Intermediate-valence compounds with heavy fermions viewed as two-component systems

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A two-component model is used to analyze the properties of intermediate-valence compounds with heavy fermions. Expressions for the thermodynamic quantities—compressibility, heat capacity, thermal diffusion coefficient, and magnetic susceptibility—are obtained and analyzed, and their dependences on temperature and on magnetic field are studied. The behavior of a number of kinetic characteristics is investigated. The important role of both the heavy and light components is demonstrated for a consistent interpretation of the special properties of these compounds. It is shown that the two-component model gives a good description of the regularities observed in experiment.

1. INTRODUCTION

Because they exhibit a number of interesting properties, compounds with valence fluctuations have long attracted the attention of researchers.[1] However, in recent times these same compounds of rare-earth and actinide elements have caused an explosion of interest in the literature, connected with the discovery within this class of materials of superconductors with very unusual properties—$CeCu_2Si_2$, UBe_{13}, UPt_3, and $CePb_3$ (see, e.g., Ref. 2).

However, even in the normal state these materials are very strange—they have anomalously large heat capacities and magnetic susceptibilities, and many quantities exhibit unusual kinetic properties and peculiar temperature dependences.[2]

The qualitative behavior of these materials is interpreted by using a model in which electrons at the Fermi level have a very large effective mass $m^* \sim 10^2$–$10^3 m_0$ ("heavy fermions"). However, despite the availability of a great deal of experimental material, there is as yet no correct description of the properties of these materials at the microscopic level. This is to a significant extent related to the fact that in the final analysis the nature of the "heavy fermions" themselves is not well-understood. Therefore, limited phenomenological schemes are proposed in order to analyze the properties of these materials; among these, the Fermi-liquid approach is most satisfactory. In addition to its purely heuristic value, the Fermi-liquid picture also may reflect more fundamental requirements for a correct theory, since we are dealing here with a very strongly-interacting system.

A similar approach has already been applied to systems with intermediate valence and heavy fermions (see, e.g., Ref. 4). In such systems it is customary to take into account only the presence of the heavy component. However, there are compelling reasons to believe that a number of properties of these systems are influenced not only by the heavy electrons (from here on we will be calling these "*f*-electrons," keeping in mind their origin) but also by the light electrons which are also clearly present (electrons in wide bands, e.g., the 5*d*, 6*s* bands in rare-earth compounds or the 6*d*, 7*s* bands in actinides; we will refer to these as "*d*-electrons" for brevity).

There is also direct experimental evidence for the presence at the Fermi surface of two groups of electrons with significantly different masses; study of the de Haas–van Alphen effect shows[5] that in the intermediate-valence compound $CeSn_3$ there is a group of carriers with large effective mass $m_f^* \sim 8$–$10 m_0$ while on another part of the Fermi surface there is a group of normal light electrons with $m_d^* \sim m_0$ (in systems with larger values of m_f^*, i.e., in true heavy-fermion materials, it has not yet been possible to observe the de Haas–van Alphen effect).

As we will endeavor to show, inclusion of two fermion components allows us to interpret many properties of these compounds in a rather natural way, in particular some properties which cannot be explained (or are explained only with difficulty) by a model with one heavy component. In some cases, where it is necessary and leads to qualitative consequences, we will also include Fermi liquid effects, although the basic results of the article do not depend on these effects, but rather are simply consequences of the presence of two components with very different effective masses (and densities of states). In this regard our approach is rather close to a model of transition metals developed long ago,[6] with the fundamental difference that the disparity in scales (e.g., for characteristic temperature or bandwidth) between light and heavy fermions is in this case significantly larger and thus the corresponding effects are much more marked.

2. THE SINGLE-COMPONENT APPROACH

Let us consider certain consequences which follow from a one-component model. First of all, the heavy Fermi liquid is associated with the large density of states $\rho = m^* p_F V / \pi^2 \hbar^3$, as a result of which the heat capacity C, magnetic susceptibility χ, and compressibility $\varkappa$ turn out to be proportional to ρ and are large in magnitude (three to four orders of magnitude larger than in normal metals). In reality, however, C and $\chi \sim \rho \sim m^*$, while $\varkappa$ is not at all proportional to m^*. Furthermore, in heavy-fermion systems with near-integer valence ($CeCu_2Si_2$, $CeAl_3$) the compressibility turns out to be almost the same as in rare-earth compounds with stable *f*-shells.[7] It is still possible to correct this problem with the compressibility if we take into account correlation effects, which lead to an expression of the form $\varkappa = \rho / Vn^2(1 + {}^sF_0)$, if for these systems the zero-order symmetric Landau coefficient grows as the effective mass increases, i.e., ${}^sF_0 \sim m^*$ (Refs. 8, 9). However, explaining the behavior of

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the coefficient of thermal expansion α within the one-component approach is a still more complicated problem. It has been established experimentally that in many cases (e.g., in $CeAl_3$,[10,11] $CeCu_2Si_2$[12]) α behaves in an anomalous fashion at low temperatures and changes sign, becoming negative. The usual interpretation of this is based on an analogy with ^3He, where Fermi-liquid theory leads to an expression of the form[13]

$$\alpha = \varkappa C\left(\frac{2}{3} + \frac{\partial \ln m^*}{\partial \ln V}\right), \tag{1}$$

from which it follows that for a negative sign of the derivative $\partial m^*/\partial V$ (which actually occurs in ^3He[8,13]) α can become negative. However, in solids the effective mass satisfies $m^* \sim \Gamma^{-1}$ or T_f^{-1}, where Γ is the width of the virtual f-level and T_f is a characteristic temperature (for example, the temperature of spin fluctuations or the Kondo temperature). Also well-established is the fact that all these quantities increase with pressure, so that $\partial m^*/\partial V > 0$, as a result of which it is necessary to introduce some other considerations to explain the anomaly in the coefficient of thermal expansion. Of additional significance is the difficulty in interpreting the changes in sign of the thermoelectric power, and the correlation of these anomalies with the behavior of the thermal expansion coefficient.[12,14]

The above-mentioned difficulties are not restricted to the one-component Fermi-liquid approach; the other popular description of heavy fermions in rare-earth and actinide compounds—the model of almost-localized electrons[8,9]—also leads to the same result. In this approach, the narrow f-band is described by a Hubbard-type model, and the effective mass is proportional to the expression

$$m_f^* \sim [1-(U/U_c)^2]^{-1}, \quad U_c \sim t \tag{2a}$$

for a half-filled band $n_f = 1$; here U is the energy of electronic repulsion from a single center and t is the band width; or else,

$$m_f^* \sim \delta^{-1}, \quad \delta = |n_f - 1| \tag{2b}$$

in the case of a partially-filled band with $\delta \ll 1$ and for strong correlation $U \gg U_c$. In this case too we find that $\partial m^*/\partial V > 0$ under pressure, due to the growth in the band width t, or to the increase in valence (i.e., a decrease in the number of f-electrons, which is to say a decrease in δ).

Still another often-used phenomenological approach is to describe the properties of a system with heavy fermions with a model which includes a resonance level; an expression of Lorentzian form is used for the density of states of the f-level (see Ref. 34):

$$\rho_f(\varepsilon) = \frac{2}{\pi}\frac{\Gamma}{[(\varepsilon-\varepsilon_f)^2+\Gamma^2]}. \tag{3}$$

Here ε_f is the position of the f-level relative to the Fermi level and Γ is the width of the f-band. The characteristic temperature satisfies $T_f \approx (\Gamma^2 + \varepsilon_f^2)^{1/2}$, for the case of interest to us, i.e., $\varepsilon_f < \Gamma, T_f \sim \Gamma$. It is not difficult to show that even in this case if we limit ourselves to only one f-level, the thermal expansion coefficient α of Ce-based systems is found to be positive (see Ref. 15). Thus, we see that a simple one-component model does not allow us to explain all the properties of a heavy-fermion system.

3. THE TWO-COMPONENT MODEL

It is beyond dispute that a better approach to this problem must include correctly the specific properties of the compounds under consideration, in particular the complex character of their band structures and densities of states near the Fermi level. In this paper we want to propose a phenomenological scheme in order to describe systems with intermediate valence and heavy fermions, which is based on a two-component model.

Let us consider a system consisting of electrons from two bands—a "heavy" component from the narrow f-band and a light component corresponding to the conduction band. In this case the numbers N_f, N_d of heavy and light electrons are not conserved individually (it is this aspect in particular which distinguishes this model both from nuclear matter[16] and from metallic hydrogen[17]), while at the same time their sum $N = N_f + N_d$ remains constant (this is a consequence of our neglecting from this point on the influence of the other band states). The ratio between N_f and N_d is determined by the equilibrium condition of the system, i.e., equality of the chemical potentials $\mu_f = \mu_d$. The possibility of electrons flowing from band to band turns out to be an important feature of these systems, and along with the interband interaction it plays a key role in interpreting a number of peculiar properties of the compounds under study.

In view of the complexity of the problem and the wide class of phenomena which require explanation, it is expedient to simplify its formulation as much as possible. With this goal in mind we will sometimes employ very simple models, in particular those used in the theory of transition metals and especially the model of two isotropic bands centered at the same point in k-space and intersected by the overall Fermi level. We will further assume a quadratic dispersion law

$$\varepsilon_i(p) = p^2/2m_i^* + \Delta_i \quad (i=f,\ d), \tag{4}$$

where the effective masses of the carriers satisfy $m_f^* \gg m_d^*$. We remark that in the general case the Δ_i are functions of the specific volume. Choosing the sign of the dispersion law in form (4) is not an essential limitation and is used only for clarity; in fact all the responses will depend only on the densities of states at the Fermi level $\rho_f(\varepsilon_f)$, $\rho_d(\varepsilon_f)$ and their derivatives $\rho'(\varepsilon_f)$, $\rho''(\varepsilon_f)$. We will often use expression (3) for $\rho(\varepsilon_f)$.

Within this approach, the interaction of quasiparticles can in principle be described by using the Fermi liquid model. The Landau functional in this case is a matrix in band-space. We can introduce the coefficients of a Legendre polynomial expansion of the kernel $\hat{f}$ in the standard fashion ${}^{s,a}F_l^{ij} = \rho_j^{s,a} f_l^{ij}$, where l is the orbital angular momentum and i, j are band indices.

In the general case, the F^{ij} are unknown parameters whose number is determined by relations derived from symmetry, hermeticity and sum rules. In our case, however, the situation is simplified due to the presence of the large effective mass $m_f^* \gg m_d^*$. This allows us to reduce substantially the degree of arbitrariness of the F^{ij}, and in this limit the responses depend only on a small number of free parameters. In practice we can neglect entirely the correlation coefficients of the light components, i.e., set $F^{dd} = 0$, without loss of generality. Assuming that hybridization (one- or two-particle) is included in determining the f- and d-quasiparticle states, we will also neglect (as is usually done) amplitudes which change the numbers of particles in the bands (for more detail, see, e.g., Ref. 18). In the approach which describes the heavy component as an almost-localized Fermi liquid,[8,9] we obtain the following expressions for the corresponding parameters of the Landau theory in the limit $m_f^* \to \infty$: ${}^aF_{0.1}^{ff} \approx -3/4$, ${}^sF_1^{ff} \sim m_f^*$, and ${}^sF_0^{ff} \sim (m_f^*)^2$ or $\sim m_f^*$, depending on whether relation (2a) or (2b) holds. In point of fact, it is apparently the second situation which is realized in compounds with heavy fermions,[9] i.e., the Landau coefficients grow no faster than m_f^*. We will keep in mind these results below, although there are other possibilities (see, e.g., Ref. 19).

Thus, we have the interband coefficients ${}^{s,a}F^{fd}$ to determine. The investigation in Refs. 8, 9 was limited to the one-band case, and so we can draw no direct conclusions about the behavior of the analogous model with interband coefficients F^{fd}. However, simple qualitative considerations show that here too one can hardly expect the dependence to be stronger than m_f^*. (Thus, even the most dangerous terms ${}^sF_0^{fd}$ will be proportional to

$$f_0^{df} \sim \int |\psi_f(\mathbf{r})|^2 |\psi_d(\mathbf{r})|^2 W(\mathbf{r}, \mathbf{r}'),$$

and by virtue of the delocalized character of the d-electrons and the weak overlap of the d- and f-wave functions this factor remains finite in the approach to localization, i.e., ${}^sF_0^{fd} = \rho_f^s f_0^{fd} \sim m_f^*$). As yet there is no explicit calculation of these "crossed" coefficients.

4. THERMODYNAMIC QUANTITIES IN THE TWO-COMPONENT MODEL

Let us turn to an investigation of the fundamental thermodynamic quantities in this model.

a) It is obvious that the entropy of the electrons has the usual combinatoric form, and $S = S_f + S_d$ is adequate. Correspondingly, having found the heat capacity in the usual way $C = 1/T(\partial S/\partial T)$, we obtain the following simple expression[1)]:

$$C = C_f + C_d = \gamma T, \quad \gamma = \gamma_f + \gamma_d,$$
$$\gamma_i = \pi^2 \rho_i / 3, \quad \rho_i = m_i^* p_{Fi} V / \pi^2 \hbar^3. \tag{5}$$

Thus, as $T \to 0$ the heat capacity is simply additive and for $m_f^* \gg m_d^*$ is wholly determined by the heavy component.

In the simplest version, if we neglect the Fermi-liquid effects it is easy to investigate the behavior of the heat capacity over an even wider temperature interval. For an arbitrary dependence of the density of states $\rho_f(\varepsilon)$ on the energy we can take into account the next correction in powers of T; then $C(T)$ takes the form (see Ref. 4):

$$C(T) = \gamma_f T \left\{ 1 + \frac{\pi^2 T^2}{3} \left[\frac{7}{5} \frac{\rho_f''}{\rho_f} - \left(\frac{\rho_f'}{\rho_f} \right)^2 \right] \right\}. \tag{6}$$

(Fermi-liquid theory leads to a correction $\sim T^3 \ln T$; however, only one among the large number of compounds with valence fluctuations is observed to have such a contribution to $C(T)$ in experiments—Upt$_3$—and we will not discuss it in what follows).

In the general case, the occupation of the f-band is incomplete. When the sum is carried out for the T^2 coefficient in (6) [e.g., for a density of f-states of the form (3)], its sign can depend on the occupation of the f-band (which is to an important degree determined by the degree of degeneracy of the underlying f-level[2)]).

Once we have chosen a specific form for $\rho_f(\varepsilon)$, it is easy to calculate the dependence of $C(T)$ for all temperatures (see Ref. 34). In Fig. 1a we present the results of a calculation of $\gamma(T) = C(T)/T$ using a density of states of the form (3) with $\varepsilon_f = 0$; we also present there the experimental values of γ for UBe$_{13}$ and CeCu$_2$Si$_2$. It is clear that agreement is very good for relatively low temperatures. In Fig. 1b the corresponding results are presented for $\varepsilon_f \neq 0$, along with experimental data from CeAl$_3$. For computational simplicity we chose a symmetric density of states:

$$\rho_f(\varepsilon) = (1/2)[\rho_f(\varepsilon, \varepsilon_f) + \rho_f(\varepsilon, -\varepsilon_f)],$$

where $\rho_f(\varepsilon, \varepsilon_f)$ is given by expression (3); in fact this corresponds to locating the Fermi level inside the pseudogap in the density of states, whose presence was postulated in Ref. 14 for the coherent regime. It is clear that the qualitative behavior of $C(T)$ is correctly described; however, the quantitative disagreement is substantial, especially at high temperatures.[3)]

b) Analogously, once we have calculated the magnetization M taking into account the change in quasiparticle energies in a magnetic field, we can obtain expressions for the magnetic susceptibility:

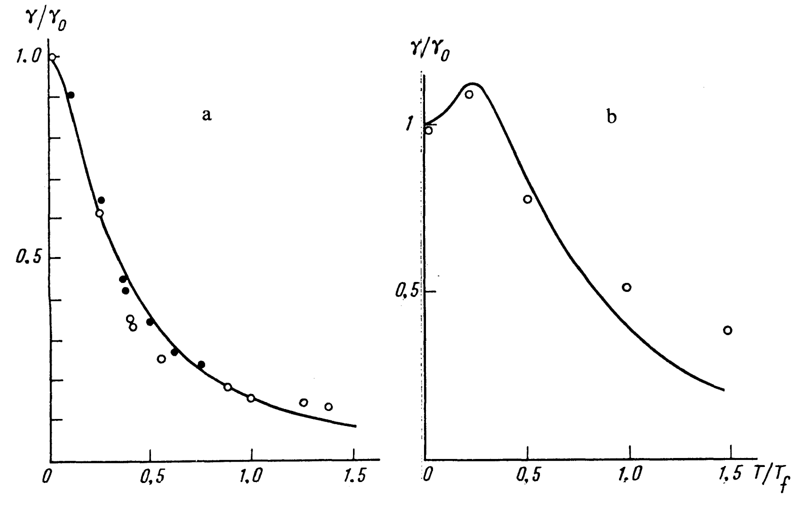

FIG. 1. (a) Temperature dependences of $C(T)/T = \gamma(T)$ [normalized by $\gamma_0 = \gamma(0)$] in the symmetric case $\varepsilon_f = 0$. The continuous curves are calculated; ○—experimental data for UBe$_{13}$ and CeCu$_2$Si$_2$ from Ref. 3 (they practically coincide); ●—experimental data for UBe$_{13}$ according to data from Ref. 9; $T_f = 8$ °K. (b) The same for $\varepsilon_f \neq 0$. Continuous curve—calculated ($\varepsilon_f/\Gamma = 1$); ○—experimental data from CeAl$_3$ (from Ref. 3); $T_f = 2$ °K.

$$\chi=\chi_f+\chi_d,\quad \chi_f\sim m_f^*,\quad \chi_d\sim m_d^*\ll\chi_f. \tag{7}$$

In the usual way, we can also include the Fermi-liquid corrections in χ (see Ref. 21), which here do not lead to any qualitative consequences (let us recall that in our case the corresponding correlation parameters ${}^aF_0$ are limited by $|{}^aF_0|<1$.[8,9,19]

At finite temperatures, it is also simple to find the next term in the expansion of $\chi(T)$ in T. Again we discard the Fermi liquid parameters and find (see Refs. 4, 22):

$$\chi(T)=\chi(0)\left\{1+\frac{\pi^2T^2}{6}\left[\frac{\rho_f''}{\rho_f}-\left(\frac{\rho_f'}{\rho_f}\right)^2\right]\right\}, \tag{8}$$

where naturally only the contribution from the heavy component is left. The sign of the term in T^2, as with the heat capacity (10), depends on the detailed structure of the density of states $\rho_f(\varepsilon)$ near the Fermi level. It is not hard to see that in the case of a negative correction to $C(T)$ (the Kondo regime), $\chi(T)$ will decrease as T increases; conversely, if $\gamma=C/T$ grows with temperature (in a system with a high degree of degeneracy, i.e., the intermediate-valence regime) the susceptibility must also increase. In this case the susceptibility will have a maximum at some finite temperature T^* [for lower temperatures it is obvious that $\chi(T)$ will follow Curie's law, $\chi(T)\sim T^{-1}$], Such behavior of $\chi(T)$, along with the correlation in the behavior of $C(T)$ and $\chi(T)$, also agrees with the experimental data.

Having found the above temperature dependence of the magnetic susceptibility, we can also obtain the heat capacity $C(H)$ in a magnetic field. Specifically, using the thermodynamic relation $\partial M/\partial T=\partial S/\partial H$, we obtain

$$\frac{\partial C}{\partial H}=TH\frac{\partial^2\chi}{\partial T^2}, \tag{9}$$

from which it follows that for small H

$$C(H,T)-C(0,T)=\frac{TH^2}{2}\frac{\partial^2\chi}{\partial T^2}=\frac{H^2}{T}\left[\chi(T)-\chi(0)\right], \tag{10}$$

where the last equation is obtained by taking (8) into account, and is correct only in the region over which this relation is valid.

From formula (9) and (10) it follows that $\Delta C(H)=C(H)-C(0)$ is proportional to H^2 and can be both positive and negative; furthermore, it can change sign with temperature depending on the behavior of the magnetic susceptibility $\chi(T)$.

Study of the behavior of the heat capacity in a magnetic field has recently become a very popular method for investigating heavy-fermion systems.[3] It appears, however, that experimentally such information is much more easily obtained, at least in weak fields, with the help of relations (9) and (10), using much easier and more standard methods to measure the magnetic susceptibility. Relations (9) and (10) can also be used to verify the mutual consistency of the results of different experiments. A comparison of data on the functions $C(H,T)$ and $\chi(H)$ presented in Ref. 3 shows that as a rule the correlation required by (9) does occur, whereas the sign of $\Delta C(H)$ itself, and the dependence of ΔC on temperature, change from material to material.

c) Whereas for the heat capacity or susceptibility the results of the one- and two-component models coincide qualitatively when the approximation is made that the density of states is large for the heavy component, the situation is otherwise for the compressibility. Here a decisive role is played by the indistinguishability of the electrons, along with Fermi-liquid correlations, and the possibility of their flow from one band to the other.

The definition of the compressibility $\varkappa=-(1/V)(\partial V/\partial P)$ can be written in the form $\varkappa^{-1}=-N\partial\mu/\partial N$, using the fact that for low temperatures $VdP=Nd\mu$. By varying the chemical potential we obtain

$$\delta\mu_i=\rho_i^{-1}\delta n_i+\sum_j {}^sf_0^{ij}\delta n_j+\delta\Delta_i. \tag{11}$$

When we calculate the derivative $\partial\mu/\partial V$ the term

$$\frac{\partial n_i}{\partial V}=\frac{\partial(N_i/V)}{\partial V}=-\frac{N_i}{V^2}+\frac{1}{V}\frac{\partial N_i}{\partial V},$$

appears, in which the last term is not zero as it is in the one-band case due to the possibility of transfer of electrons between bands.

Using the equality of chemical potentials $\delta\mu_f=\delta\mu_d$ and calculating from it the derivative $\partial N_f/\partial V=-\partial N_d/\partial V$, we finally obtain the following expressions for the compressibility:

$$\varkappa=\frac{1}{Vn}\frac{\rho_d(\beta_f-{}^sF_0^{df})+\rho_f(\beta_d-{}^sF_0^{fd})}{n(\beta_d\beta_f-{}^sF_0^{fd}\,{}^sF_0^{df})-\Delta_d'(\rho_d\beta_f-\rho_f{}^sF_0^{fd})-\Delta_f'(\rho_f\beta_d-\rho_d{}^sF_0^{df})}\,. \tag{12}$$

Here $\beta_i=1+{}^sF_0^{ii}$, $\Delta_i'=\partial\Delta_i/\partial V$, and $n=n_f+n_d$ is the total electron density. In its structure expression (12) is reminiscent of the corresponding expression for the magnetic susceptibility[12]; in the case of rigid bands ($\Delta_i'=0$) it coincides with the results of Ref. 23. It is significant that, thanks to the two peculiarities alluded to above, i.e., the correlation between components and the displacement of the bands ($\Delta_i'\neq0$), the magnitude of $\varkappa$ in the general case remains finite even when $m_f^*\to\infty$.

Expression (12) has different limiting forms for $m_f^*\gg m_d^*$, depending on different possible behaviors of the Landau coefficients ${}^sF_0^{ij}$. In the simplest case, $F^{ij}=0$ and $\rho_f\gg\rho_d$,

$$\varkappa=-1/Vn\Delta_f', \tag{13}$$

and the compressibility is found to be finite due to the band shifts [usually the f-band shifts upward with pressure, i.e., $\Delta_f'=\partial\Delta_f/\partial V<0)$].

If, however, relation (2a) were correct for example, we would then obtain

$$\varkappa=\frac{\rho_d}{Vn}\left[n(1+{}^sF_0^{dd})-\rho_d\Delta_d'\right]^{-1}, \tag{14}$$

i.e., the compressibility would be determined by the light component. In the general case the characteristics of both components enter in. In order of magnitude the compressibility for this case, generally speaking, is found to be close to the compressibility of analogous systems with one light component. On the other hand, specifically because of the mutual influence of the two components, a situation is possible in which for certain parameter ratios $\varkappa$ becomes negative, which will correspond to instability of the system relative to a transition to one with variable valence.

We note that the result (12) differs significantly from analogous expressions for metallic hydrogen,[17] which as we have already noted is connected with the identity of particles of the different components and with the possibility that they can pass from band to band under compression.

Using the relations between the derivatives of the thermodynamic quantities, we can study the dependence of the compressibility $\varkappa$ on the modulus of hydrostatic compression $B = \varkappa^{-1}$ on magnetic field. In analogy with (9) we obtain

$$\frac{\partial B}{\partial H} = -VH\frac{\partial^2 \chi}{\partial V^2}.$$

However, since the dependence of the susceptibility on pressure or volume is not as easy a quantity to measure, this relation turns out to be less useful than (9) and (10).

d) An expression for the thermal expansion coefficient α can be obtained as usual[13] from the Maxwell relation:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T = \varkappa\left(\frac{\partial S}{\partial V}\right)_T. \qquad (15)$$

Using the explicit expression for the entropy

$$S = (\pi/3)^{2/3}\hbar^{-2}VT(m_f^* n_f^{1/3} + m_d^* n_d^{1/3}), \qquad (16)$$

where $n_i = N_i/V$ is the density of the ith component, we find from (15) that

$$\alpha = \varkappa\sum_i C_i\left(\frac{2}{3} + \frac{\partial \ln m_i^*}{\partial \ln V} + \frac{1}{3n_i}\frac{\partial N_i}{\partial V}\right), \qquad (17)$$

where C_i is the heat capacity, and $\partial N_i/\partial V$ will in the general case contain Fermi-liquid correlations.[24]

In the simplest case Fermi-liquid effects other than those contained in m_f^* are absent, and for $\rho_f \gg \rho_d$ we obtain in this case the simple expression[24]

$$\alpha = \varkappa C_f\left[\frac{2}{3} + \frac{\partial \ln m_f^*}{\partial \ln V} - \frac{n_d}{3n_f} + \frac{\rho_d(\Delta_d' - \Delta_f')}{3n_f}\right]. \qquad (18)$$

It is clear that due to the third term in (18) α can become negative (as was already noted above, the second and fourth terms in these systems are positive). The meaning of these terms can be made more transparent if we rewrite expression (15) in terms of the density of states. Assuming for simplicity that the Δ_i are constant, we obtain

$$\alpha = \varkappa C_f\left(\frac{2}{3} + \frac{\partial \ln m_f^*}{\partial \ln V} - \frac{Vn_d}{3\rho_f^2}\frac{\partial \rho_f}{\partial \varepsilon}\right). \qquad (19)$$

We can show that in this form the expression for α does not depend on our special choice of the dispersion law (4).

Expression (19) is found to be in agreement with the general treatment of thermal expansion of metals with arbitrary band structures.[25] From expressions (18), (19) it is clear that the situation which favors a negative thermal expansion is one in which the Fermi level is located in a region of increasing density of states $\partial\rho_f/\partial\varepsilon > 0$, and in this case the total electron concentration will be large compared to the concentration of the heavy component. One may suppose that both of these conditions are realized in $CeAl_3$ and $CeCu_2Si_2$, and that the negative sign of α observed in these compounds for $T \lesssim 0.5$ °K is explained by the mechanism considered above, which is essentially related to the multiband property and to the complex structure of the density of states in these compounds.

An additional factor in favor of this explanation is the correlation between the behavior of the thermal expansion coefficient and that of the thermoelectric power in these systems. As was found in Refs. 12, 14, in $CeAl_3$ and $CeCu_2Si_2$, for $T \gtrsim 0.5$ °K we have $\alpha > 0$ and the Seebeck coefficient satisfies $Q < 0$; for $T \approx 0.5$ °K, both of these quantities change sign, and at low temperatures $\alpha < 0$ and $Q < 0$. In the two-component model the expression for Q takes the form[26]

$$Q = \frac{\pi^2 T}{3|e|\rho_f}\frac{\partial \rho_f}{\partial \varepsilon}, \qquad (20)$$

i.e., Q is proportional to the same derivative of the density of states and the condition of negative α for $\partial\rho_f/\partial\varepsilon > 0$ coincides with the condition that the quantity Q be positive. [In Ref. 14 the thermoelectric power was investigated within the one-band scheme in which $Q \sim -\partial\rho/\partial\varepsilon > 0$, and the sign change and transition to positive Q at low temperatures were treated as evidence of the appearance in the electron spectrum of a pseudogap and the entrance of the Fermi level into a region where $\partial\rho/\partial\varepsilon < 0$. We claim, however, that a two-band description of the kinetic properties of these systems is more satisfactory (see also Ref. 12) and that formula (20) applies, i.e., even if a pseudogap does form, the Fermi level enters a region $\partial\rho/\partial\varepsilon > 0$.]

5. KINETIC PROPERTIES

The kinetic properties of the two-component model have been investigated repeatedly in the context of transition-metal applications. As was already noted, by virtue of the significant disparity in scale between these systems and systems with heavy fermions and intermediate valence, the effects of the two-band character in the latter can be considerably more marked. The degeneracy temperature of the heavy f-component is in these systems on the order of $T_f \sim 1$–100 °K, and thus for experimentally attainable temperatures we can easily satisfy the condition $T \sim T_f$ and even $T \gg T_f$, which is impossible as a rule in other systems. In this case we can expect a significant temperature-dependent correction to the various kinetic coefficients.

As an example, we will investigate below the impurity contribution to the resistivity of a system with fluctuating valence. One special feature of such systems is the large density of states of the heavy component. This implies that the most effective scattering mechanism for the light component, which gives the most important contribution, e.g., to the conductivity, will be scattering with a transition from the d- to the f-band, in full analogy with transition metals and their compounds[6] (see Ref. 35 for A-15 compounds). As a result, the impurity resistance turns out to be large and, which is no less important, possesses a strong temperature dependence.

Actually, for scattering by impurities the conductivity is given by the usual expression:

$$\sigma = \frac{n_d e^2}{m_d}\int\left(-\frac{\partial \varphi}{\partial \varepsilon}\right)\tau(\varepsilon)\,d\varepsilon, \qquad \tau^{-1}(\varepsilon) = \frac{2\pi}{\hbar}c|M|^2\rho_f(\varepsilon), \qquad (21)$$

where c is the impurity concentration, φ is the Fermi function, $|M|^2$ is the square of the matrix element for f-scattering, averaged over angle, and ρ_f is the density of states, for which we will use expression (3). Taking into account the variation of the chemical potential with temperature, at low temperature it is not difficult to obtain from (21) the following result for the impurity resistance:

$$R_{imp}(T)=R_0\left[1-\frac{\pi^2}{3}\frac{T^2(\Gamma^2+3\varepsilon_f^2)}{(\Gamma^2+\varepsilon_f^2)^2}\right]\approx R_0\left[1-\frac{\pi^2}{3}\left(\frac{T}{T_f}\right)^2\right], \tag{22}$$

where $R_0=4m_dc|M|^2\Gamma[n_de^2\hbar(\Gamma^2+\varepsilon_f^2)]^{-1}\sim T_f^{-1}$.

It is easy to see that because of the large density of states in the f-band the residual resistance is actually large, $R_0\sim T_f^{-1}$ (see the result in Ref. 27; here, of course, $R_{\text{imp}}<R_M\sim 100$–$300\ \mu\Omega$-cm is the maximum metallic resistance). In addition, the impurity resistance falls off quadratically with temperature over a range $\sim T_f$, which is perfectly understandable on qualitative grounds; for $T>T_f$ the fraction of electrons which satisfy the resonance condition for d-f scattering decreases. We note further that the resistance of a "pure" system is determined by the same scaling, $R=AT^2, A\sim T_f^{-2}$.

The conclusions we arrived at above agree well with the experimental data for the system CePd$_3$:La,[28] i.e., in this system $R(T)=R_M(T/T_f)^2$ in "pure" samples, with $T_f=45$ °K, while the impurity contribution decreases with temperature according to $R_{\text{imp}}=R_0[1-(T/T_f')^2]$, with roughly the same scale $T_f'=31$ °K. The result (22) also explains the remarkable correlation between the decrease in R_0 and the increase of A in the function $R=R_0+AT^2$ for CeCu$_6$ [29]; the second term in (26) renormalizes the coefficient A, $A\to A(1-aR_0)$. In still another system, Ce$_{0.9-x}$La$_x$Th$_{0.1}$, it was observed in Ref. 30 that as the pressure increases R_0 and A fall off simultaneously, while A falls off more rapidly than R_0. This is also explained by (22), if we note that the characteristic temperature T_f increases with temperature ($R\sim T_f^{-1}, A\sim T_f^{-2}$).

The falloff of R_{imp} with T can lead to the following effect: for $T>T_f$, when scattering by f-centers becomes incoherent, the resistance of a system with impurities can become smaller than that of a pure system—the replacement of resonant ions, e.g., Ce, by impurities without f-electrons (for example La) will lead to a decrease in the resistance. Such behavior is observed in many systems, e.g., CeCu$_6$:La [31] or CeBe$_{13}$:La [32]. Thus, within the framework of the two-component approach it is possible to explain in a quite natural way the observed peculiarities of the impurity resistance.

Within the same model it is easy to explain also the impurity part of the magnetoresistance. Considering that the g-factor of the f-electrons is large, i.e., $g_f\gg g_d$, and hence that the basic influence of a magnetic field turns out to be its effect on the heavy component—the field splits its spectrum $\varepsilon_{fs}\to\varepsilon_f+g_f\mu_BsH$, where $s=\pm1$ is the f-electron spin—we obtain in place of (21)

$$\sigma=\sigma_\uparrow+\sigma_\downarrow=\frac{n_de^2}{m_d}\int\left(-\frac{\partial\varphi}{\partial\varepsilon}\right)[\tau_\uparrow(\varepsilon)+\tau_\downarrow(\varepsilon)], \tag{23}$$

where

$$\tau_s^{-1}(\varepsilon)\sim\rho_{fs}(\varepsilon)\sim(\Gamma/\pi)[(\varepsilon-\varepsilon_f+g_f\mu_BsH)^2+\Gamma^2]^{-1},\quad \Gamma\sim T_f.$$

To sum up, for the symmetric case $\varepsilon_f=0$ (henceforth we will measure H in energy units and omit the constant $g_f\mu_B$) we find

$$\frac{\Delta R(H)}{R(0)}=-\frac{H^2}{H^2+T_f^2+\pi^2T^2/3}=-\frac{x^2}{1+x^2}, \tag{24}$$

where $x=H(T_f^2+\pi^2T^2/3)^{-1/2}$. Thus, for $\varepsilon_f=0$ the magnetoresistance is negative, and for small fields is proportional to $-H^2$, while for $H\sim T_f$ it approaches saturation. It is also clear that $\Delta R/R$ is a universal function of the reduced temperature $H(T^2+T_f^2)^{-1/2}$. Such behavior is in good agreement with experimental data for UBe$_{13}$ (see Ref. 3, p. 370), where in particular it is pointed out that for UBe$_{13}$ $\Delta R/R=f[H/(T+T^*)]$, $T^*\approx 1$ K. It is also clear that the mechanism under discussion here works the same way both for the longitudinal and the transverse magnetoresistance.

The situation can change for $\varepsilon_f\neq 0$. In particular, if the Fermi level lies within the pseudogap in the density of states,[14] e.g., for a ρ_f of the form

$$\rho_f(\varepsilon)=\frac{\Gamma}{\pi}\left[\frac{1}{(\varepsilon-\varepsilon_f)^2+\Gamma^2}+\frac{1}{(\varepsilon+\varepsilon_f)^2+\Gamma^2}\right], \tag{25}$$

it is easy to obtain the magnetoresistance at $T=0$:

$$R(H)\sim\Gamma\left[\Gamma^2+\varepsilon_f^2+H^2\frac{\Gamma^2-3\varepsilon_f^2+H^2}{\Gamma^2+\varepsilon_f^2+H^2}\right]^{-1}, \tag{26}$$

from which it is clear that the function $\Delta R(H)$ can be nonmonotonic. For small fields,

$$\frac{\Delta R(H)}{R(0)}=-H^2\frac{\Gamma^2-3\varepsilon_f^2}{(\Gamma^2+\varepsilon_f^2)^2}, \tag{27}$$

and the sign of ΔR is determined by the ratio of the width of the pseudogap $2\varepsilon_f$ to the width of the peak Γ. For small ε_f the magnetoresistance for $T\ll T_f$ is always negative; if, however, $\varepsilon_f>\Gamma/\sqrt{3}$, ΔR is positive for small fields $H\lesssim(3\varepsilon_f^2-\Gamma^2)^{1/2}\sim T_f$ while according to (26) it becomes negative for stronger fields. Thus, there are two possible types of function $\Delta R(H)$, which are shown schematically in Fig. 2. The dependence of $\Delta R/R$ on temperature is also similar.

Experimentally, the change in sign of $\Delta R/R$ from negative to positive as the temperature decreases and the system passes into the coherent regime [in which we also postulate the presence of a pseudogap and a density of states of the form (25)] is observed in CeAl$_3$ [33] in the same range of temperatures $T<0.5$ °K where other anomalous quantities are present. Such behavior has a natural explanation within this picture, which, as was shown in Section 3a, easily explains the behavior of the heat capacity of CeAl$_3$, too.

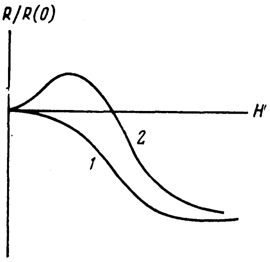

FIG. 2. Qualitative dependence of $\Delta R(H)/R(0)$ on magnetic field at low temperatures $T\ll T_f$. Curve 1: $\varepsilon_f<3^{-1/2}\Gamma$, curve 2: $\varepsilon_f>3^{-1/2}\Gamma$.

In a similar fashion we can also treat the other kinetic characteristics, for example, the thermal conductivity. We will not present the corresponding analysis here; our basic goal in this article was to demonstrate the possibility in principle of obtaining within this simple model a satisfactory description not only of the thermodynamic but also the kinetic properties of a system with valence fluctuations.

6. CONCLUSIONS

In many respects, the present article has a practical aim. It seems to us that there is an indubitable advantage to developing a general scheme of this sort, and in particular to analyzing the available experimental data based on this scheme, in order to clarify the role of the second (light) component and to elucidate the relative contribution of each component to a given phenomena.

The assumption in this paper of a two-component model is a natural generalization of the one-component approach, which is widely applicable to describing systems with intermediate valence and heavy fermions. It allows us to take advantage of all the properties obtained in the one-component model in those cases where this model correctly describes the behavior of these systems (for example, the specific heat and susceptibility). At the same time, our approach also provides an interpretation of such properties as the compressibility and thermal expansion of this class of compounds, for which the usual approach is inadequate.

We should also note that the two-component Fermi liquid model shows promise for describing other properties of these materials, especially the kinetic properties. A striking example of this is the possibility of a perfectly natural explanation of the correlation between the behavior of the coefficient of linear expansion and that of the thermoelectric power at low temperatures, and also the temperature dependence of the impurity resistance and negative magnetoresistance.

We can also link a number of superconducting properties of these compounds to the presence of a light component. For example, the London penetration depth λ_L [given in the simplest case by the expression $\lambda_L^2 = m^* e^2/4\pi n c^2$)] turns out in these compounds to be the same order of magnitude as that of normal superconductors, which can be explained by screening of the field by the light carriers.[2]

It is also not hard to investigate the collective modes of systems with heavy fermions within this approach. Finally, let us note the possibility in principle of extending the model into the semi-quantum mechanical region of higher temperatures $T_{Ff} < T < T_{Fd}$, where the heavy component is nondegenerate and the temperature dependences of the kinetic coefficients are changed.

In conclusion, it seems advisable to note that despite the fruitfulness of the two-component model in interpreting the properties of heavy-fermion systems, the resulting treatment is phenomenological and can conceal the far-from-trivial origins of the two-component system. Further development of the theory must show to what extent the phenomenological scheme developed here can be justified, and how much meaning we should ascribe to the heavy and light components.

1) The effective mass m_i^* of a component is related in the following way to the first harmonics of an expansion of the symmetric part of the kernel f:

$$m_i^* = m_i \left(1 + \frac{{}^sF_1{}^{ii}}{3} + \frac{v_j m_j}{v_i m_i} \frac{{}^sF_1{}^{ij}}{3} \right),$$

where m_i is the crystal mass and $v_i = \rho_{Fi}/m_i^*$.

2) As is easy to see, in agreement with this investigation for $n_f = 1$ the sign of the T^3 component changes for $J = 3/2$,[4] which is related to the result of an exact solution to the Kondo problem for arbitrary impurity spins.[20]

3) This calculation, which was carried out without any detailed fitting, is presented exclusively for purposes of illustration, using reasonable values of the parameters ε_f and Γ.

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