

Energy Balance of Mixed-Valent Eu Ions

J. Röhler and D. Wohlleben

II. Physikalisches Institut, Universität zu Köln, D-5000 Köln 41, Germany

and

G. Kaindl

Institut für Atom- und Festkörperphysik, Freie Universität Berlin, D-1000 Berlin, Germany

and

H. Balster

Abteilung für Physik und Astronomie, Ruhr-Universität Bochum, D-4630 Bochum, Germany

(Received 10 July 1981; revised manuscript received 3 February 1982)

The interconfigurational mixing and excitation energies, Γ and E_x , of the Eu ions in EuCu_2Si_2 are determined experimentally as functions of pressure and temperature. Γ seems to depend only on E_x , and the strongly nonlinear $\Gamma(E_x)$ reflects the intra-ionic multiplet splittings and degeneracies of $4f^6$. The observed pressure and temperature dependence of E_x is analyzed self-consistently in terms of contributions from mixing, elastic, and conduction-electron energies, which arise from the temperature and pressure dependence of the valence.

PACS numbers: 75.20.Hr, 72.15.Eb, 76.80.+y

The valence (ν) of rare earth (RE) fluctuating or intermediate valence systems is known to change strongly sometimes with temperature and pressure. This causes large shifts of the Fermi energy of the conduction electrons (ϵ_F), of the elastic energy (F_L), and of the energy of interconfigurational mixing (Γ). Clearly all these shifts need to be considered simultaneously in any attempt to understand the observed temperature and pressure dependence of the valence. In this Letter we derive the energy balance for EuCu_2Si_2 from experiments over a wide temperature and pressure range and then analyze it self-consistently in terms of temperature and pressure dependence of the above energy parameter.

In the ionic model of valence fluctuations two configurations $4f^j$ of the RE ion are competing for stability when their overall energy difference, the interconfigurational excitation energy E_x , becomes sufficiently small.¹ Thermodynamically the valence, or equivalently the fractional occupation ν of the $4f^n$ configuration, is then determined in first approximation by

$$\frac{1-\nu}{\nu} = \frac{N_{n+1}}{N_n} = \frac{\zeta_{n+1}'}{\zeta_n'} \exp\left(\frac{-E_x}{k_B T}\right). \quad (1)$$

Here the ζ_j' are the partition functions of $4f^j$ with energies counted from the lowest intraconfigurational levels $E_{j,0}$, and $E_x \equiv E_{n+1,0} - (E_{n,0} + \epsilon_F)$ with the Fermi energy ϵ_F .

When $k_B T \gg E_x$ the valence is determined only

by the intra-ionic spectra, i.e., by entropy and not by E_x .² In real systems the valence will be described by Eq. (1) the less accurately the lower the temperature and E_x , because for small $|E_x|$ the ion can gain energy by interconfigurational mixing, i.e., by partial occupation of both configurations via quantum fluctuations (in addition to the usual thermal fluctuations) which will persist to $T=0$. In first approximation, this energy gain Γ will be a function of E_x only; $\Gamma(E_x)$ will have a maximum near configurational crossover ($E_x=0$) and will tend to zero for $E_x \rightarrow \pm\infty$. In a phenomenological thermodynamic treatment^{2,3} the mixing energy was introduced through the fluctuation temperature $T_f \equiv \Gamma/k_B$ in the effective temperature $T^+ \equiv (T^2 + T_f^2)^{1/2}$ which replaces T in Eq. (1). Given E_x the observed valence can then be described at all temperatures by Eq. (1) with the appropriate choice of T_f .

Because of the large difference between the volumes V_j of the unit cell with the ion in $4f^j$, E_x depends strongly on the available volume. In the limit of integral valence ($k_B T^+ \ll |E_x|$) Johansson⁴ finds for the isothermal dependence of E_x on external pressure $\partial E_x / \partial p|_T = V_{n+1} - V_n$. Isobaric temperature-driven valence changes and thermal expansion of the matrix will also cause volume changes of order $V_{n+1} - V_n$, which will bring about correspondingly large changes of the internal pressure and therefore make E_x and $\Gamma(E_x)$ strong functions of temperature. In the following

we neglect all pressure and temperature dependences of the intra-ionic spectra against those of E_x and Γ .

In short, the spectrum underlying Eq. (1) will depend on pressure and temperature through $E_x(T, p)$ and $T_f(T, p)$.

Clearly E_x and T_f may not be assumed to remain constant when the valence changes strongly, as, e.g., in EuCu_2Si_2 and YbAl_2 .³ We shall now describe an unambiguous experimental determination of the two functions $E_x(T, p)$ and $T_f(p, T)$ of EuCu_2Si_2 by simultaneous evaluation of two inde-

pendent physical quantities, the Mössbauer isomer shift $\delta(T, p)$ and the susceptibility $\chi(T, p)$ (Fig. 1). We shall then evaluate $E_x(T, p)$ in terms of ϵ_F , $\partial(F_L + pV)/\partial v$, and $\partial\Gamma/\partial v$, which can be calculated with use of the observed valence changes and parameters measured independently on integral valent reference compounds. The isomer shift δ measures the valence via⁵

$$\delta(T, V) = \delta_2(T, V) + (\delta_3 - \delta_2)\nu(T, V), \quad (2)$$

where δ_3 and δ_2 are the isomer shifts of stable Eu^{2+} and Eu^{3+} and V is the volume. The static susceptibility is given by

$$\chi(T, p) = [1 - \nu(p, T)]\chi_7(T^+(p, T)) + \nu(p, T)\chi_6(T^+(p, T)). \quad (3)$$

χ_7 and χ_6 are the Curie and Van Vleck susceptibilities of $4f^7$ and $4f^6$. In the ζ_j' and χ_j we have used the following intra-ionic spectra: in $4f^7$ one level at 0 K (with $g=8$); in $4f^6$ levels at 0 K ($g_0=1$), 480 K ($g_1=3$), 1330 K ($g_2=5$), and 2600 K ($g_3=7$).⁶

In Fig. 1(a) the isomer shift and the relative volume^{7,8} are plotted as functions of pressure at 300 K together with the pressure dependence of

the susceptibility.⁹ In Fig. 1(b) the isobaric variation of δ for our sample of EuCu_2Si_2 (Refs. 7 and 8) is plotted as a function of temperature at atmospheric pressure together with the isomer shift of Ref. 5 (shifted by -0.4 mm/s for reasons discussed in Ref. 8) and with the temperature dependence of the susceptibility measured at atmospheric pressure by Sales and Viswanathan.⁹ In

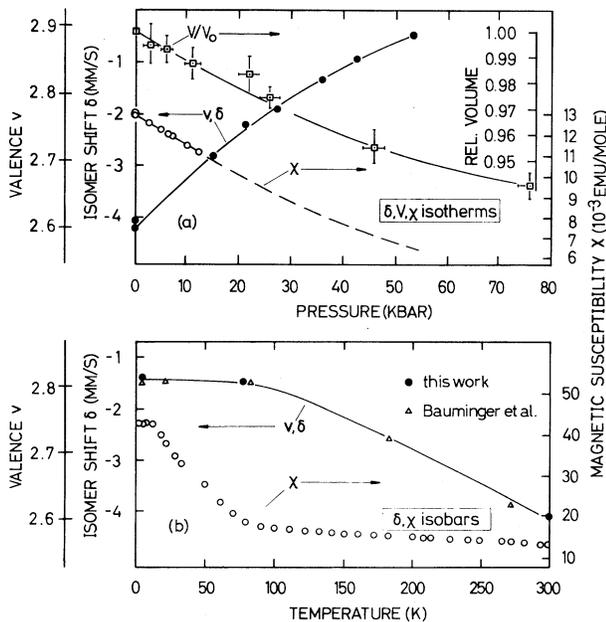


FIG. 1. (a) Pressure and (b) temperature dependence of the ^{151}Eu isomer shift δ (relative to $^{151}\text{SmF}_3$) and of the magnetic susceptibility χ for EuCu_2Si_2 . In (a) also the relative volume at 300 K is given as a function of pressure. Next to the δ ordinate a scale is added for the mean valence ν .

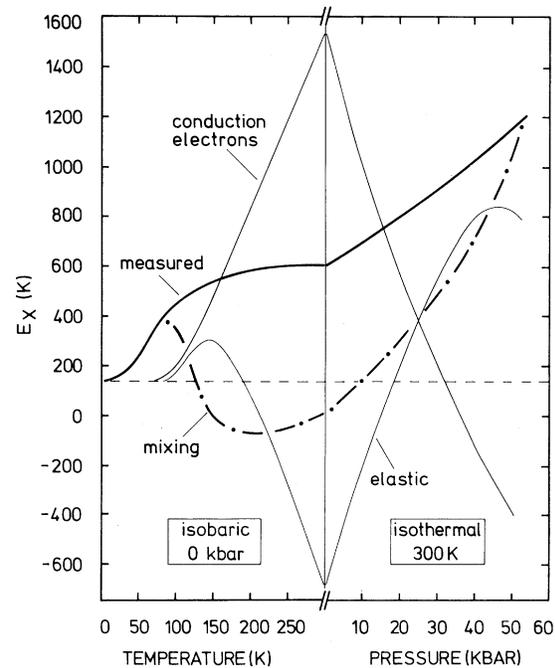


FIG. 2. Temperature and pressure dependence of the interconfigurational excitation energy E_x and its decomposition into mixing, conduction electron, and elastic energies.

deriving the valence from the isomer shift via Eq. (2) small corrections were applied^{7,8} which take into account the normal volume dependence of δ_2 .^{10,11} δ_2 was set equal to -12 mm/s at $p=0$ and $T=300$ K and $\delta_2 - \delta_3 = 13$ mm/s. From the data in Fig. 1 $E_x(T, p)$ and $T_f(T, p)$ were extracted via Eqs. (1)–(3). $E_x(T, p)$ is exhibited in Fig. 2 and $T_f(E_x)$ in Fig. 3 (heavy lines). The thin lines in Fig. 3 give $T_f(E_x)$ for two choices of δ_2 which shift the valence scale by $+4\%$ and -1% .

All curves have the following common features: (a) $T_f(E_x)$ exhibits a maximum (or bump) near $E_x \approx 500$ K. (b) T_f and E_x show a tendency to cluster near this maximum over a considerable temperature range. (c) The curves $T_f(E_x)$ from the isobaric data smoothly join those from the isothermal data.

Feature (a) suggests that the mixing energy goes through a maximum where the $4f^7$ energy $E_{7,0}$ crosses $E_{6,1}$, the $J=1$ sublevel of $4f^6$ (a crystal-field splitting of $E_{6,1}$ in the tetragonal EuCu_2Si_2 by about 150 K may be hidden in the asymmetric shape of this maximum). The shape of $T_f(E_x)$ is consistent with the expectation that similar maxima exist at $E_x=0$ and at $E_x=1330$ K, where $E_{7,0}$ crosses the $J=0$ and $J=2$ sublevels of $4f^6$, $E_{6,0}$ and $E_{6,2}$. Since the mixing energy is proportional to the degeneracies of the crossing levels, the height of these maxima should scale as $g_0:g_1:g_2=1:3:5$. The relationship $T_f(E_x)$ in Fig. 3, although determined with the aid of a rather coarse approximation (implied in the way in which the mixing energy $k_B T_f$ enters our thermodynamic formalism), seems to reflect fairly well what is expected.

In order to carry out a complete analysis of all contributions to $E_x(T, p)$ we consider the free enthalpy of the fluctuating valence system, similar to some previous workers (see, e.g., Jeffer-son¹²), but replacing T by T^+ :

$$G(T, p, \nu) = F_{n+1} + F_n + F_e + F_L + pV. \quad (4)$$

$$-E_x + E_{n+1,0,0} - [E_{n,0,0} + \epsilon_F(\nu)] + N^{-1} \partial(F_L + pV) / \partial \nu + E_{xm} = 0,$$

with

$$E_{xm} = k_B T^+ [(1-\nu)S_{n+1}(T^+) + \nu S_n(T^+) + \nu S_e(T^+)] \\ \times \left\{ \nu(1-\nu) \left[\frac{dE_x}{dT_f} \right]_{T,p} \frac{T^+}{T_f} - \frac{E_x + E_{n+1}(T^+) - E_n(T^+) - (\pi k_B T^+)^2 / 6\epsilon_F}{T^+} \right\}^{-1}.$$

The term E_x in Eq. (5) denotes at first nothing but an abbreviation for

$$E_x \equiv k_B T^+ \ln[\zeta_{n+1}' \nu / \zeta_n' (1-\nu)] - (\pi k_B T^+)^2 / 6\epsilon_F(\nu). \quad (6)$$

But if one neglects the last (small) term on the right-hand side of Eq. (6) and solves for $(1-\nu)/\nu$,

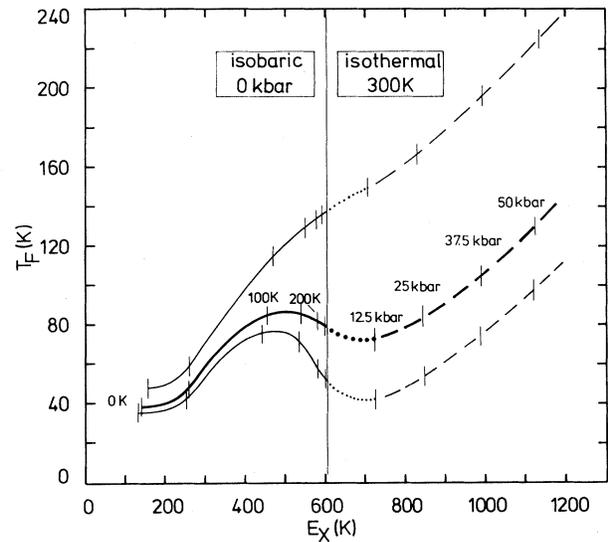


FIG. 3. Dependence of the fluctuation temperature T_f on the interconfigurational excitation energy E_x . Level crossings occur at $E_x = 0, 480, 1330$ K. The three curves correspond to three choices of valence calibration. Full curves from data at $p=0$ and $4.2 < T < 300$ K, dotted curves at $T=300$ K and $0 < p < 12.5$ kbar, dashed curves at $T=300$ K and $12.5 < p < 53$ kbar. Dashed curves are based on extrapolated $\chi(p, 300)$ above 12.5 kbar [Fig. 1(a)]. Bars indicate typical experimental error and temperature and pressure values in steps of 50 K and 12.5 kbar, respectively.

Here the

$$F_j = N_j \{ E_{j,0,0} - k_B T^+ [\ln(\zeta_j' / N_j) + 1] \}$$

are the intra-ionic free energies of the N_j ions in the configurations j , and F_e is the free energy of the conduction electrons. The contribution to the $E_{j,0}$ which are due to the volume strains are absorbed in $F_L(\nu, T, p)$, leaving the constants $E_{j,0,0}$. $V(\nu, T, p)$ is the actual volume. We have $N_n = \nu N$, $N_{n+1} = (1-\nu)N$, $N_e = \nu N$, where N is the total number of RE ions and $\nu = 2 + \nu$ is the valence. The condition for chemical equilibrium, $\partial G / \partial \nu|_{T,p} = 0$, yields

(5)

one obtains Eq. (1). So the abbreviation Eq. (6) has the physical meaning of the overall energy difference $E_x(T, p)$ defined by Eq. (1). The last term in Eq. (5), E_{xm} , is a contribution from the configurational mixing. This term arises in our treatment because the mixing energy $k_B T_f$ depends on ν through E_x . The $E(T^+)$ and $S(T^+)$ in E_{xm} are the intraconfigurational and conduction-electron energies and entropies, all at temperatures T^+ .

We now analyze the derived $E_x(T, p)$ labeled "measured" in Fig. 2 with Eq. (5). The dot-dashed curve labeled "mixing" is the term $E_{xm}(T, p)$ calculated from Eq. (5) with use of $E_x(T, p)$ and $T_f(T, p)$. dE_x/dT_f is obtained from Fig. 3 with the assumption that $T_f(E_x)$ is independent of T and p , i.e., that there is *only one* independent parameter to determine the valence (and to be determined by it) at all T and p . The dashed line is the zero of E_{xm} . Clearly E_{xm} constitutes a force which tends to stabilize E_x at the crossover of $E_{7,0}$ with $E_{6,1}$ on the isobaric curve. Below 70 K, the upward motion of E_x with increasing temperature without change of valence is obviously a consequence of this mutual attraction of $E_{7,0}$ and $E_{6,1}$. Viewing the situation in reverse "the effective f level, as you go to lower temperatures, gets scaled away from the Fermi surface to the side favoring the lower degeneracy state, at the expense of the higher degeneracy state."¹³ Above 70 K the Fermi level and the elastic energy begin to move because of the beginning valence change. We have generated $\Delta\epsilon_F(\nu)$ (the curves labeled "conduction electrons") using the valence changes of Fig. 1 with $\Delta\epsilon_F \equiv \epsilon_F(\nu) - \epsilon_F(\nu_0) = \rho^{-1}(\epsilon_F)(\nu - \nu_0)$. Here $\rho(\epsilon_F)$ is the density of states [$\rho = 1.65$ states/eV from the linear specific-heat coefficient of LuCu_2Si_2 (Ref. 8)] and $\nu_0 = 0.81$ at $T = 0$ and $p = 0$. Subtracting E_{xm} and $\Delta\epsilon_F(\nu)$ from $E_x(T, p)$, we end up with the curves labeled "elastic." The curves fit, within the noise, the expression $\partial(F_L + pV)/\partial\nu|_{T,p}$ derived from the *Ansatz*

$$F_L = C[V(T, p, \nu) - V_0]^2 B(\nu)/2V_0, \quad (7)$$

where V_0 is a constant volume and $B(\nu)/V_0 \equiv \nu B_6/V_6 + (1 - \nu)B_7/V_7$. For the bulk modulus B_6 of Eu^{3+} we take 1240 kbar from the high-pressure end of $V(p)$ in Fig. 1 and for B_7 of Eu^{2+} 930 kbar from a

measurement on CaCu_2Si_2 .⁸ For $V(\nu)$ we take into account the deviations from Vegard's law discussed elsewhere.⁸ We find $V_0 = 40.8 \text{ \AA}^3$ and $C = 2$. Note that the large valence-driven changes of E_x due to the conduction electron and the elastic term tend to cancel each other. This seems to be the reason why valence changes in concentrated⁵ and dilute⁶ systems are so similar: The shifts of E_x due to shifts of elastic and Fermi energy tend to cancel, leaving changes of thermal and mixing energy to dominate the observed valence changes.

This work was partly supported by Sonderforschungsbereiche 161 and 125 of the Deutsche Forschungsgemeinschaft. The authors gratefully acknowledge valuable discussions with I. Nowik, W. B. Holzapfel, and J. Schilling. We especially thank B. Sales for letting us use his sample of EuCu_2Si_2 .

¹L. L. Hirst, *Phys. Kondens. Mater.* **11**, 255 (1970).

²D. Wohlleben, in *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 1.

³B. C. Sales and D. K. Wohlleben, *Phys. Rev. Lett.* **35**, 1240 (1975).

⁴B. Johansson and A. Rosengren, *Phys. Rev. B* **14**, 361 (1976).

⁵E. R. Bauminger, D. Froindlich, I. Nowik, S. Ofer, I. Felner, and I. Mayer, *Phys. Rev. Lett.* **30**, 1053 (1973).

⁶W. Franz, F. Steglich, W. Zell, D. Wohlleben, and F. Pobell, *Phys. Rev. Lett.* **45**, 64 (1980).

⁷J. Röhler, Diplom thesis, Ruhr-Universität Bochum, 1979 (unpublished).

⁸J. Röhler, G. Kändl, and D. Wohlleben, in *Proceedings of the International Conference on Valence Instabilities*, Zürich, April 1982 (to be published).

⁹B. C. Scales and R. Viswanathan, *J. Low Temp. Phys.* **23**, 449 (1976).

¹⁰G. M. Kalvius, U. F. Klein, and G. Wortmann, *J. Phys. (Paris)*, Colloq. **35**, C6-136 (1974).

¹¹U. F. Klein, Ph.D. thesis, Technische Universität, München, Germany, 1976 (unpublished).

¹²J. H. Jefferson, *J. Phys. C* **9**, 269 (1976).

¹³P. W. Anderson, in *Valence Fluctuations in Solids*, edited by L. M. Falicov, W. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 452.