Intermediate Valence on Dilute Europium Ions

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Dilute alloys of Eu in $ScAl_2$ show single-ion anomalies in their transport properties. The susceptibility is intermediate between Eu^{2+} and Eu^{3+}. The Mössbauer isomer shift is intermediate as well as strongly temperature dependent. This is the first case of microscopically confirmed configurational instability in any dilute rare-earth alloy.

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It is well known that certain metals containing Ce, Pr, Sm, Eu, Tm, and Yb (either as partners in an intermetallic compound or in high dilution) exhibit large anomalies of their macroscopic physical properties.[1-4] These anomalies are alternatively discussed in terms of the Kondo effect or of intermediate valence, both of which can be regarded as different regimes of configurational instability: The Kondo effect can occur, when the instability is incipient,[5] i.e., when the valence is nearly integral. Configurational instability (existence of *two separate* ionic configurations in the ground state) can be established unambiguously only by microscopic methods, i.e., by x-ray absorption,[6] by photoemission,[7] or by the Mössbauer isomer shift.[8] Unfortunately, these microscopic methods fail because of signal-to-noise problems in compounds with nearly integral valence and in the usual macroscopically anomalous dilute alloys. This is a severe handicap for all interpretations of macroscopic anomalies, especially in dilute alloys, where in the absence of evidence to the contrary one usually assumes that the instability is only incipient and bases one's interpretation on the results of the traditional s-d-type Kondo theories. Another reason for this course of action is lack of theoretical work based on the more fundamental concept of configurational instability. Early suggestions in this direction[9] have only recently produced some interesting results.[10]

Obviously it is an urgent experimental task to establish the degree of configurational instability (the intermediacy of the valence) by microscopic methods in as many macroscopically anomalous metals as possible, especially in dilute alloys. The best microscopic method for this task is the measurement of the Mössbauer isomer shift, since it establishes simultaneously the ratio of both configurations (the valence) and the homogeneity (or dynamic nature) of their mixture. Unfortunately, this method is difficult or impossible to apply to the above rare-earth (RE) ions except for europium. For alloys with dilute EU impurities on the other hand, no macroscopic anomalies have been reported so far, although there are some well-established cases of microscopically confirmed intermediate valence of Eu ions in compounds and concentrated alloys.[8] Thus, in order to study the degree of valence mixing in dilute Eu alloys by the Mössbauer effect, we had to search first for a suitable dilute europium alloy. We have found macroscopic anomalies in susceptibility and transport properties of dilute alloys of Eu in $ScAl_2$, using dilute Gd as stable reference impurity in the same matrix. The idea was to increase the lattice pressure on the Eu ion in $ScAl_2$ ($a = 7.53$ Å) in comparison to $EuAl_2$ ($a = 8.11$ Å), where it is divalent, to induce a valence change towards the smaller Eu^{3+} ion.

$ScAl_2$, $EuAl_2$, and $Sc_{1-x}Gd_xAl_2$ alloys were molten together from the weighed constituents in an induction furnace (in the case of $EuAl_2$ compensating weight losses with surplus Eu). $Sc_{1-x}Eu_xAl_2$ alloys were then molten from $ScAl_2$ and $EuAl_2$. Weight losses recorded after this procedure indicate preferential evaporation of about one-third of the europium. No such losses occurred in the Gd alloys. The Eu concentrations quoted below are values obtained after correcting the nominal concentration first for the measured weight losses (leaving an error of ±0.05 at.%) and then to within ±0.02 at.% by scaling with the high-temperature susceptibility (see below). Rods were cut from the ingots ($0.15 \times 0.15 \times 2$ cm^3), and annealed in high vacuum at 600 or 1000 °C for 96 or 48 h, respectively. Test samples cut from these rods were investigated by reflection microscopy and powder x-ray diffraction. The solubility limit of Eu in $ScAl_2$ lies near 1 at.%. The resistivity, thermopower, and susceptibility were measured between 1.5 and 300 K on equipment described elsewhere.[11,12] The Mössbauer spectra were obtained with a ^{151}Sm source in Sm_2O_3, with use of the stable ^{151}Eu isotope of the natural isotopic mixture of the Eu impurities as absorber.

Figure 1 shows the temperature dependence of the ^{151}Eu isomer shift in alloys of 0.68 and 0.22 at.% Eu in $ScAl_2$. The *isomer shift is intermediate* between the usual values for Eu^{2+} (-12 to -8 mm/sec) and Eu^{3+} (-1 to $+3$ mm/sec) in metals, *and depends strongly on temperature,* which is the most convincing indication of an intermediate valence. The linewidth is 2.6 ± 0.2 mm/sec, and changes only very slightly with temperature between 325 and 4.2 K. Thus there is no indication of a slowdown of the fluctuation rate or of any hyperfine splitting.[8] The 0.68-at.% sample exhibits a second line which is three times weaker than the first one. It has a temperature independent position of -9.2 mm-sec down to 50 K, then broadens and eventually splits. This line is due to an $EuAl_2$ contamination in our sample which has Eu in the divalent state and orders magnetically below 50 K. No second line was found in the 0.22-at.% alloy to within 0.02 at.%.

Figure 2 shows $x^{-1}\Delta\chi(T)$, the temperature dependence of the impurity susceptibility per at.%, for alloys of 0.68, 0.22, and 0.18 at.% Eu and of 1.0 at.% Gd. The Eu susceptibility is clearly intermediate between $4f^7$ (Eu^{2+}, Gd^{3+}) and $4f^6$ (Eu^{3+}) and follows a Curie-Weiss law between 300 and 100 K with a *Curie-Weiss temperature of* $\Theta = (-40 \pm 5)$ K. In contrast, the 1 at.% Gd alloy has $\Theta = (1 \pm)$ K, [with $p_{\mathrm{eff}} = (7.94 \pm 0.03)\mu_B$], and $EuAl_2$ has $\Theta = (0 \pm 2)$ K. Below 100 K there are considerable variations of the impurity susceptibility between Eu alloys which depend on annealing and show structure near 30 and 15 K reminiscent of the structure of the susceptibility of $EuAl_2$. The susceptibility of the 0.68-at.% alloy, as shown, is corrected by subtracting the susceptibility of 0.17 at.% $EuAl_2$, the fraction found in the Mössbauer spectra. Although for the other two alloys the upper limit of 0.02 at.% $EuAl_2$ is more than sufficient to explain the excess of their low-temperature susceptibility over the corrected values of the most concentrated alloy, we have refrained from applying such corrections.

We have fitted the isomer shift and the susceptibility simultaneously with a model applied successfully to intermediate-valence compounds in the past.[8,13] We assume that the Eu^{2+} configuration has an energy E_{ex} above the $J = 0$ ground state of the Eu^{3+} configuration, and that all sub-

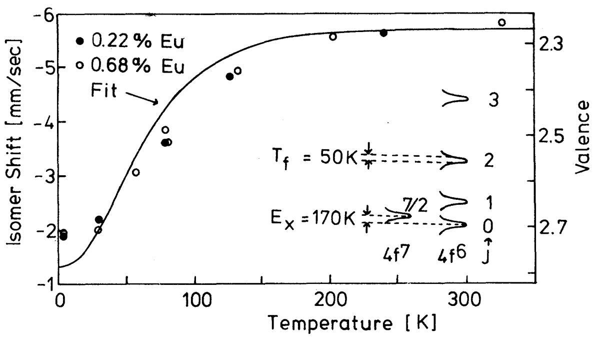

FIG. 1. Mössbauer isomer shift of dilute europium impurities in $ScAl_2$ as function of temperature. The analysis leads to a temperature-dependent valence which can be read off the right-hand scale. The chosen values of E_{ex} and T_f yield the best simultaneous fit of Mössbauer and susceptibility data (see also Fig. 2).

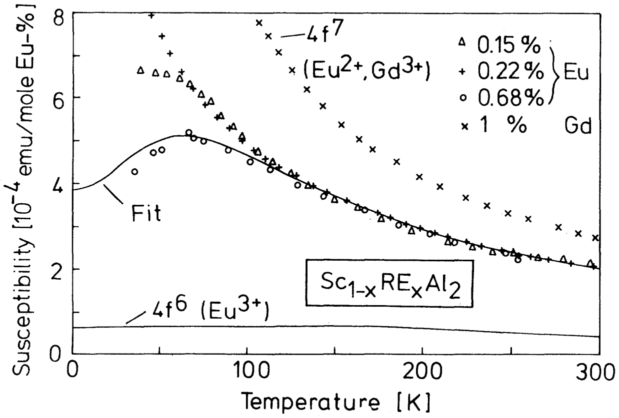

FIG. 2. Temperature dependence of the susceptibility per at.% of dilute Eu and Gd impurities in $ScAl_2$. The data of the 0.68-at.% Eu sample (but not the others) are corrected for a contribution of residual $EuAl_2$ detected in the Mössbauer spectra.

levels of both configurations have a width $k_B T_f$ due to the configurational instability. This width is introduced phenomenologically by replacing the thermodynamic temperature T by an effective $T^+ = (T^2 + T_f^{\,2})^{1/2}$ in the Boltzmann factors when calculating thermodynamic averages. Both E_{ex} and T_f are assumed to be independent of temperature, which is an approximation. The ratio of 2^+ to 3^+ ions is given by the ratio of the partition functions of Eu^{2+} and Eu^{3+} ions:

$$\frac{p_2}{p_3} = \frac{8\exp(-E_{ex}/k_B T^+)}{1 + 3\exp(-480/T^+) + 5\exp(-1330/T^+) + 7\exp(-2600/T^+)},$$

with $p_2 + p_3 = 1$; one obtains isomer shift and susceptibility through

$$\delta(T) = p_2(T^+)\delta_2 + p_3(T^+)\delta_3,$$

$$\chi(T) = p_2(T^+)\chi_2(T^+) + p_3(T^+)\chi_3(T^+),$$

where χ_2 is the (Curie) susceptibility of $4f^7$ ions and χ_3 the (Van Vleck) susceptibility of $4f^6$ ions (with T replaced by T^+ and with the same set of multiplet energies as in p_3). We obtain the fits shown in Figs. 1 and 2 with $E_{ex} = 170$ K and $T_f = 50$ K with $\delta_2 = -8$ mm/sec, and $\delta_3 = +0.5$ mm/sec. The value of − 8 mm/sec was obtained by scaling the measured isomer shift of $EuAl_2$ ($\delta = -9.2$ mm/sec) to the volume of $ScAl_2$. The choice of δ_3 affects the magnitude of E_{ex} and T_f but not their ratio, which is the essential fit parameter. The quality of the data and fits is sufficient for us to state confidently that we have intermediate-valence europium ions in dynamic mixture, with a strong temperature dependence of the valence from about 2.7 at 4.2 K to about 2.3 at 300 K.

The thermoelectric power (TEP) is shown in Fig. 3. For the compounds $ScAl_2$ and $EuAl_2$, the TEP can be decomposed into $S = S_D + S_{ph}$. For simple metals the diffusion part S_D is proportional to T and at low temperatures the phonon drag part $S_{ph} \sim T^3$. While we can fit our data of $ScAl_2$ below 30 K by $S/T = A + BT^2$, this is not possible in antiferromagnetic $EuAl_2$. But here the measured TEP is proportional to T above 200 K. In Fig. 3 we have indicated $S_D = AT$ by dashed straight lines with the coefficients A as given in Table I. After subtraction of these straight lines from the raw data, we obtain the usual maxima of $S_{ph}(T)$ for $ScAl_2$ and $EuAl_2$ at 90 and 50 K, respectively. The temperatures T_m of these maxima scale with the Debye temperatures, i.e., $T_m(EuAl_2)/T_m(ScAl_2) = 0.55 \simeq \Theta_D(EuAl_2)/\Theta_D(ScAl_2) \simeq (M_{Eu}/M_{Sc})^{-1/2} = 0.54$. For the two Eu alloys we observe a different *type of pronounced nearly concentrated independent peaks of the TEP near 40* K, with a large initial slope of $A = 0.3$ μV/K². The peak temperature correlates well with the Curie-Weiss temperature $\Theta = -40$ K found in the impurity susceptibility. Note that Gd impurities do not show this anomaly. These TEP peaks must be due to electron diffusion dominated by the scattering from the intermediate-valence (IV) Eu ions.

From the resistivity measurements we have extracted the temperature-dependent part of the impurity resistivity per at.%, as shown in the inset of Fig. 3. By use of Matthiessen's rule, this quantity is defined as $x^{-1}\Delta\rho(T) \equiv x^{-1}\{[\rho(T) - \rho_0]_{\rm alloy} - [\rho(T) - \rho_0]_{ScAl_2}\}$. The last term is the

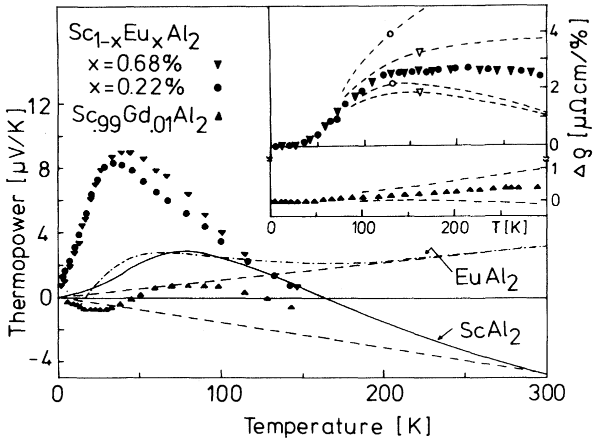

FIG. 3. Thermopower vs temperature for two alloys of Eu and one of Gd in $ScAl_2$, and for $ScAl_2$ and $EuAl_2$. Dashed lines indicate diffusion part, S_D, of TEP. Inset shows temperature-dependent part of the incremental impurity resistivity per at.% for two alloys with Eu and one with Gd.

TABLE I. Results and analysis of transport measurements (for details see text).

Sample	x (at.%)	ρ_0 (μΩ cm)	$\rho_{300}/\rho_{4.2}$	S_D/T (μV/K²)
$ScAl_2$	0	0.315	53.9	-0.01
$(Eu_x Sc_{1-x})Al_2$	0.22	0.334	54.4	+0.3
$(Eu_x Sc_{1-x})Al_2$	0.68	0.517	35.0	
$(Gd_x Sc_{1-x})Al_2$	1.0	0.761	23.1	-0.015

phonon resistivity of the matrix and ρ_0 is the residual resistivity as listed in Table I. The systematic error of $\Delta\rho(T)$ due to the geometry factor of alloys and matrix becomes large above 100 K. By measuring ρ_0 and $\rho(300\text{ K})$ in about ten independent runs for each sample, the systematic error could be reduced to the indicated limits. *Outside* this error, and contrary to $\Delta\rho_{\text{Gd}}$, $\Delta\rho_{Eu}$ *increases with temperature to 2–3 $\mu\Omega$ cm/at.% at 130 K,* with an inflection point near 80 K, and with a tendency to saturation above 150 K. Because of the systematic error, we cannot be sure of the sign of $d(\Delta\rho)/dT$ at high temperature. However, staying within the systematic limits, we are free to scale $\Delta\rho(T)$ at one temperature, which we did at 300 K in Fig. 3. In this way we obtain congruence of both curves over the entire temperature range within the much smaller relative scatter of $\Delta\rho(T)$ and find $\Delta\rho(0.68\text{ at.\%})/\Delta\rho(0.22\text{ at.\%}) = 1.75 \pm 0.2$, close enough to the ratio of IV ions determined by susceptibility and Mössbauer data $(0.68 - 0.17 \pm 0.02)/(0.22 \pm 0.02) = 2.3 \pm 0.3$. In contrast to the usual Kondo-type behavior ($d\Delta\rho/dT < 0$ because of negative effective exchange integral, $\Gamma < 0$), we have $d\Delta\rho/dT > 0$ near the characteristic temperature and below. One might wish to invoke another case of a reverse Kondo anomaly ($\Gamma > 0$), but this is only expected[14] and has only been observed on integral-valence $4f$-shell ions like Gd (Ref. 14) and Nd (Ref. 15). Also, one must bear in mind the clear tendency of the Eu ions to depopulate the magnetic $4f^7$ configuration and to condense into the ionic singlet ground state $J = 0$ of the $4f^6$ configuration. This new feature highlights the need for fundamental theoretical work on the transport properties of dilute IV ions. From the point of view of intermediate valence, the positive resistance anomaly, $d\Delta\rho/dT > 0$, may simply be due to an increase of charge, spin, and volume of the Eu ions, which accompanies the drastic valence change with increasing temperature. Note that $\Delta\rho(T)$ accurately traces the temperature-dependent isomer shift $\delta(T)$, i.e., the valence. The concentration independence of the TEP anomaly and the scaling of the resistance anomaly with concentration strongly suggest that the IV Eu ions are in fact dissolved as isolated impurities in ScAl_2. In conclusion, we have for the first time found macroscopic anomalies in a dilute Eu alloy, which are similar to those found previously in dilute alloys of Ce, Pr, Sm, Tm, and Yb, except for the resistance anomaly. Via the Mössbauer isomer shift, these anomalies have been traced unambiguously to configurational instability for the first time in a dilute alloy. Surprisingly, the valence, rather than being nearly integral as expected for dilute alloys (where pinning of the $4f$ resonance to the Fermi level due to electron transfer from the local $4f$ shell to the conduction band cannot occur), is very nonintegral and varies strongly with temperature in a manner very similar to that of Eu IV compounds.[8]

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