = \pi(2n + 1)/\beta$, n being an integer, which replaces the continuous variable ω . The mass operator corresponding to Fig. 1 is then given by

can be performed at once. One merely has to use the fact that close to the Fermi surface the Landau quasiparticle picture holds:

$$S(\vec{p}', E) \cong \delta(E - E_{\vec{p}'}) / \left[1 - \text{Re} \frac{\partial \Sigma}{\partial E_{\vec{p}'}} \right], \quad (10)$$

where

$$E_{\vec{p}'} = \epsilon_{\vec{p}'} + \text{Re} \Sigma(\vec{p}', E_{\vec{p}'})$$

is the energy of a quasiparticle with momentum \vec{p}' . Hence neglecting $\text{Im} \Sigma(\vec{p}', E_{\vec{p}'})$ we obtain, after analytically continuing $\Sigma(p, i\omega_n) = \Sigma(i\omega_n)$,

$$\text{Re} \Sigma(\omega) = g^2 N(0) \frac{1}{2p_F^2} \int_0^{2p_F} dq q P \left[\int_{-\infty}^{\infty} dE \int_{-\infty}^{\infty} dE' r(q, E') \frac{f(E) - \frac{1}{2}}{E + E' - \omega} \right], \quad (11)$$

where P indicates the principal part of the integral. Furthermore, $f(E) = (1 + e^{\beta E})^{-1}$ is the Fermi function, and $r(q, E')$ is the average of $r(\vec{q}, E')$ with respect to the direction of \vec{q} corresponding to Eq. (9). The neglecting of the term proportional to $\coth(\beta E'/2)$ in Eq. (7) and the extension of the integration over dE to $\pm \infty$ imply only corrections of the order ω/D , where D is the conduction-electron bandwidth. By making use of the property $r(q, -E') = -r(q, E')$, which follows from time reversal symmetry, and introducing

$$r(q, E') = -\frac{1}{\pi} \text{Im} R(q, E' + i0^+)$$

one finds the temperature-dependent mass enhancement

$$\frac{m^*(T)}{m} = 1 - g^2 N(0) \frac{\beta}{2\pi^2 p_F^2} \int_0^{2p_F} dq q \int_0^{\infty} dE' \text{Im} R(q, E') \text{Re} \left[i\psi' \left[\frac{1}{2} + i \frac{\beta E'}{2\pi} \right] \right] \quad (12)$$

when expressed in terms of the first derivative of the digamma function $\psi(z)$. In the $T \rightarrow 0$ limit this simplifies into

$$\frac{m^*(0)}{m} = 1 - g^2 N(0) \frac{1}{2p_F^2} \int_0^{2p_F} dq q R(q, 0) \quad (13)$$

with the use of the asymptotic relation $\psi'(z) \rightarrow z^{-1}$ for $z \rightarrow \infty$. Notice that m^* only depends on the static part of the boson propagator at $T=0$. Next we want to discuss the behavior of the electronic excess specific heat $\Delta C_e(T)$ due to interactions of the electrons with the bosons. Experimentally it is, of course, not possible to separate the total excess specific heat ΔC due to those interactions into an electronic part ΔC_e and a boson part ΔC_{bos} . Therefore, if one is interested in ΔC itself one should start out from an expansion of the thermodynamic potential to second order in the coupling constant g and calculate ΔC from it. Here, instead, we want to consider $\Delta C_e(T)$ only, in order to study the effect of the

frequency- and temperature-dependent self-energy on it. There is a simple and natural way to derive an expression for ΔC_e by observing that $\text{Im} \Sigma(\omega)$ only introduces corrections of the order E'/D in the expression for m^*/m , provided that $T \ll T_F$, where T_F is the Fermi temperature. This must also be the case when considering the specific heat or the entropy. Hence neglecting $\text{Im} \Sigma(\omega)$ the electronic entropy is determined by the statistical behavior of fermions with an excitation energy given by

$$E_{\vec{p}} = \epsilon_{\vec{p}} + \text{Re} \Sigma(E_{\vec{p}}, T).$$

Therefore

$$S = 2k_B \int \frac{d\vec{p}}{(2\pi)^3} \{ \ln[1 + \exp(-\beta E_{\vec{p}})] + \beta E_{\vec{p}} f(E_{\vec{p}}) \}. \quad (14)$$

With this expression for the entropy the electronic specific heat is

$$\begin{aligned} C_e &= T \frac{\partial S}{\partial T} = 2 \int \frac{d\vec{p}}{(2\pi)^3} E_{\vec{p}} \left[\frac{\partial f}{\partial T} + \frac{\partial f}{\partial E_{\vec{p}}} \frac{\partial E_{\vec{p}}}{\partial T} \right] \\ &= C_0 + 2N(0) \int_{-\infty}^{\infty} d\omega \omega \left[\frac{\partial f}{\partial \omega} \frac{\partial \text{Re} \Sigma}{\partial T} - \frac{\partial f}{\partial T} \frac{\partial \text{Re} \Sigma}{\partial \omega} \right], \end{aligned} \quad (15)$$

where $C_0 = \gamma_0 T$ plus corrections of the order $(T/T_F)^3$.

The result for $\Delta C_e = C_e - C_0$ is the same as obtained by Grimvall⁷ and corresponds to the excess electronic entropy

$$\Delta S = 2N(0) \frac{1}{T} \int_{-\infty}^{\infty} d\omega \omega \frac{\partial f}{\partial \omega} \text{Re}\Sigma(\omega). \quad (16)$$

The term proportional to $\coth(\beta E'/2)$ in the total expression for $\Sigma(\omega)$, Eq. (7), can still be neglected, as the contribution of this term to ΔS is of the order E'/D . Neglecting terms of this order of magnitude, $\text{Re}\Sigma(\omega, T)$ given by Eq. (11) can be used, and we finally obtain

$$\Delta C_e = -2k_B [gN(0)]^2 \frac{1}{2p_F^2} \int_0^{2p_F} dq q \int_{-\infty}^{\infty} dE' \left[\text{Im}R(\vec{q}, E') \frac{\beta E'}{2\pi} L'(\beta E'/2\pi) - T \frac{\partial \text{Im}R(q, E')}{\partial T} L(\beta E'/2\pi) \right] \quad (17a)$$

with

$$L(y) = y \text{Re}[iy\psi'(iy) - 1]. \quad (17b)$$

We shall now specify the boson propagator. We remind the reader that for phonons

$$R(\vec{q}, \omega) = \omega_{\vec{q}}^2 / (\omega^2 - \omega_{\vec{q}}^2), \quad (18)$$

where $\omega_{\vec{q}}$ describes the phonon dispersion. Here we have adopted the definition of the phonon propagator as given in Ref. 1 which has the advantage that the electron-phonon coupling constant is frequency independent. For paramagnons^{2,3}

$$R(\vec{q}, \omega) = \frac{-2N(0)}{\left[1 - N(0)V - \frac{i\pi}{2} \frac{\omega}{qv_F} + \frac{1}{12} \frac{q^2}{p_F^2} \right]}, \quad (19)$$

where V is the electronic exchange interaction and $N(0)V$ is less than but close to 1 (v_F is the Fermi velocity). The factor g^2 has to be identified with the square of the electron-phonon coupling constant and with V^2 , respectively (in the latter case there is a correction factor of $\frac{3}{4}$ in the expression for $m^*/m - 1$).

In the case of rare-earth systems the interaction Hamiltonian for the conduction electrons interacting with the localized rare-earth moments may be written

$$H_{\text{int}} = -I_{sf}(g_L - 1) \sum_n \vec{\sigma}(\vec{R}_n) \cdot \vec{J}_n, \quad (20)$$

where I_{sf} is an exchange integral, g_L is the Landé factor, \vec{J}_n is the total angular momentum of a rare-earth ion at site \vec{R}_n , and $\vec{\sigma}$ are the Pauli matrices. With this Hamiltonian we can make the following identifications:

$$g = -(g_L - 1)I_{sf}, \quad (21)$$

$$R(\vec{q}, \omega) = -\text{Tr}\chi_{\alpha\alpha}(\vec{q}, \omega),$$

where Tr indicates the trace of the susceptibility tensor $\chi_{\alpha\beta}$.

In order to illustrate the above results we shall consider the simplest possible case, namely, a crystal-field level scheme consisting of two singlets only, separated by an energy δ , which are coupled through a matrix element M . Neglecting any dispersion effects one can write (see, for example, Ref. 8)

$$\text{Tr}\chi_{\alpha\alpha}(\vec{q}, \omega) = \frac{2|M|^2\delta}{\delta^2 - \omega^2} \tanh\left[\frac{\beta\delta}{2}\right]. \quad (22)$$

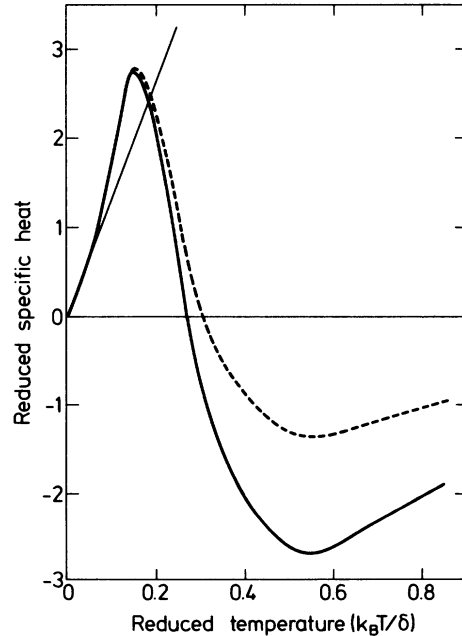


FIG. 2. Reduced specific-heat contribution which arises due to the coupling of the conduction electrons with a singlet-singlet system, i.e., K given by Eq. (24) as a function of the reduced temperature $k_B T/\delta$. The straight line shows the asymptotic behavior in the low-temperature limit. The dashed line indicates the "pure" electronic part obtained when the derivative of the magnetic population factor in Eq. (24) is neglected.

At $T=0$ one finds from Eq. (13)

$$\frac{m^*}{m} = 1 + (g_L - 1)^2 I_{sf}^2 N(0) \frac{2|M|^2}{\delta}. \quad (23)$$

This shows that for small excitation energy δ we can

$$K(1/\beta\delta) = \Delta C_e \frac{1}{k_B} [(g_L - 1) I_{sf} N(0) |M|]^{-2} = 4\pi y [\tanh(\pi y) L'(y) + \pi \cosh^{-2}(\pi y) L(y)]_{y=\beta\delta/2\pi} \quad (24)$$

is shown in the singlet-singlet case; $L(y)$ is the function given by (17b). The dashed line in the figure shows the result if the second term proportional to $\cosh^{-2}(\pi y)$ is neglected. The difference between the solid and the dashed lines gives rise to a minor scaling of the magnetic specific heat, as $L(y) \approx -y$ for $k_B T \geq 0.4\delta$, in which case this term is simply $-(m^*/m - 1)_{T=0} 2N(0)\delta$ times the magnetic heat capacity. The behavior of the electronic specific heat is going to be masked completely by the magnetic contributions for $k_B T \geq 0.2\delta$. There should, however, be the chance that the maximum at $k_B T = 0.15\delta$ might show up as a minute anomaly in an accurate measurement of $\partial C/\partial T$. ΔC_e and $m^*/m - 1$ are both zero for $k_B T \gg \delta$, which means that elastic scattering processes due to degenerate crystal-field levels do not contribute to ΔC_e and to be subtracted from $R(q,0)$ in Eq. (13).

Next we consider a system in an external magnetic field or in a magnetically ordered state. In that case the self-energy can become spin dependent. When a magnetic field is applied we must calculate

$$\text{Re}\Sigma_{\uparrow}(\omega) = (g_L - 1)^2 I_{sf}^2 N_{\uparrow}(0) \frac{1}{2p_F^{\uparrow} p_F^{\downarrow}} \int_{|p_F^{\uparrow} - p_F^{\downarrow}|}^{p_F^{\uparrow} + p_F^{\downarrow}} dq p \left[\int_{-\infty}^{\infty} dE \int_{-\infty}^{\infty} dE' \frac{1}{\pi} \text{Im}\chi^{+-}(q, E') \frac{f(E) - \frac{1}{2}}{E + E' - \omega} \right] \quad (26)$$

and the similar expression for $\text{Re}\Sigma_{\downarrow}(\omega)$ in which $\chi^{-+}(q, E')$ replaces $\chi^{+-}(q, E')$. The symmetry relation

$$\text{Im}\chi^{+-}(q, -E') = -\text{Im}\chi^{-+}(q, E')$$

implies

$$N_{\uparrow}(0) \text{Re}\Sigma_{\uparrow}(-\omega) = -N_{\downarrow}(0) \text{Re}\Sigma_{\downarrow}(\omega). \quad (27)$$

This equation shows that $(m^*/m)_{\uparrow}$ and $(m^*/m)_{\downarrow}$ might differ from each other but only if the density of states at the spin-up and spin-down Fermi surfaces, $N_{\uparrow}(0)$ and $N_{\downarrow}(0)$, are different. This corrects a statement made in Ref. 4 where it was erroneously suggested that in an external magnetic field along

expect large effects in m^* . In the low-temperature limit, $\Delta C_e = (m^*/m - 1)\gamma_0 T$. An analysis of Eq. (17) shows that this holds true approximately as long as $k_B T < 0.15\delta$, at which temperature $\Delta C_e(T)$ starts to decrease rapidly. In Fig. 2 the reduced specific heat

$$R(\vec{q}, \omega) = -\text{Tr}\chi_{\alpha\alpha}(\vec{q}, \omega)$$

[see Eq. (21)] in the presence of the field. The crystalline electric field levels are then Zeeman split by the effective field, which consists of the external field and the molecular field from the neighboring sites. For a detailed discussion we refer to Refs. 4 and 9. As far as magnetically ordered materials are concerned there have been earlier attempts by Kasuya¹⁰ and in particular by Nakajima¹⁰ to treat the influence of magnons on the electronic low-temperature specific heat. We want to improve on those studies and also simplify them. We restrict ourselves to the ferromagnetic case, where the moment $\langle J_z \rangle$ produces a splitting between the spin-up (majority spins) and spin-down electron bands. This means that p_F^{\uparrow} differs from p_F^{\downarrow} as determined by

$$\Delta = \epsilon_{p_F^{\uparrow}} - \epsilon_{p_F^{\downarrow}} = 2(g_L - 1) I_{sf} \langle J_z \rangle - \Sigma_{\uparrow}(0) + \Sigma_{\downarrow}(0). \quad (25)$$

When $\langle J_z \rangle \approx J$, then $\text{Im}\chi_{\alpha\alpha}(\vec{q}, \omega)$ can be neglected, and instead of Eq. (11) we obtain

the c axis Pr should have a spin-dependent m_{σ}^* . $\Sigma_{\uparrow}(0)$ is not necessarily zero, as is the case for $\Sigma(0)$ in the unpolarized case, although it is presumably small in comparison with Δ in Eq. (25). However, the actual value of $\Sigma_{\uparrow}(0)$ depends on the electronic properties also far away from the Fermi surface, which means that Eq. (26) is not sufficiently accurate for calculating this quantity. We also remark that the perturbation of the electronic bands, which is due to $\Sigma_{\sigma}(\omega)$, does not affect (at least to leading order) the relation which exists between $I_{sf} \langle J_z \rangle$ and the degree of polarization of the conduction electrons when the unperturbed density of states is used.

In the low-temperature limit we obtain, in generalization of Eq. (4),

$$C = \frac{\pi^2}{3} k_B^2 T \left[N_{\uparrow}(0) \frac{m_{\uparrow}^*}{m} + N_{\downarrow}(0) \frac{m_{\downarrow}^*}{m} \right] = \frac{\pi^2}{3} k_B^2 T [N_{\uparrow}(0) + N_{\downarrow}(0) + 2(g_L - 1)^2 I_{sf}^2 N_{\uparrow}(0) N_{\downarrow}(0) \langle \chi \rangle]. \quad (28)$$

Here we have made use of the expression (26) and the equivalent form for $\text{Re}\Sigma_i(\omega)$ from which, through Eq. (3), m_i^* and m_i^* are obtained. For $T \rightarrow 0$ those expressions can be integrated which respect to dE and dE' as demonstrated before for Eq. (11). The average value of the trace of the susceptibility is given by

$$\langle \chi \rangle = \frac{1}{2p_F^\uparrow p_F^\downarrow} \int_{|p_F^\uparrow - p_F^\downarrow|}^{p_F^\uparrow + p_F^\downarrow} dq q \frac{2JA_q}{A_q^2 - B^2}. \quad (29)$$

Remember that $\chi_{zz}(\vec{q}, 0)$ does not contribute to the trace in the low-temperature limit. The form of Eq. (29) is obtained by using the conventional form for $\chi_{xx}(\vec{q}, 0) + \chi_{yy}(\vec{q}, 0)$ for ferromagnets in an applied field. It is

$$A_{\vec{q}} = J[\mathcal{J}(\vec{0}) - \mathcal{J}(\vec{q})] + A + g_L \mu_B H. \quad (30)$$

$(A_{\vec{q}}^2 - B^2)^{1/2}$ is the dispersion relation for an anisotropic ferromagnet in a field H , applied along the direction of magnetization. $\mathcal{J}(\vec{q})$ is the Fourier transform of the Heisenberg interaction between the angular momentum of the rare-earth ions, and A and B are single-ion anisotropy constants (see, for instance, Ref. 11).

III. MASS RENORMALIZATION IN RARE-EARTH METALS

The importance of mass renormalization in rare-earth metals due to the interaction of the conduction electrons with the localized $4f$ moments has recently been discovered experimentally by Forgan.⁵ He found that the effective density of states $N^*(0)$, in Pr metal, as deduced from heat-capacity measurements between 1 and 6 K, was about a factor of 4 larger than predicted by band calculations.¹² More significantly, he observed that this enhancement factor was reduced by as much as $\sim 25\%$ in an applied field of 4 T, which shows that the effect must be of magnetic origin. White and Fulde⁴ subsequently showed that the exchange interaction between the conduction electrons and the $4f$ electrons modifies the effective mass in Pr in a way which agrees in order of magnitude with the experiment. Their estimate can be improved quantitatively when utilizing the fact that the dispersion of the magnetic excitations in Pr (Ref. 9) only introduces minor correlation effects between 1 and 6 K.¹³ Within an estimated error of less than 10% we can use the following approximation in Eq. (17):

$$\begin{aligned} & \frac{1}{2p_F^2} \int_0^{2p_F} dq q R(q, \omega) \\ &= -\frac{1}{2p_F^2} \int \frac{d\Omega_{\vec{q}}}{4\pi} \int_0^{2p_F} dq q \text{Tr}\chi(\vec{q}, \omega) \\ &\simeq -\text{Tr}\chi_0(\omega), \end{aligned} \quad (31)$$

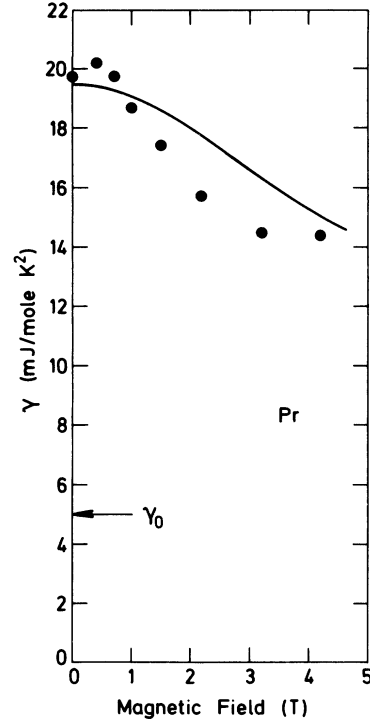


FIG. 3. Specific-heat coefficient γ of Pr metal as a function of a magnetic field applied in the basal plane. The solid circles are the experimental results of Forgan (Ref. 5). The solid line shows the behavior predicted by Eq. (33) when the molecular-field model of Houmann *et al.* (Ref. 9) is being used.

where $\chi_0(\omega)$ is the noninteracting susceptibility appearing in the random-phase expression

$$\chi(\vec{q}, \omega) = \chi_0(\omega) / [1 - \mathcal{J}(\vec{q})\chi_0(\omega)]. \quad (32)$$

With this simplification we find that the Sommerfeld constant γ is

$$\begin{aligned} \gamma &= \gamma_0 \{ 1 + (g_L - 1)^2 I_{sf}^2 N(0) \\ &\quad \times \frac{1}{2} \text{Tr}[\chi_0^{\text{hex}}(0) + \chi_0^{\text{cub}}(0)] \} \end{aligned} \quad (33)$$

when we make the plausible assumption that the effective exchange coupling between the conduction electrons and the Pr ions is independent of whether an ion is situated at a "hexagonal" or a "cubic" site.⁹ The molecular-field model for Pr developed by Houmann *et al.*⁹ predicts $\text{Tr}\chi_0^{\text{hex}}(0) = 11.4 \text{ meV}^{-1}$ and $\text{Tr}\chi_0^{\text{cub}}(0) = 4.8 \text{ meV}^{-1}$ at zero field and temperature. $\text{Tr}\chi_0^{\text{hex}}(0)$ is strongly dependent on the field applied in the basal plane, and the solid line in Fig. 3 shows the behavior predicted by Eq. (33) when the field dependence of $\chi_0^{\text{hex}}(0)$ and $\chi_0^{\text{cub}}(0)$ is calculated according to Refs. 9 and 13. Thereby $\gamma_0 = 5.0 \text{ mJ/mole K}^2$, corresponding to $N(0) = 1.06 \text{ eV}^{-1}$ per atom and spin, and $I_{sf} = 0.092 \text{ eV}$ is used.

TABLE I. The electronic specific-heat coefficients of the heavy rare-earth metals in units of mJ/mole K². The first row, γ_{expt} are the experimental values. γ_0 are the noninteracting values predicted by band-structure calculations (Ref. 18) according to the results shown in Fig. 4 when the band splittings given in the caption are used. With these values of γ_0 the theory predicts the modified coefficients γ_{calc} when the mass enhancement due to the spin waves is introduced.

	Gd	Tb	Dy	Ho	Er
γ_{expt}	3.7 ^a	4.35 ^b	< 4.5 ^c	6±1 ^c	< 9.5 ^c
γ_0	2.1	2.8	3.7	4.2	4.2
γ_{calc}	3.7	5.0	7.0	8.4	8.4

^aAfter Ref. 15.

^bAfter Ref. 16.

^cAfter Ref. 17.

The calculated field dependence of γ agrees reasonably well with the experimental results of Forgan. The minor, but systematic, deviations may be only partly due to our approximation in Eq. (31). The temperature interval 1–6 K corresponds to $k_B T/\delta$ lying between 0.025–0.15 and 0.01–0.06 for the hexagonal and cubic ions, respectively. Referring to Fig. 2 we expect the hexagonal contribution to be effectively ~25% larger than that given by Eq. (33). This effect does not change the field dependence of γ , but suggests that $I_{sf}=0.085$ eV instead of the value given above. At 4 T the uniform band splitting is about 0.08 eV, which might produce a reduction of the density of states by ~2% (see later) compared with the zero-field value. This small shift would reduce the calculated value of γ at 4 T by 0.5

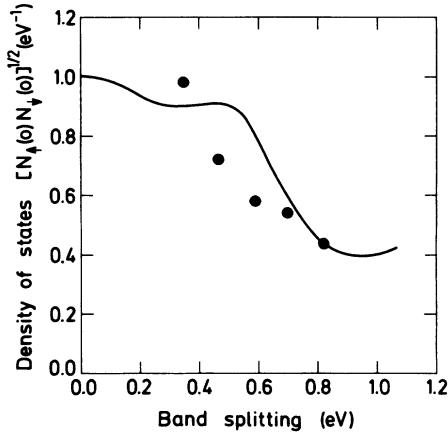


FIG. 4. Mean value of the densities of states at the spin-up and spin-down Fermi surfaces, $[N_{\uparrow}(0)N_{\downarrow}(0)]^{1/2}$, in Gd metal determined by band-structure calculations (Ref. 18) as a function of the rigid band splitting Δ . The solid circles show the densities of states in the different heavy rare-earth metals predicted by γ_{expt} in Table I as discussed in the text. The zero-temperature band splittings in the different metals are assumed to be proportional to $(g_L - 1)J$ with $\Delta=0.82$ eV in the case of Gd metal.

mJ/mole K², and would improve systematically the comparison with the experimental behavior.

In the heavy rare-earth metals both the experimental results and the theoretical predictions are more uncertain. At low temperatures Gd, Tb, and Dy are ferromagnets, and Ho and Er are ordered in conical structures. Owing to the contributions of the low-frequency part of the spin-wave spectrum and the nuclear hyperfine interaction it is difficult to isolate the linear electronic term in the experimental heat capacity. Furthermore, the γ value depends critically on the purity of the sample.¹⁴ In Table I the experimental results obtained in recent years on highly purified samples of the heavy rare earths are given.^{15–17}

Band-structure calculations performed on ferromagnetic Gd (see the review of Harmon¹²) indicate quite a strong dependence of $N_{\uparrow}(0)$ and $N_{\downarrow}(0)$ on the band splitting Δ . The solid line in Fig. 4 shows the variation of $[N_{\uparrow}(0)N_{\downarrow}(0)]^{1/2}$ with Δ obtained in the case of Gd.¹⁸ These results are determined by rigid shifts of the energy bands from those of paramagnetic Gd. The polarization of the band electrons in Gd gives rise to a moment of 0.63 μ_B /atom. Depending on whether the s - p electrons do not participate or whether they are polarized just as much as the d electrons, this moment corresponds to Δ equal to 0.97 or 0.72 eV, respectively. de Haas–van Alphen experiments¹⁹ indicate an intermediate value of 0.82–0.88 eV. Here we use $\Delta=0.82$ eV, which, according to Fig. 4, predicts

$$[N_{\uparrow}(0)N_{\downarrow}(0)]^{1/2}=0.44 \text{ eV}^{-1}$$

per atom and spin in Gd. This value is less than half the density of states at the Fermi surface in paramagnetic Gd and agrees with the value given by Harmon.¹² For the densities of states in the other heavy rare earths we shall use the results obtained for Gd and shown in Fig. 4 but with a band splitting Δ scaled according to Eq. (25) (neglecting the self-

energy correction). This is a reasonable procedure in the case of Tb and Dy, but it is somewhat questionable in the case of the conically ordered metals Ho and Er (to a lesser degree in Er where the ferromagnetic component is large). On the other hand, the superzone gaps in the electron bands produced by the periodic modulation of the magnetic moments are going to reduce the effective $N(0)$, and one might consider the present procedure to give an estimate of this reduction.

In view of the approximations already made in the theory and the experimental uncertainties, the following simplifying description of the averaged magnetic response in the heavy rare earths should be sufficiently accurate. $\langle \chi \rangle$ in Eq. (29) is being replaced by the molecular-field value $\langle \chi_0 \rangle$. It is obtained by setting $\mathcal{J}(\vec{q}) \equiv 0$ in the equation, and we use $\mathcal{J}(\vec{0}) = (g_L - 1)^2 (4.8) \text{ meV}$ corresponding to $T_c = 293 \text{ K}$ in Gd. This is equivalent to a replacement of the spin-wave spectrum in the different metals by a flat level lying just above the energy of the spin wave at $q = 2\pi/c$ in the c direction.

In Table I a comparison is given of the experimental specific-heat coefficients γ_{expt} , with the unperturbed values γ_0 , and the results γ_{cal} , obtained from Eq. (28) when the above procedure is used. An alternative comparison between theory and experiment is given in Fig. 4 where we have plotted the effective densities of states predicted by γ_{expt} when inserted in Eq. (28). In both comparisons we have fitted to the result of Gd, i.e., we have used $I_{sf} = 0.065 \text{ eV}$. As in the case of Pr a crucial test of the theory might be obtained by studying the field dependence of γ . The present estimate predicts a linear reduction of γ , when a field is applied along the direction of magnetization, which in the case of Tb should amount to $\sim 4\%$ in a field of 10 T. Unfortunately, this is on the borderline of the experimental capability, although a test of this prediction would be very valuable. The comparison between the experiments and the results obtained from band-structure calculations, as given in Table I or in Fig. 4, is clearly improved when the mass renormalization is taken into account. The only exception seems to be the case of Dy metal. This discrepancy might be due either to the experimental uncertainties, or alternatively, to the simple scaling of the results for Gd to the case of, e.g., Dy, without considering other individual properties.

The coupling constant I_{sf} was found to be equal to 0.085 and 0.065 eV in the respective cases of Pr and the heavy rare earths. When trying to relate the effective coupling constant $I_{sf}(\gamma)$ to other properties depending on the exchange interaction, the interaction Hamiltonian, Eq. (20), is found to be too simplified. Modifications result from the finite exten-

sion of the 4f-electron cloud, as well as from the deviations of the wave functions of the band electrons from plane waves.²⁰ The band splitting $\Delta = 0.82 \text{ eV}$ together with Eq. (25) indicates $I_{sf} = I_{sf}(\Delta) = 0.12 \text{ eV}$. If we consider only the effect of the nonzero 4f radius, as determined by magnetic form-factor measurements, then we find

$$I_{sf}(\gamma) \simeq 0.85 I_{sf}(\Delta) = 0.10 \text{ eV} .$$

A more uncertain estimate of an effective coupling constant is obtained from

$$\mathcal{J}(\vec{0}) \simeq 2N(0)(g_L - 1)^2 I_{sf}^2 .$$

This relation could be wrong by a factor of 2 or more, but with $\mathcal{J}(0) = 4.8 \text{ meV}$ in Gd we have $I_{sf}(\mathcal{J}) \simeq 0.05 \text{ eV}$. The effects introduced when modifying the wave functions of the conduction electrons indicate that $I_{sf}(\gamma)$ is most strongly related to the effective coupling constant appearing in the linewidth of the magnetic excitations due to their interaction with the electron-hole pair excitations. This scattering effect has been detected experimentally in Tb in the low-temperature limit.²¹ A theoretical account of these measurements²² is obtained using $I_{sf} = 0.08 \text{ eV}$ (together with $[N_1(0) \times N_1(0)]^{1/2} = 0.60 \text{ eV}^{-1}$). Combining the different estimates we conclude that $I_{sf}(\gamma) = 0.08 \pm 0.01 \text{ eV}$ seems to give a fair assessment of the effective coupling constant. Again one should have in mind that there might be individual differences, especially between Pr and the other heavy rare-earth metals.

IV. CONCLUSION

The mass enhancement of the conduction electrons due to their interaction with the magnetic excitons has been derived both in the paramagnetic and in the spin-polarized ferromagnetic cases. The modification of the electronic mass is found to be proportional to the static susceptibility of the magnetic system. It becomes large if the magnetic excitation energies are small. The theory accounts for the leading-order contribution to m^* , but neglects terms of the order of δ/D , where δ is the magnetic excitation energy and D is the electronic bandwidth. By this assessment we have also included the approximations made in, for instance, Eqs. (3) or (8). The most significant feature of the correction to the temperature-dependent electronic specific heat, as exemplified in Fig. 2, is the narrow peak around $k_B T \simeq 0.15\delta$. The position of this maximum does not depend very much on the actual population factor, that is, on $\tanh(\beta\delta/2)$ in the singlet-singlet case. The temperature dependence of γ is normally very difficult to extract from experimental measurements

because the deviation of ΔC_e from the linear behavior occurs at temperatures where other non-linear contributions of the solid dominate. For this purpose Pr metal might be one of the best qualified systems, and we propose a careful examination of C in Pr, which might, it is hoped, reveal a small change of slope at about 6 K. Because of the field dependence of the crystal-field splittings the position of the maximum should be shifted upwards in temperature with an amount of about 0.9 K in a field of 4 T.

In Sec. III the theory is applied to the cases of paramagnetic Pr and the magnetically ordered heavy rare-earth metals. Pr is quite an ideal system for studying the enhancement effect, because it is a singlet ground-state system in which the exchange coupling has a value just below the one which would force the system to order magnetically.⁹ This means that the coupling constant is of substantial magnitude, although the system stays paramagnetic, and that the magnetic response is strongly influenced by an applied magnetic field. Experimentally⁵ the mass-enhancement factor was found to be around 4 at zero field, and it was reduced to about 3 in a field of 4 T. Both these results are reproduced by the theory with a value of the coupling constant which compares well with other estimates. In the case of the heavy rare-earth metals the situation is more uncertain, both for experimental and theoretical reasons. Band-structure calculations^{12,18} indicate a substantial reduction in the density of states at the Fermi surface when the spins of the conduction electrons are being polarized. The experimental values of γ in all the heavy rare earths are larger than the noninteracting γ_0 predicted by the band-structure calculation. With the exception of Dy our comparison indicates the presence of a mass-enhancement factor lying between 1.5–2. This indication agrees reasonably well with the effect expected due alone to the interaction of the conduction electrons with the spin waves. In these comparisons we have left out the mass enhancement due to the electron-phonon interaction. The experimental result of $\gamma=8.2$ mJ/moleK² for both Lu (Ref. 23) and Y (Ref. 14) might be used as an indication of $\lambda \simeq 0.8$ in the rare-earth metals, where λ is the phonon contribution to m^*/m . A phonon term of this magnitude would only slightly affect our comparison in the case of Pr, but it would account for most of the differences between γ_{expt} and γ_0 in the heavy rare-

earth metals given in Table I. Here we have taken into consideration that λ is reduced proportional to $N(0)$, i.e., $\lambda \simeq 0.4$ in Gd. In the spin-polarized metals λ might be reduced further because the band splitting introduces a lower cutoff at $|p_F^\uparrow - p_F^\downarrow|$, see Eq. (26), which diminishes the influence of the long-wavelength part of the phonon spectrum. We can add that there are indications^{21,22} of such a cutoff in the spin-wave spectrum of Tb lying around 0.3 \AA^{-1} . However, this minor correction cannot alter the indication that the above estimate of λ must be exaggerating the influence of the phonons. Our modest estimate of the mass enhancement in the heavy rare earths due to the spin waves is not compatible with experiments unless the above phonon contribution is reduced at least by a factor of 2. This claim is consistent with the result that $\lambda \simeq 0.3$ in Lu metal, which has been deduced from the superconducting transition temperature as a function of an applied pressure.²⁴

In conclusion, we can say that the magnitude and the field dependence of γ in Pr clearly indicate a renormalization of the electronic mass due to the magnetic excitons, and that the effects agree with the theory. The comparison between γ_0 as derived from band-structure calculations and the experimental values of γ in the heavy rare-earth metals (with the exception of Dy) shows differences which compare well with the mass enhancement due alone to the electron-spin-wave interaction. This comparison indicates that λ due to the electron-phonon interaction must be smaller than ~ 0.4 in the unpolarized metals. As in the case of Pr metal the most direct way of referring a mass-enhancement effect to the magnetic excitons in a rare-earth system would be a study of the field dependence of γ . This dependence is estimated to be small in the heavy rare-earth metals.

We do not consider Pr metal to be unique with respect to the magnitude of the mass enhancement. Nor do we consider the (isotropic) exchange interaction as given by Eq. (20) as a necessary prerequisite for it to occur. For example, PrCu₂ is known to be a singlet ground-state system with an induced Jahn-Teller phase transition.²⁵ In that case the aspherical Coulomb charge scattering is more important than the isotropic exchange interaction. When PrCu₂ is diluted with La such that the Jahn-Teller phase transition is suppressed one would expect a large electron-mass enhancement.

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