Evidence for valence fluctuations in CeAs

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Anomalous temperature and pressure dependences for the ^{75}As Knight shift in CeAs are interpreted within the framework of Hirst's model for fluctuating valence. A 30-K-wide peak in the density of states, located 85 K below E_F, is inferred from the analysis. The area under the peak represents 1% of the Ce^{3+} valence, but due to the nature of the hyperfine interaction this is less than the actual number of electrons which would be involved in the fluctuation from Ce^{3+} to Ce^{4+}.

Experimental anomalies in magnetic[1-4] and transport[5] properties of the systems CeP and CeAs have stimulated the construction of a variety of explanatory models. A partial valence change provides a model for some experiments, but apparently has not been useful for others. In particular, our interpretation for the temperature and pressure dependence[4] of Knight shifts required the introduction of a sharp feature into the conduction-electron density of states, very near the Fermi energy (E_F). Such a feature had no easily identifiable relation to ambiguities in the Ce valence. Recently, however, Hirst[6] showed that such a change in the density of states is, in fact, a consequence of fluctuating valence.[7] Since our original analysis was entirely phenomenological, and the shape of the feature arbitrarily taken to be a step, we have, in this paper, reanalyzed available nuclear resonance data using Hirst's results and, as a consequence of the analysis, demonstrated that the fluctuating valence model semiquantitatively reproduces our data.

Our analysis is based upon the following physical picture.[6] Under some circumstances, two ionic configurations can occur with appreciable amplitudes, such that a mixed configuration exists as the system ground state. Fluctuations between these configurations introduce excitations near E_F, and for suitable choices of the respective configuration ground-state ionic splittings and interconfiguration fluctuation (ICF) rates, a single band of quasiparticles occurs. While the bandwidth (W) is determined by ICF rates, the band position relative to E_F is determined by the relative amplitude of the two configurations. Hirst used a Lorentzian shape for this band, but for our purposes a simple rectangular shape, shown in Fig. 1, is assumed.

The model used for fitting NMR data assumes that the fraction of valence 4+ remains constant, while temperature and pressure are varied.[8a] Volume changes affect the relative position of the quasiparticle band and E_F. We assume this position-volume relation is linear. In the Hirst single band picture, some overlap with E_F occurs, and varying the band position is equivalent to small valence changes. Although the quality of the fits could be improved by allowing the area of the peak in Fig. 1 to be pressure and temperature dependent, we have elected to ignore this possible mechanism and demonstrate that the principal cause of the observed NMR anomalies is simply the existence of the peak. Given this interpretation, our experiments, to good approximation, do not affect the valence, but strongly reflect valence fluctuations which occur naturally in this material.

We will consider only CeAs since a complete set of data on thermal properties is available, and essentially the same results are found for CeP. In this compound, the two competing configurations are $4f^0$ and $4f^1$. Since nuclear resonance or susceptibility experiments sample on a time scale much longer than inverse ICF rates, both types of measurements respond to an average susceptibility (χ). Bulk χ data for CeAs can be successfully analyzed[2] assuming Ce^{3+} ions, so that the fraction of time in which the $4f^0$ configuration occurs, must be of the order of a few percent. Thus for evaluation purposes, χ is taken as $\chi(Ce^{3+})$.

Knight-shift calculation is accomplished using the uniform polarization model[8b]

$$K = K_0(1 + \Gamma\chi)\,, \tag{1}$$

where K_0 is the Pauli shift and Γ is the coupling constant defined elsewhere.[8b]

The nature of hyperfine interactions in rare-earth (RE) pnictides is not certain. There is evidence that s-electron character is responsible,[8b] ultimately, for K. Certainly the conduction-electron f character is not an effective hyperfine mechanism. It is, therefore, reasonable to suppose that the NMR effects are due to changes in the s character, which in turn are produced indirectly by the fluctuating f-electron number. This can occur via s-f hybridization or generally by s-f interactions outside the scope of our model.

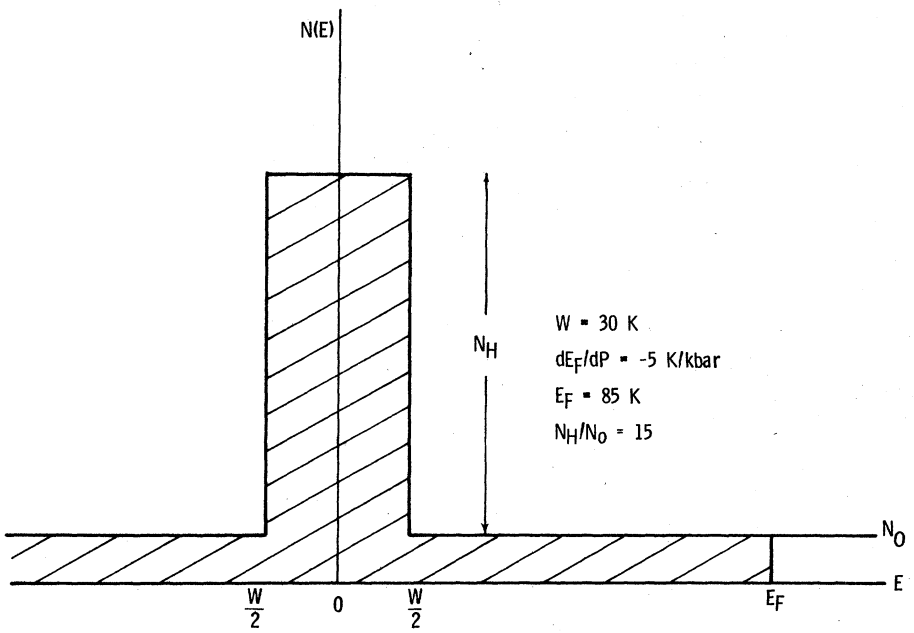

FIG. 1. Schematic of conduction-electron density of states $N(E)$ showing a peak of width W and height N_H located at the arbitrarily chosen zero energy. The bandwidth is assumed large compared to the separation of the peak and band edge. The parameter values are for the data fits shown in Figs. 2 and 3.

These phenomena occur on a rapid time scale compared to the NMR measurement, and the density of states to which the NMR is responsive is considered static. We have described the system with a uniform polarization model, which includes a temperature-independent s-f exchange constant Γ. We also assume that Γ is independent of pressure (or volume). Normally, both Γ and χ vary with volume roughly as the material compressibility. This is small compared to the magnitude of the anomaly in the NMR data. The value of Γ is undoubtedly affected by changing electron character, but the temperature dependence of our data cannot be accounted for by any such effects. We simply treat Γ as a model parameter that is determined by fitting data.

Restrictions of the uniform polarization model are not important to this problem. All that is necessary is that the coupling of the Ce spin to the As nucleus occurs through the conduction electrons. That is, K is a product of the conduction electron density of states and χ. For independent electrons[9]

$$K_0 = \tfrac{1}{2}\gamma_e^2 H_{\rm hf}(s)\,\frac{1}{4T}\int_{-\infty}^{\infty} N(E)\,\mathrm{sech}^2\frac{E-E_F}{2T}\,dE\,, \tag{2}$$

where the factors have their usual meanings and are defined elsewhere.[9] Note that the integral has appreciable value only in the energy range $2(E-E_F)\sim T$. Thus the flat conduction band of Fig. 1 is not a severe restriction.

Numerical data fits for the temperature and pressure dependence of K for CeAs are shown in Figs. 2 and 3. The Jones fit for the susceptibility data was used for χ. For K there are five parameters: (i) position of peak relative to E_F, (ii) rate of change of E_F with pressure, (iii) width of peak (W), (iv) the overall multiplier for $K[N_0 H_{\rm hf}(s)]$, and (v) the ratio N_H/N_0 (Fig. 1). The effect of volume change with temperature is included using published thermal-expansion[5] and compressibility[10] data. Parameter values are also summarized in Fig. 1. We note that the quality of the fit is somewhat better than in Ref. 4.

The width parameter (W) is much smaller than the crystal-field splitting[11] ($\Delta_{\rm CF} = 140$ K). This means that the ionic splitting of the ground state (the cubic crystal field splits the Ce^{3+} $J = \frac{5}{2}$ level into a doublet and quartet[12]) is larger than the configurational mixing interaction and the assumption of a single quasiparticle band is suspect. Furthermore, the density-of-states structure should change as the temperature increases from $T \ll$ to $T \gtrsim \Delta$. Our model is only sensitive to the structure for $T \leq 50$ K whereas $\Delta = 140$ K. As a consequence, our data fits are not affected by possible changes in the density-of-states peak at or or near Δ. We have attempted data fits with two bands separated by the crystal-field splitting. Qualitative failures for the fits are found if the second band is located above the Fermi energy. However, should a second quasiparticle band lie lower in the conduction band, its effect on the NMR results would probably not be detectable.

There are some interesting features of the fit

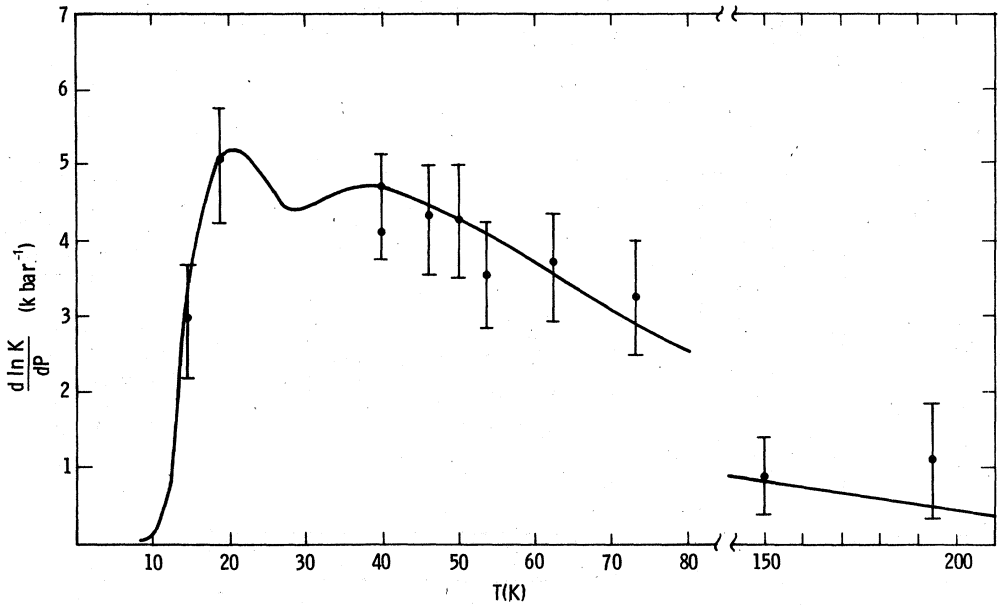

FIG. 2. Knight shift of ^{75}As in CeAs as in a function of temperature. The data are from Ref. 3 and solid curve is obtained using model parameters shown in Fig. 1. See text for details of model.

parameters. First, the value of $H_{hf}\chi$ is 7.7 G emu/mole, which is roughly a factor of two smaller than deduced from Knight-shift work[8b] on LaAs and YAs. This suggests a failure in rigid-band models between CeAs and these nonmagnetic compounds. Second, for an assumed $H_{hf} = 10^6$ G, which is typical for s-contact hyperfine interactions in metals, values of 0.12 and 3.6 states/(eV atom) are found for N_0 and N_H, respectively. With W = 30 K, there are roughly 0.01 s-states/atom added to the conduction band by the quasiparticle interaction.

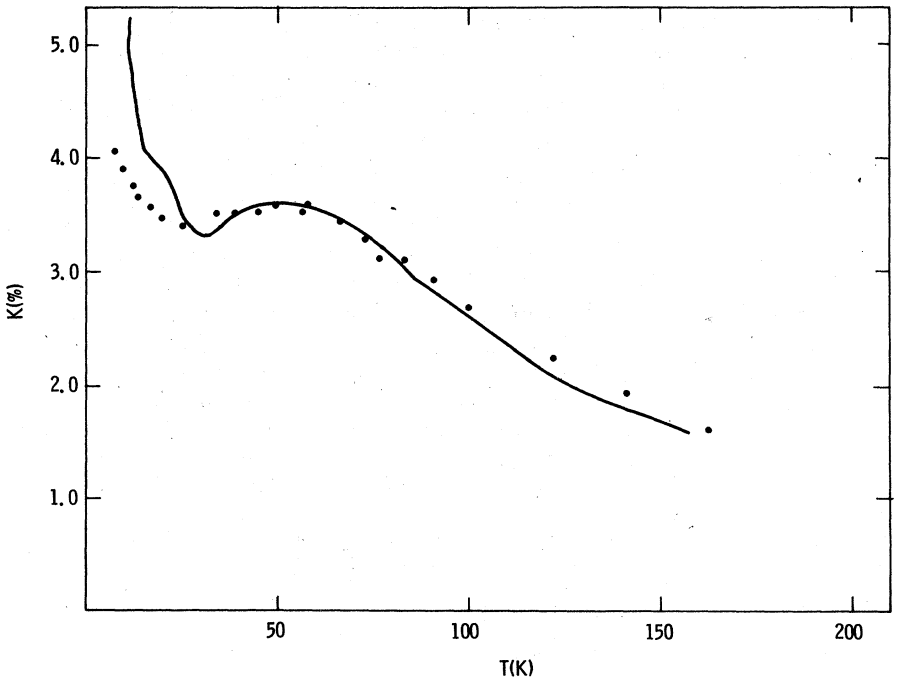

FIG. 3. Pressure derivatives of the ^{75}As Knight shift as a function of temperature. The solid curve is derived from parameters shown in Fig. 1 using the model described in text.

Since the valence fluctuations are due to f-electron changes, the principal character of the added conduction electrons is mostly f-state relative to the RE site. The s-state enhancement to which the nuclear resonance is sensitive, can be due simply to the component of these new states which possess s symmetry about the pnictide site. However, it is probably the interaction of these new states with the conduction-electron system, which gives rise to the observed structure in the density of states. This second alternative is supported by the very narrow width of the peak needed for the data fit. Certainly the credence of such a conclusion is affected by the number of parameters used in the fitting procedure. However, the narrow peak was definitely better than the step used earlier.[4] If the peak is assumed narrow, direct interactions of RE f electrons with pnictide nuclei as a Knight-shift mechanism would be unlikely. In any case, the NMR will underestimate the degree of valence fluctuation since it is only sensitive to one symmetry type. The 0.01 s states/atom detected in our experiments thus represent the minimum valence fluctuation which, in fact, may be several percent.

Finally, we note that configuration crossover (change to valence 4 +) has been achieved in CeP at 100 kbar pressures and room temperature.[13] This is consistent with the low-percentage valence fluctuation at low pressure. However, our result shows an intersection of E_F and the quasiparticle band at something in excess of 15 kbar at low temperature or ~ 30 kbar at room temperature. Although the compressibility undoubtedly decreases in the high-pressure range, the factor of 3 difference between our inferred value and the observed crossover pressure suggests nonlinearity for $E_F(P)$.

In summary, our results indicate a peak in the density of states of CeAs about 30 K wide and located 85 K below E_F. The area under the peak represents 0.01 states/atom. Since the crystal-field splitting is much larger than the width of this peak, a splitting is possible. If a second peak exists, it lies deeper in the conduction band and does not affect the NMR. We emphasize that within this model our interpretation of the NMR experiments is based upon the occurrence of configuration fluctuations which are, to good approximation, not altered (that is, W and N_H are constant) within the experimental pressure and temperature ranges.

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[7]The phenomena of valence fluctuations have been investigated by a large number of workers. We do not intend to review in any manner this work, but simply to focus on one particular aspect. Reference 6 contains a good list of pertinent papers.
[8](a) An alternative approach is to fix the position of the density-of-states peak relative to E_F and allow its area to change with temperature and pressure. Although this approach has qualitative numerical equivalence to our model, volume changes are known to alter the position of E_F within the band in specific areas. (b) See E. D. Jones, Phys. Rev. 180, 455 (1969).
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