

ing that the second-order Born scattering term ($G^{(3)}$) of Appelbaum's theory is decreasing with temperature and has vanished by 1 K. It is as though the exchange parameter J were decreasing to zero. The magnetic field and interaction effects could come from the first-order Born terms ($G^{(2)}$). The explanation of this shrinking conductance peak is not understood.

Although we have been discussing high-concentration junctions because these show the largest and most dramatic effects of interactions, their effect can be present in lower-concentration junctions which do not show a conductance minimum. Their effect will be to cause deviations from $\ln(|eV|+kT)$, and it will look as though there is an extra-large thermal smearing. These effects are probably the main reason why Appelbaum's expression has not been found to fit the data for some magnetically doped junctions.³

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Study of Hyperfine Field Data on Actinide Impurities in 3d Ferromagnetic Hosts

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Hyperfine-field data on actinide impurities in ferromagnetic transition hosts are analyzed in terms of conduction-electron polarization and d -electron contributions, except for Np, Pu, and Cm. For these special impurities, it is necessary to invoke the hyperfine-field contribution due to magnetic localized $5f$ shells.

We present a study of the magnetic behavior of actinides diluted in a ferromagnetic host from an analysis of their hyperfine-field data. The hyperfine fields of radium,¹ thorium,² uranium,^{2,3} and plutonium⁴ have been measured by a perturbed-angular-correlations technique⁵ in an iron host; the hyperfine fields of neptunium⁶ and curium⁷ have been measured in a nickel host. These values are given in Fig. 1. The hyperfine field is negative and slowly decreasing from Ra to U, while it becomes positive for Np and Pu and roughly zero for Cm.

Actinide metals are not magnetic until americium, while curium and berkelium have magnetic moments corresponding roughly to the $5f$ ionic values. The absence of magnetism in the beginning of the series is connected to a large d - f hybridization.^{8,9}

The situation is different in the case of alloys with actinide impurities. From the decrease of the superconducting temperature of lanthanum due to small amounts of actinides,¹⁰ and also from

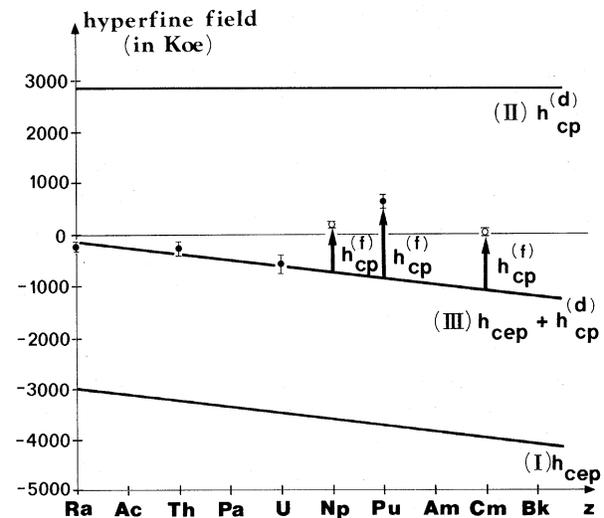


FIG. 1. Plot of the hyperfine field (in kOe). The experimental points are given by closed circles for actinides in a Fe host and by open circles in a Ni host. The curves I, II, and III are described in the text.

susceptibility and resistivity measurements on Y:A,¹¹ La:A,¹² Zr:A,¹³ and Pd:A¹⁴ (where A stands for any actinide), we may conclude that Th, U, and Am are not magnetic while Np and Pu are with magnetic moments of order $2\mu_B$ and $1\mu_B$, respectively.

For the case of actinide impurities in a ferromagnetic matrix, the only available data are hyperfine-field measurements. The hyperfine field has several contributions:

(i) The first contribution comes from the polarization of the s - p conduction band,

$$h_{cep} = A(Z)m_s^{(0)}. \quad (1)$$

$A(Z)$ is a positive s -electron hyperfine coupling parameter and $m_s^{(0)}$ is the conduction-electron polarization at the actinide impurity. A table of the coefficients $A(Z)$ is given by Campbell¹⁵ for all the elements except for the actinides. To find $A(Z)$ for the beginning of the actinide series, we can extrapolate the values for the first elements of the $7s$ series from the values for the corresponding elements of the $4s$, $5s$, and $6s$ series. Hence we deduce $A(Z) \sim (10-20)\mu_B^{-1}$ MOe for Ra. Assuming that $A(Z)$ increases along the actinide series with the same relative variation $A^{-1}(Z)dA(Z)/dZ$ as in the rare-earth series, we can take

$$A(Z) = [15 + 0.6(Z - Z_0)] \times 10^3 \mu_B^{-1} \text{ kOe}, \quad (2)$$

where Z_0 is the atomic number of Ra. We take here $m_s^{(0)} = -0.2\mu_B$ as in transitional elements. This assumes implicitly that the s band remains unchanged by the impurity or that the screening is entirely made within the d band.¹⁵ Thus, h_{cep} is given by the curve I in Fig. 1:

$$h_{cep} = -3000 - 120(Z - Z_0) \text{ kOe}. \quad (3)$$

(ii) The second contribution comes from the d -like electrons,

$$h_{cp}^{(d)} = -\alpha_d m_d^{(0)}; \quad (4)$$

α_d is constant in each d series and of order $50\mu_B^{-1}$ kOe for the $3d$ series, $400\mu_B^{-1}$ kOe for the $4d$ series and $1000\mu_B^{-1}$ kOe for the $5d$ series,¹⁵ and $m_d^{(0)}$ is the d magnetic moment at the impurity site. For the evaluation of $m_d^{(0)}$, we apply here the well-known results¹⁶ of $3d$ impurities. For $3d$ impurities in Fe or Ni, $m_d^{(0)}$ becomes negative when the difference of charge ΔZ between the impurity and iron is of order -1 and remains of order $-1\mu_B$ for $\Delta Z = -2, -3, -4$.¹⁶ It should be remembered that here one has a large period effect which gives a larger impurity potential

than for pure charge effects; in any case, the variation of $m_d^{(0)}$ is almost unchanged, except that it becomes more rapidly negative when ΔZ decreases. Since the s - d hybridization is usually important in transitionlike metals, which implies small numbers of s electrons, we consider that both s and d electrons are screened within the d band in the actinide case (the case of Ra is perhaps a special one, like sp impurities, since only s atomic states are present). In actinides, the number of s electrons is 2 and the number of d electrons remains smaller than 2.5 or 3, so that $\Delta Z \leq -2$ if we do not take into account the $5f$ electrons in the screening. At this point, it is important to distinguish, as far as f screening is concerned, the case of magnetic f states and nonmagnetic ones. In the first case, it seems clear that, since the $5f$ states are far from the Fermi level, their contribution to the screening is negligible. The case of nonmagnetic $5f$ shells for actinide impurities is a very delicate problem, since the role of the d - f hybridization is not precisely known in transition-based alloys. However, neglecting their participation in the screening seems to be consistent with our analysis of experimental data. Since $\Delta Z \leq -2$ for actinides, $h_{cp}^{(d)}$ has to remain roughly constant because α_d is assumed to be constant along the series and $m_d^{(0)}$ remains of order $-1\mu_B$, according to our preceding considerations.¹⁶

The constancy of $h_{cp}^{(d)}$ is checked by the experimental variation of the hyperfine fields up to U, which is roughly parallel to the curve I. This result is consistent with only two contributions h_{cep} and $h_{cp}^{(d)}$ to the hyperfine field in the case of Ra, Th, and U; it leads to an estimation of $h_{cp}^{(d)}$ which is of order 3000 kOe and remains roughly constant in the whole actinide series (curve II). We deduce an empirical constant α_d of order $3000\mu_B^{-1}$ kOe for the $6d$ series, in agreement with its extrapolation from the other d series.¹⁵ We can also notice that changing slightly the $A(Z)$ value leaves unchanged the physical result of the constancy of $h_{cp}^{(d)}$ and only changes the value of α_d .

(iii) Since the experimental values for Np, Pu, and Cm lie above the curve III, giving $h_{cep} + h_{cp}^{(d)}$, it is necessary to invoke, for these special impurities, an extra contribution to the hyperfine field. The extra contribution is due to the occurrence of an f localized moment $m_f^{(0)}$ on these impurities and can be written as

$$h_{cp}^{(f)} = -\alpha_f m_f^{(0)}, \quad (5)$$

where α_f is a positive constant.

The f magnetic moment has probably both spin and orbital contributions in Np and Pu due to the large spin-orbit coupling. Since the exchange coupling between the d magnetic moment on the impurity site and the f magnetic moment is positive ("ferromagnetic alignment"), it follows from (5) that $h_{cp}^{(f)}$ is positive because $m_f^{(0)}$ is negative. This point is in agreement with the experimental data of Np and Pu, which lie above the curve III. Then, the deduced contributions $h_{cp}^{(f)}$ are of order 750 kOe for Np and 1500 kOe for Pu. We can estimate α_f by using experimental data in good local-moment cases, such as NpC,¹⁷ or UP, USb, US,¹⁸ where one knows both $m_f^{(0)}$ and $h_{cp}^{(f)}$. The deduced α_f value is of order 1500 to $2000\mu_B^{-1}$ kOe, which seems a good value for the case of an Fe matrix, because it leads to an f magnetic moment of order $1\mu_B$ for Pu, in good agreement with the other experimental results for Pu systems. For Np, we have to remember that the measurements have been done in Ni. Since, for rare earths $h_{cp}^{(f)}$ is roughly 3–5 times smaller in Ni than in Fe,⁵ α_f is probably of order $500\mu_B^{-1}$ kOe in Ni. Also, $|m_d^{(0)}|$ for $3d$ impurities in Ni is a little smaller than in Fe,¹⁶ and extending this result to our case would reinforce $|m_f^{(0)}|$ for Np. So, the resulting f magnetic moment for Np is certainly near the $2\mu_B$ value found in other Np systems. We have to notice that our estimated value for α_f , larger than for the rare earths, is consistent with a smaller localization of the $5f$ electrons than of the $4f$ electrons.

The f magnetic moment has probably only a spin contribution in the case of Cm, with a $5f^7$ configuration as in pure metal case; therefore, $h_{cp}^{(f)}$ would also be positive. This is verified by the experimental value of the hyperfine field, which lies above the curve III. If we consider more quantitatively the data of Falk *et al.*⁷, the deduced value for $h_{cp}^{(f)}$ would be of order 1000 kOe. This value can be accounted for by (5) by taking $\alpha_f \sim 150$ kOe in Ni, roughly 3 times smaller here in a case of only a spin contribution than in the case of both orbital and spin contributions as in Ni:Np. We cannot be more precise quantitatively this point, but the same qualitative behavior is observed in the case of rare earths.

So, our analysis of the experimental hyperfine-field data of actinides diluted in $3d$ ferromagnetic hosts is consistent with no f magnetism for Ra, Th, and U, with the occurrence of a spin and orbital f magnetic moment of order $2\mu_B$ for Np and $1\mu_B$ for Pu and with only a spin contribution to

the magnetism of Cm.

Within the preceding framework, we can point out some predictions:

(1) For Np and Cm we can deduce that the hyperfine field measured in a Fe host would be certainly larger than the experimental values reported here. For Fe:Np it would be ~ 2000 – 3000 kOe and for Fe:Cm it would be ~ 2000 – 4000 kOe.

(2) If we assume that americium is nonmagnetic in a ferromagnetic host, as it is observed either in La:Am¹⁰ or in pure Am metal, its hyperfine field would lie on the curve III, i.e., of order ~ 1000 kOe.

(3) Berkelium and the following elements are certainly magnetic with both spin and orbital contributions. The orbital moment is parallel to the spin in the second half of the series of actinides as for rare earths, and leads to a negative and very large (in absolute value) hyperfine field.

Finally, there is a theoretical point concerning the connection between the magnetic moments in the first half of the series and the d - f hybridization.^{9,19} The more the d band is important, the smaller the magnetic moments in Np and Pu seem to be, and even the magnetism can completely disappear for a large d character as in pure actinides. We can finally suggest a study of the magnetic properties of actinide impurities in a host which has no d character, in order to see if the magnetic moments of plutonium and neptunium are larger and also if even the uranium impurity can become magnetic.

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Electron Energy States in Sb_2Se_3 †

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The transition strength $(h\nu)^2\epsilon_2$, computed by Kramers-Kronig analysis of optical reflectance spectra, is compared with x-ray photoelectron spectra for both single-crystal and amorphous Sb_2Se_3 . The similarity of the data from x-ray photoelectron spectra for the two modifications suggests that the valence-band structure is essentially the same, whereas differences in the spectral dependence of $(h\nu)^2\epsilon_2$ suggest that the conduction-band density of states is lower in the amorphous material, or that the matrix elements for optical transitions are suppressed.

As part of a study of the optical properties of Sb_2Se_3 , we have compared the energy dependence of the transition strength $(h\nu)^2\epsilon_2$ with x-ray photoelectron spectra (electron spectroscopy by chemical analysis) for both the amorphous and orthorhombic crystalline (D_{2h}^{16}) modifications of the same composition. The single crystals were prepared in a horizontal zone refiner¹ and the amorphous films by vacuum evaporation² onto room-temperature fused quartz for the optical reflectance spectra, or aluminum substrates for the x-ray photoelectron spectra (XPS). An electrically conducting substrate of aluminum was used to

facilitate cleaning by sputtering. The films were verified to be amorphous by x-ray diffraction.

Values for the function $(h\nu)^2\epsilon_2$, where $h\nu$ is the photon energy, were calculated by Kramers-Kronig analysis³ of reflectivity data from 0 to 24 eV⁴ and are plotted in Fig. 1. The most striking difference between the amorphous and single-crystal curves is that the peak observed at ~ 3 eV for both polarizations of the electric light vector for the single crystal appears to be strongly depressed for the amorphous material. This peak and the next major one at ~ 9 eV also are less well resolved for the amorphous solid.