CONF-721114--4

72-102

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W. C. Koehler, R. M. Moon, and H. R. Child

SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE CORPORATION
for the
U. S. Atomic Energy Commission
Oak Ridge, Tennessee 37830

October 1972

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W. C. Koehler, R. M. Moon, and H. R. Child
Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

Neutron scattering experiments have been carried out on a polycrystalline rod of ^{147}Pm at temperatures ranging from 320°K to 7.5°K. The double hexagonal close-packed structure characteristic of Pr and Nd was observed over this entire temperature range. Evidence for magnetic ordering in ^{147}Pm was sought in a variety of neutron scattering experiments. From conventional measurements it appears that any ordered moment must be less than about 0.4 μ_B. Neutron depolarization measurements indicate a small ferromagnetic moment at low temperatures and a transition temperature of about 98°K. The observations are qualitatively consistent with point charge model crystal field calculations which predict a singlet ground state for ions on both hexagonal and cubic sites.

INTRODUCTION

In recent years the magnetic properties of a number of the light rare earth metals have been intensively studied both by classical macroscopic methods and by neutron scattering techniques. The element promethium, falling between Nd and Sm in the periodic table, has been little studied by any means primarily because it is not a naturally occurring element. However, the isotope ^{147}Pm is found, in relatively copious amounts, as a by-product of fission in nuclear reactors. It has a relatively long half-life for easily shielded β-emission, and a not unreasonable neutron capture cross section.

Highly pure metal can be obtained from the Target Development Center of the Oak Ridge National Laboratory in which methods have been developed and facilities built for the production, purification, and fabrication of gram quantities of elemental ^{147}Pm. Finally, since the crystal structure of ^{147}Pm appeared to be the relatively simple dhcp structure[1] characteristic of Nd rather than the more complex structure characteristic of Sm, we were encouraged to carry out a number of neutron scattering experiments on a polycrystalline specimen in an attempt characterize this material.

SAMPLE PROPERTIES

A reduction-distillation technique was used to produce high purity ^{147}Pm according to the reaction

$$2\ Pm_2O_3 + 3\ Th \xrightarrow{1600°C} 3\ ThO_2 + 4\ Pm\uparrow \qquad (1)$$

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

Prior to the collection of Pm in a hemispherical quartz dome just above the reactor still, the reactor temperature was held at 1400°C for 30 minutes which was sufficient to reduce and distill off the ^{147}Sm daughter impurity in the oxide. The metallic ^{147}Pm was subsequently arc melted and drop cast to form a cylinder 0.635 cm in diameter and 2.54 cm long. The arc melting and casting process removed any ^{147}Sm decay product formed since the distillation; thus "time zero" for ^{147}Sm growth in the diffraction specimen could be accurately known. (With a half-life of 2.62 years, the β decay produces about 2.2% ^{147}Sm per month. The data to be reported here were collected one month after the casting of the specimen, and are thus for an alloy containing about 2% ^{147}Sm.)

The diffraction specimen was placed in an aluminum capsule, sealed with an epoxy cement, and loaded into one of the cryostats at HB-1 of the HFIR. The β activity was effectively shielded by the aluminum capsule and the Bremsstrahlung radiation level (greater than 100 rem at a distance of 1.5") was under 100 mrem at 15 feet from the instrument. A total number of 5159 curies was in the sample. The thermal power of the specimen was 1.85 watts and this presented something of a challenge to obtaining low sample temperatures. Nevertheless, we were able to reach a temperature, as measured by a sensor located close to the specimen, of 7.5°K.

A transmission experiment on our specimen yielded a value for the total neutron cross section $\sigma_T = 110 \pm 2b$ at a neutron energy of 0.07 eV in good agreement with recent measurements of the total cross section of ^{147}Pm in the thermal region.[2]

A neutron diffraction pattern taken at room temperature showed lines characteristic of the double hexagonal close-packed structure with $a \approx 3.65$ Å, $c \cong 11.65$ Å in accord with the room temperature x-ray diffraction data.[1] Patterns taken at various lower temperatures show that this structure is retained to 7.5°K. From the intensities observed in a pattern taken at 97°K, calibrated in the usual way against a standard scatterer, the coherent scattering amplitude and cross section for the alloy were found to be $b = 1.26 \pm 0.04 \times 10^{-12}$ cm and $\sigma_{coh} = 20.0 \pm 1.3$ barns.

According to Hund's rules the free ion ground state for the $4f^4$ configuration of Pm^{+3} is $^5I_4$ ($L = 6$, $S = 2$, $J = 4$) for which the fully ordered moment gJ is $3/5 \cdot 4 = 2.4\ \mu_B$. The degeneracy of this free ion ground state can be lifted by the crystal field and Pm^{+3} with an even number of electrons can have a singlet, non-magnetic ground state in both the hexagonal and cubic sites of the dhcp structure.

RESULTS

We turn now to results of the several neutron scattering experiments which we have carried out in an effort to investigate the magnetic properties of promethium.

1. Search for Antiferromagnetic Ordering. In the absence, to our knowledge, of magnetic susceptibility or of other physical data indicating a magnetic ordering transition, we first made diffraction patterns at room temperature, and at a low temperature, 7.5°K, and

looked for additional reflections of magnetic origin. Patterns were made as well at 97°K. Except for slight changes in the intensities of the nuclear reflections, these patterns were not significantly different from each other, and this suggests that the ordered moment in any antiferromagnetic structure of Pm must be very small or zero.

If we assume, for definiteness, that the magnetic structure of Pm is the same as that of polycrystalline Pr[3] which in turn is supposed to be similar to that of Nd,[4] and if only one set of sites is ordered, then from the sensitivity of the data we conclude that the ordered moment must be smaller than about 0.3 μ_B.

2. Search for an Ordered Structure of Any Type. When a transition from the paramagnetic state to a magnetically ordered state occurs it is sometimes possible to assess the magnitude of the moment in the ordered state from the difference in magnetic diffuse scattering observed at temperatures well above and well below the transition without a detailed knowledge of the structure. The method gives reliable results when the neutron energy is very high compared to the overall splitting of the ground state. This is probably only approximately true for Pm with an incident neutron energy of 70 meV. Assuming the method to be applicable, a background difference which is just significant would correspond to an ordered moment of 0.6 μ_B.

3. Search for a Ferromagnetically Ordered State. A very sensitive probe for the detection of small ferromagnetic moments is a beam of polarized neutrons. When such a beam is transmitted through an unmagnetized ferromagnet, the random direction of the magnetic domains produces depolarization of the beam. According to Halpern and Holstein[5] this depolarization depends upon the thickness of the sample, d, the mean domain size $\bar{\Delta}$, and the spontaneous induction, B, in the domains according to the relation

$$P/P_o = D = \exp - (\gamma_n^2 B^2 \bar{\Delta} d/3v^2) \qquad (2)$$

where γ_n is the gyromagnetic ratio and v the velocity of the neutron and P and P_o are the beam polarizations with and without the specimen. Neutron depolarization measurements on Ni[6] near its Curie point have shown that the variation of $(B^2\bar{\Delta})^{\frac{1}{2}}$ with temperature follows the bulk magnetization data, and experiments on Dy[7] showed that in zero applied field the magnetic domains were very small, between 10^{-6} and 5×10^{-5} cm.

In order to check for a weak ferromagnetic moment in the ^{147}Pm specimen we made measurements of the polarization ratio R_T of the neutrons transmitted through the specimen as a function of temperature. The quantity R_T is simply the ratio of the intensity of neutrons detected when the flipper is off to those counted when the flipper is activated; that is, the ratio of neutrons in the + spin state to those in the - spin state, and it is directly related to the polarization of the transmitted beam $R_T = (1 + P)/(1 - P)$. As shown in Fig. 1, the polarization ratio increases with temperature becoming constant above about 98°K. Such behavior is typical of a ferromagnet with a Curie point of 98°K.

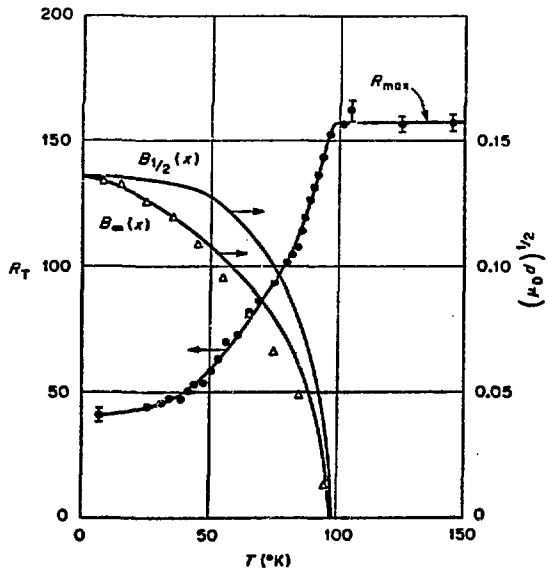

Fig. 1. Variation of R_T and $(\mu_D d)^{\frac{1}{2}}$ with temperature. For comparison with the $(\mu_D d)^{\frac{1}{2}}$ data are shown Brillouin functions for $J = 1/2$ and $J = \infty$.

When the instrumental corrections are small, as is the case when R is over 100, one may express P_o, P_f, and P_A, the efficiencies of the polarizer, flipper, and analyzer as $1-2\delta_o$, $1-2\delta_f$, and $1-2\delta_A$, respectively. It is easy to show that the inverse flipping ratio with the sample out (actually sample in but above 98°K) is approximately $1/R_{max} \cong \delta_o + \delta_f + \delta_A$. Below 98°K there is depolarization of the beam and the sample can be characterized by a small linear depolarization coefficient μ_D. Then $D = P/P_{max} = 1 - 2\,\mu_D d$ and $1/R_T \cong \delta_o + \delta_f + \delta_A + \mu_D d$. Thus the difference between the inverse polarization ratio at temperature T and the maximum is directly a measure of the depolarization.

At the lowest temperature the observed value of $\mu_D d = 0.01806$. If we assume all atoms have the same moment, μ, expressed in Bohr magnetons we find from Eq. (2) $\mu^2\Delta = 5.7 \times 10^{-6}$. With a mean domain size of 10^{-4} cm, say, this would imply a moment of 0.24 μ_B.

Having obtained evidence for weak ferromagnetism in the specimen from the depolarization experiment, we measured the intensity of the strong (102) reflection as a function of temperature in order to detect a possible magnetic contribution to this reflection. An estimated Debye-Waller correction factor was applied to the intensities after which it appeared that a ratio of low temperature to high temperature intensities of 1.003 would not be significant. If all atoms carry the same moment this result means that a moment $\mu \leq 0.4\ \mu_B$ would not have been detected.

The ideal way to measure the magnetic contributions to Bragg reflections is to measure the flipping ratio of a series of Bragg peaks. Such a measurement is best carried out with a magnetic field strong enough to saturate the specimen directed normal to the scattering vector. At present we are not equipped to apply a vertical field to a specimen at very low temperatures so we attempted to measure the flipping ratio of the (102) reflection by applying a horizontal field at an angle to the scattering vector and making use of a small normal component of the sample magnetization. We estimate that a moment per atom $\leq 0.3\ \mu_B$ would not have been detected.

SUMMARY AND DISCUSSION

None of the diffraction experiments that we have carried out on ^{147}Pm has shown any evidence for magnetic ordering in this substance, and this is consistent with the results of point charge model crystal field calculations which we have made which predict a singlet ground state for Pm^{+3} in both the cubic and hexagonal sites of the structure. Qualitatively the existence of a small net moment, as suggested by the depolarization experiments can be understood as arising from exchange induced admixture of an excited level into the ground state. Quantitatively, however, it is difficult, at present, to reconcile a low moment with such a high transition temperature.

As we have mentioned, our sample contains a few atomic percent ^{147}Sm, which is present in the double hexagonal structure. The susceptibility of pure dhcp Sm[8] shows a sharp maximum characteristic of an antiferromagnet at 27°K and a kink of undetermined origin between 100° and 120°K. While it is not likely that a ferromagnetic transition at 98°K can be attributed to a 2% ^{147}Sm impurity, it is disturbing that we have no direct diffraction evidence for ferromagnetism. We propose, in the near future, to repeat the flipping ratio experiments with the aid of a 60 kOe split coil superconducting magnet.

ACKNOWLEDGMENT

The authors are grateful to E. H. Kobisk, Target Development Center, Oak Ridge National Laboratory, for preparing and encapsulating the specimen.

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