

perhaps, be artificially created.<sup>1,26</sup> Since the thermalized portion of any distribution is isotropic, the importance of orbital quantization considerations is essentially the same for isotropic and anisotropic distributions.

We offer no explanation for the difference between the experimental results of Dousmanis *et al.* and Dexter *et al.*, except, perhaps, to point out that, due to the

<sup>26</sup> If the strongly anisotropic distribution envisioned in reference 1 were actually achieved, the emissive effect would be enhanced by a factor of about  $(1+\omega^2r^2)$  by the application of a magnetic field to resonate the negative masses.

quantization, a region of energy allowed for negative-mass carriers in the former experiment is not allowed at the higher magnetic fields of the latter.

#### ACKNOWLEDGMENTS

We are very grateful to S. Kahng for his advice and assistance in setting up the problem for machine computation. We would also like to thank G. C. Dousmanis, F. Herman, and D. O. North for many interesting and helpful discussions.

### Internal Fields at Low Temperatures in CoPd Alloys\*

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(Received September 5, 1961)

The hyperfine splitting of the 14.4-keV gamma ray line in  $Fe^{57}$  has been measured for a series of sources, each containing  $Co^{57}$  activity doped into a host lattice of CoPd. Although Pd itself is not ferromagnetic, the alloys with Co are all ferromagnetic, with Curie temperatures ranging from 1404°K for pure Co down to 130°K for a 3% Co alloy (the most dilute which we have studied). The internal field associated with the hyperfine splitting is a function of temperature for a given alloy; however, at temperatures small compared to the Curie temperature, we find that each source shows very nearly the same internal field, namely -308 kgauss. The relationship of this behavior to current theories of the internal field in Fe and to the nature of ferromagnetism in CoPd is briefly discussed.

THE ferromagnetism of alloys of Pd with the iron series elements has been extensively studied.<sup>1-3</sup> The Co-Pd alloys are a continuous series of random substitutional solid solutions.<sup>4</sup> The dilute Co alloys at room temperature are fcc in structure and show no superlattice structure.<sup>4</sup> They have the interesting property that, although Pd itself is not ferromagnetic, the addition of as little as 0.1% Co makes an alloy which is ferromagnetic.<sup>1</sup> This raises the question of the mechanism for this very long range ferromagnetism.

The experimental information presently available for the cobalt-palladium alloys concerns bulk properties such as the Curie temperature  $T_c$ , the saturation magnetization, and the magnetic susceptibility. Recently, however, the Mössbauer effect has been used to study the internal magnetic field  $H_i$  at  $Fe^{57}$  impurities in various materials. For  $Fe^{57}$  in a lattice<sup>2</sup> of pure Fe, we have reported the temperature dependence of the hyperfine

splitting.<sup>5</sup> The absorption spectrum at all temperatures from 1026° to 0.35°K showed six well-resolved lines, indicating  $H_i$  must be very nearly the same at all lattice positions. (The Curie temperature of Fe is 1046°K.) Furthermore,  $H_i$  and the saturation magnetization have the same temperature dependence, within the accuracy of the experiment. For the Co-Pd alloys, because of their random character, it seemed interesting to investigate with the Mössbauer effect whether  $H_i$  would still be unique, and what would be the temperature dependence.

A series of Co-Pd alloys were prepared ranging in Co concentrations from 100% to 3% Co. Each sample was rolled to about 5 mils thickness and electroplated with  $Co^{57}$ , which was then diffused into the lattice for 1 hour at 1000°C. The Mössbauer effect spectrum was obtained at several temperatures for each alloy. Some of the 8% samples in the interval  $T_c > T > 0.7 T_c$  show anomalous spectra, which appear to be the superposition of a six-line hyperfine pattern and a single-line (unsplit) pattern. This effect is still being studied. However, for  $T < 0.5 T_c$ , every sample showed a spectrum of six well-defined emission lines, indicating that  $H_i$  was very nearly the same at all lattice positions for a given sample. From the splitting, we obtain  $H_i$  in kilogauss,

\* Work performed under the auspices of the U. S. Atomic Energy Commission.

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<sup>2</sup> E. O. Wollan, *Phys. Rev.* **122**, 1710 (1961).

<sup>3</sup> J. Crangle and D. Parsons, *Proc. Roy. Soc. (London)* **255A**, 509 (1960).

<sup>4</sup> M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), 2nd ed., p. 491.

<sup>5</sup> D. E. Nagle, H. Frauenfelder, R. D. Taylor, D. R. F. Cochran, and B. T. Matthias, *Phys. Rev. Letters* **5**, 364 (1960). J. G. Dash *et al.*, *Phys. Rev.* **122**, 1116 (1961).

TABLE I. Hyperfine field  $H_i$  in Co-Pd Alloys at low temperatures ( $T/T_c$ ).

Atom per cent cobalt	Curie temperature ( $^{\circ}$ K)	Temperature for $H_i$ measurement ( $^{\circ}$ K)	$H_i$ (kgauss)	Bulk moment/Co atom (Bohr magnetons)
100	1404	297	$-312 \pm 5$	1.7
30	673	80	$-305 \pm 10$	2.6
15	423	4	$-296 \pm 8$	4.1
8	275	4	$-315 \pm 4$	5.5
3	130	4	$-310 \pm 9$	7.4

using as a reference standard the previously determined value of 333 kgauss for  $\text{Fe}^{57}$  in Fe at  $300^{\circ}\text{K}$ .<sup>6</sup>

Table I gives our experimental values of  $H_i$  at low temperatures. The Curie temperatures  $T_c$  are those reported by Grube and Winkler<sup>7</sup> and by Bozorth *et al.*<sup>1</sup> The temperature of the measurement  $H_i$  was in each case chosen to be very small compared to  $T_c$ . The values of  $H_i$  obtained appear to be nearly constant. A small extrapolation could be made to  $H_i(T)$  to obtain  $H_i$  at  $T=0$ , using our knowledge of the temperature dependence. An approximate formula for this is<sup>8</sup>

$$H_i(0) = H_i(1 - T^2/T_c^2)^{-\frac{1}{2}}$$

from which we see that the measurements of  $H_i$  for the 100% alloy would be increased by about 2%, and the others only negligibly. The 100% Co internal field agrees well with Wertheim's value of  $3.1 \times 10^5$  gauss.<sup>9</sup>

The negative sign of  $H_i$  for  $\text{Fe}^{57}$  in an Fe lattice has been of considerable interest.<sup>10</sup> We have made a determination of the sign of  $\text{Fe}^{57}$  in a 100% Co lattice at room temperature. When the sample is placed in an external field of about 30 kgauss,  $H_i$  decreases by about 10%. Thus  $H_i$  is in the opposite direction to the magnetization, i.e., negative. Dash *et al.* report that  $H_i$  for  $\text{Co}^{57}$  impurities in a 100% Fe lattice is also negative.<sup>11</sup> From low-temperature specific heat measurements Arp, Edmonds, and Peterson show that the magnitude of  $H_i$  for  $\text{Co}^{57}$  in Fe-Co alloys varies smoothly from  $219 \pm 4$  (100% Co) to  $314 \pm 9$  (4.8% Co) koe.<sup>12</sup>  $H_i$  then cannot change sign, so it is also negative for Co in Co.

Johnson *et al.*<sup>13</sup> have studied  $H_i$  at room temperature at  $\text{Fe}^{57}$  impurity centers in Fe-Co and Fe-Ni alloys.

<sup>6</sup> S. S. Hanna, J. Heberle, C. Littlejohn, G. J. Perlow, R. S. Preston, and D. H. Vincent, *Phys. Rev. Letters* **4**, 177 (1960).

<sup>7</sup> G. Grube and O. Winkler, *Z. Electrochem.* **41**, 52 (1935).

<sup>8</sup> C. Robert and J. Winter, *Compt. rend.* **250**, 3831 (1960).

<sup>9</sup> G. Wertheim, *Phys. Rev. Letters* **4**, 403 (1960).

<sup>10</sup> S. S. Hanna, J. Heberle, G. J. Perlow, R. S. Preston, and D. H. Vincent, *Phys. Rev. Letters* **4**, 513 (1960).

<sup>11</sup> J. G. Dash, R. D. Taylor, D. E. Nagle, P. P. Craig, and W. M. Visscher, *Phys. Rev.* **122**, 1116 (1961).

<sup>12</sup> V. Arp, D. Edmonds, and R. Peterson, *Phys. Rev. Letters* **3**, 212 (1959).

<sup>13</sup> C. E. Johnson, M. S. Ridout, T. E. Cranshaw, and P. E. Madson, *Phys. Rev. Letters* **6**, 450 (1961).

Their data for the Fe-Ni system show a monotonic decrease of about 25% as the Fe concentration decreases from 100% to zero. The above continuity argument then shows  $H_i$  for  $\text{Fe}^{57}$  in Ni is also negative.

The constancy of  $H_i$  vs concentration in the Co-Pd system and the fact that it is close to the pure Fe value are in sharp contrast to the substantial variations with concentration in the binary alloys of iron group elements. Goodings and Heine,<sup>14</sup> Freeman and Watson,<sup>15</sup> and Watson and Freeman,<sup>16</sup> have discussed the various atomic electron contributions to  $H_i$  using the results of their unrestricted Hartree-Fock calculations. They conclude that in most magnetic materials of the iron series the dominant contribution to  $H_i$  is a negative one, arising from  $3d$  exchange polarization of the core electrons. A very small spin polarization of the core electrons by this mechanism gives a large hyperfine field because the Fermi contact interaction is large. This contribution to  $H_i$  appears to be proportional to the  $3d$  resultant spin; which would imply that the  $3d$  spin contribution at the  $\text{Fe}^{57}$  nucleus remains unchanged as the Co concentration in the Pd lattice decreases.

The last column of Table I gives the bulk moment divided by the number of Co atoms in the sample, taken from Bozorth *et al.*<sup>1</sup> This moment varies with concentration and is much larger than that of Co in pure Co, namely 1.7 Bohr magnetons. The ferromagnetism of the dilute Co alloys presumably arises from an exchange interaction of the  $3d$  spin of the Co with the  $4d$  band of Pd. Bozorth *et al.* consider that the Co atoms have the same moment in the alloy as in the pure metal, and that the remainder of the average moment comes from the polarization of Pd. This is consistent with the above mechanism for  $H_i$ , if we assume that the  $\text{Fe}^{57}$  impurities also have the same  $3d$  configurations as they do in pure Co metal. We also find experimentally that the chemical shift, relative to a Fe source, of the  $\text{Fe}^{57}$  resonance in the Co-Pd compounds is constant and small ( $0.1 \pm 0.1$  mm sec<sup>-1</sup>), indicating that the  $s$ -electron charge density at the nucleus also changes little.<sup>17,18</sup>

#### ACKNOWLEDGMENTS

We wish to thank H. Frauenfelder, B. Matthias, and J. G. Dash for some very helpful discussions and C. Wagner for assistance in collecting data.

<sup>14</sup> D. Goodings and V. Heine, *Phys. Rev. Letters* **5**, 370 (1960).

<sup>15</sup> A. J. Freeman and R. E. Watson, *Phys. Rev. Letters* **5**, 498 (1960).

<sup>16</sup> R. E. Watson and A. J. Freeman, *Phys. Rev.* **124**, 1117 (1961).

<sup>17</sup> L. R. Walker, G. Wertheim, and V. Jaccarino, *Phys. Rev. Letters* **6**, 98 (1961).

<sup>18</sup> O. C. Kistner and A. W. Sunyar, *Phys. Rev. Letters* **4**, 412 (1960).