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MAGNETIC SUSCEPTIBILITY OF DELTA PLUTONIUM-ALLOYS*

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The magnetic susceptibilities χ of two series of delta-phase alloys made of high-purity plutonium and aluminum or gallium have been measured from $\sim 6^\circ\text{K}$ to room temperature. The dependence of χ upon both solute concentration and temperature are weakly negative, the behavior being monotonic in both cases.

On the assumption that χ consists only of a Pauli spin paramagnetic term and a diamagnetic one associated with the radon-like core (the Landau term is considered to be negligible by virtue of the apparently high effective carrier mass), the density of states at the Fermi level, at 0°K , is very nearly 20 states/atom-eV. The results are discussed in terms of a two-band model for the electronic structure of delta plutonium.

1. Introduction

1.1. The molar magnetic susceptibility χ of metallic plutonium, as thus far reported, is of the order of several hundred emu^(1,2,3) and varies discontinuously across the phase boundaries.⁽¹⁾ The temperature dependence is weakly

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negative for all of the phases except alpha, for which Weil et al⁽³⁾ found a very feeble maximum below about 15°K. Work has been reported⁽²⁾ on one delta alloy which showed a monotonically decreasing behavior on being warmed from about 20°K, the magnitude of the susceptibility of the alloy being comparable with that of the pure metal.

1.2. The existence of a Néel or Curie point is suggested by the appearance of anomalous maxima in the electrical resistivity-vs-temperature curves for both alpha and delta plutonium. No such points have been found, however, in either phase, even though what appears to be a similar anomaly in manganese has been definitely associated with antiferromagnetic disordering.

1.3. In light of the above information it appears reasonable to suppose that the susceptibility, aside from its diamagnetic component, is almost entirely of the Pauli spin paramagnetic variety; i.e., exchange effects are perhaps negligible. This supposition is indeed supported by an analysis⁽⁴⁾ of $\chi(T)$ and $\rho(T)$, the electrical resistivity of alpha plutonium as based upon the simple free-electron model, which yields reasonable values for the density of states at the Fermi-level $g(E_F)$ as well as for its derivative. Smoluchowski⁽⁵⁾ explained the existence of the resistivity anomaly by using a similar model.

1.4. Application of the simple free-electron model to delta plutonium, however, seems to be of doubtful validity in light of our still meager knowledge concerning the band structures of the heavy metals. Ridley's⁽⁶⁾ work on gamma uranium, which was qualitatively extended to plutonium by Lee and Hall,⁽⁷⁾ suggested that the 5f band in delta plutonium is only a few tenths of an electron-volt wide. More recent work in applying the two-band model to delta plutonium,⁽⁸⁾ as well as a tight binding calculation,⁽⁹⁾ also indicate that the 5f band is very narrow. In that case the free-electron theory as usually formulated is not applicable except at very low temperature, being restricted by the assumption that $T \ll T_F$, where T_F is the degeneracy

temperature. Were the Fermi level to lie within, or very close to, either band edge, T_F could well be less than any temperature in the delta range of stability.

1.5. The present work is concerned with measuring the susceptibility of delta-phase alloys, the primary view being to determine details of the density of states curve. By varying the amount of the solute, aluminum or gallium, the electron concentration is altered, inasmuch as the apparent valencies of these solutes are smaller than that of the plutonium atoms. Thus, the height of the Fermi level can be changed at will, it being tacitly assumed that the band system is completely rigid.

1.6. The second purpose in conducting this study is to see whether or not the experimental results are consistent with a band model in which a rather narrow 5f band lies superimposed upon a comparatively broad 6d and/or 7s band.

2. Sample Preparation

2.1. The alloys containing 3, 5 or 7 at.-% gallium or 3, 5, 7 or 9 at.-% aluminum were arc melted six times and recast in MgO crucibles in an induction furnace to form 1/2 inch diameter ingots. The ingots were then rolled at room temperature to form square cross-section rods, 0.295 inch on a side, which were sealed within evacuated Pyrex capsules and annealed at $500 \pm 8^\circ\text{C}$. The gallium alloys were heated for 72 hours; the aluminum alloys for 144 hours. After being annealed, each rod was machined to 1.000 ± 0.001 inch in length by 0.250 ± 0.001 inch OD and drilled and reamed to 5/32 inch ID.

3. Experimental Techniques

3.1. The Faraday technique was utilized to determine the magnetic susceptibility of the samples. All specimens were contained in capsules of low volumetric susceptibility. To minimize temperature gradients in the specimens, they were machined to be right circular, hollow cylinders, as described above.

3.2. The measurements were made as follows: First, the empty capsule was screwed onto the supporting chain and its weight-field-temperature characteristics were determined. Second, a 99.98 per cent pure platinum standard was run at approximately 300°K as a calibration step. Finally, the plutonium alloy was placed in the capsule and the weight-field-temperature characteristics of the capsule plus sample were determined. From the above data, the weight change due to the sample alone could be computed and converted into a volumetric susceptibility.

3.3. The weight changes were detected by an automatic recording analytical vacuum balance, the sample being so located in the field that corrections due to the balance position were negligible compared to the balance accuracy of ± 0.1 mg. The balance was calibrated before each run, and runs were conducted in helium gas at a pressure of 10 torr.

3.4. The temperature of the gas in contact with the sample was determined by a miniature platinum resistance thermometer which was supplied by a commercial vendor.* The resistance thermometer was calibrated by the method of Corruccini.⁽¹⁰⁾ The accuracy of temperature measurement, determined as the result of separate calibration runs, is believed to have been of the order of $\pm 4^\circ\text{K}$ or better over the entire range of temperatures.

3.5. Field control was effected by a Hall probe device in the magnetic field. This probe was calibrated at 0 and 9.91 kilogauss before each run by using a standard magnet.

3.6. Data were taken in the temperature range 7 to 300°K and in the field range 0 to 10 kilogauss, some 75 to 85 datum points being taken during each run. The data were fitted by means of least squares techniques to the form $\chi_M = \chi_0 - aT^2$. For this fit, the cumulative one-sigma error limits indicate a precision of approximately 1 per cent. Table I gives the parameters as determined by the least squares technique.

* Rosemont Engineering Co., Minneapolis, Minnesota.

4. Results and Discussion

4.1. Figures 1 and 2 show how the susceptibility χ depends upon temperature T and solute concentration C for the series of plutonium-aluminum and plutonium-gallium alloys. The results show only a monotonic, negative dependence for both variables. The values in the upper part of the temperature range agree well with those of Lee et al⁽²⁾ for a 3.5 at.-% aluminum-plutonium alloy. However, a departure is well evident at lower temperatures. Inasmuch as the plutonium used in the present study was probably of much higher purity than that employed in the earlier work, it seems reasonable to attribute the difference to ferromagnetic impurities--probably iron.

4.2. The Pauli susceptibility when extrapolated to 0°K provides a direct measure of the density of states g at ζ^0 , the Fermi level at 0°K . On the assumption that χ consists only of spin paramagnetic and diamagnetic terms it is possible to estimate $g(\zeta^0)$. A rather large diamagnetic term is associated with the radon-like core.⁽¹¹⁾ Inasmuch as the Landau diamagnetism of the conduction electrons varies as $(m/m^*)^2$, where m and m^* are the free electron and effective masses, respectively, this term, in view of the high electrical resistivity, can be neglected. Because the 5f electrons are highly localized,⁽¹²⁾ however, their contribution may be obtained, as for the electrons in the radon-like core. The total diamagnetic susceptibility is therefore estimated to be about -72×10^{-6} emu. Subtracting this term from χ and using the relation⁽¹³⁾

$$\chi_p = g(\zeta^0) \beta^2 \quad (1)$$

where β is the electronic magnetic moment and χ_p is the Pauli susceptibility, gives $g(\zeta^0)$ as very nearly 20 states/atom-eV.

4.3. The dependence of χ upon C indicates that dg/dE is positive. The sign of the thermoelectric power S also suggests that $dg/dE > 0$ ⁽⁷⁾ although there is some doubt as to the validity of the relationship between S and dg/dE .⁽¹⁴⁾ By using the value of 20 states/atom-eV for $g(\zeta^0)$, the change

in overall electron concentration obtained by assuming that the aluminum exists in trivalent form and also by assuming that about four of the electrons reside in the $5f_{7/2}^5$ sub-band,⁽⁸⁾ dg/dE appears to be about 10. It is not clear, however, whether the observed decrease of χ with respect to C is entirely due to a change in electron concentration. Jones⁽¹⁵⁾ has recently pointed out that significant reductions in the density of states can accompany the introduction of aperiodicity into the crystal, as in the formation of random solid solutions.

5. Conclusion

5.1. The susceptibility of delta plutonium alloys containing aluminum or gallium indicates that the density of states is about 20 states/atom-eV. This number is based upon the assumption that electronic exchange interactions are so weak that the susceptibility is composed mainly of Pauli spin paramagnetic and orbital diamagnetic terms.

5.2. The large value of $g(\zeta^0)$ is indicative of delta plutonium having a narrow 5f band of the order of a few tenths of an electron-volt. The value of dg/dE obtained from the dependence of χ upon solute concentration is consistent with a narrow $5f_{7/2}^5$ band.^(6,7,8,9) The effect upon χ of band broadening by the introduction of lattice imperfections through alloying has not been considered, however. Since the band shape is probably complicated⁽⁹⁾ the positive slope of $g(E)$ indicated by this work does not necessarily correspond to ζ^0 being below the midpoint of a simple parabolic band.

5.3. The range over which the electron concentration, and hence the Fermi level ζ^0 , can be varied by alloying is small. Not much can be done, therefore, to determine details of the band structure. The weak dependence of χ upon electron concentration is not inconsistent with the rather strong effects of aluminum and other solutes upon the phase stability range of delta plutonium and upon its negative thermal expansion coefficient. For were the narrow 5f band to have a constant density of states at low temperatures, χ

would vary hardly at all with alloy composition although the entropy and chemical potential could change quite strongly.⁽⁸⁾

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Table I. Least Squares Parameters Used in Computing χ_m

$\chi_m = \chi_o - aT^2$		
Solute Element	χ_o	$a \times 10^4$
3 Ga	600.9	2.536
5 Ga	585.9	2.463
7 Ga	566.8	2.044
3 Al	602.6	3.043
5 Al	593.7	2.358
7 Al	579.4	2.460
9 Al	559.5	1.780

FIGURE CAPTIONS

- Fig. 1 Temperature dependence of the molar susceptibility of the delta-phase, plutonium-gallium alloys.
- Fig. 2 Temperature dependence of the molar susceptibility of the delta-phase, plutonium-aluminum alloys.

Fig. 2