## Magnetization of Amorphous CoP Alloy—Spin Waves in Noncrystalline Ferromagnets\*

R. W. Cochrane

Eaton Electronics Research Laboratory, McGill University, Montreal 101, Quebec, Canada

and

G. S. Cargill, III

Department of Engineering and Applied Science, Yale University, New Haven, Connecticut 06520 (Received 16 October 1973)

The magnetization of several bulk amorphous ferromagnetic CoP alloys is shown to obey a corresponding-states law which differs significantly from comparable crystalline ferromagnets such as Co or Ni. This difference originates in an anomalously large  $T^{3/2}$ low-temperature demagnetization extending beyond  $0.2T_{\rm C}$ . The temperature and field dependence of this term provide evidence for the presence of spin-wave excitations characterized by a high density of states at low energies.

Recently, there has been an increasing experimental and theoretical interest in the structural and physical properties of noncrystalline solids in general and amorphous metallic alloys in particular.<sup>1-3</sup> The metallic compounds usually include a transition or rare-earth metal in combination with each other or with some nonmetallic element of group IV or V such as C, Si, or P in regions of limited crystalline-solid solubility. In this paper we focus on the latter type of alloy whose structure can be described as a dense random packing of hard spheres,<sup>3-7</sup> and in which the large concentrations of transition-metal atoms often give rise to long-range ferromagnetic or ferrimagnetic order.<sup>1-3</sup> In spite of the abundance of such amorphous ferromagnets, the precise effect of the noncrystalline structure on the magnetic order remains poorly understood.

The most general magnetic characteristic of the amorphous transition-metal alloys is their rapid decrease in magnetization as a function of temperature.<sup>8-10</sup> When the reduced magnetization, m(T) = M(T)/M(0), is plotted as a function of the reduced temperature,  $t = T/T_{\rm C}$  (correspondingstates curve), the results for the amorphous materials consistently fall below those for the corresponding crystalline system. This behavior has been interpreted<sup>8-12</sup> on the basis of molecularfield models incorporating a distribution of internal fields. On the other hand, theoretical attempts<sup>13-15</sup> which go beyond such simple models generally analyze crystalline systems with a random distribution in the interactions or else binary alloys with randomly substituted components having different coupling constants.

We report magnetization measurements on a series of bulk amorphous *CoP* alloys. Five al-

loys with phosphorus content<sup>3</sup> from 19 to 24 at.%have been prepared by electrodeposition from chemical solutions at  $75^{\circ}C$  and are listed in Table I. Two different sets of magnetization measurements are presented and together they span the complete regime from liquid-helium temperatures through the crystallization temperature  $T_0$ , which occurs near 600 K. The first is a series of low-field measurements in a conventional ac hysteresis loop tracer.<sup>2</sup> All the CoP alloys are ferromagnetic and magnetically soft; the magnetization saturates in fields of approximately 100 Oe for the as-deposited material and as low as 10 Oe after thermal cycling to 500 K.<sup>2</sup> The second set was taken in a vibrating-sample magnetometer (VSM) from 4.2 to 300 K in a highfield NbTi superconducting solenoid. At liquidhelium temperatures, the high-field data show that the low-field saturation is complete; the

TABLE I. Sample composition, Curie temperature  $T_C$ , zero-temperature magnetization M(0), and  $T^{3/2}$  demagnetization slope *B* for amorphous *CoP* alloys, Co, and Ni.

Sample	Composition (at.% P)	Т <sub>С</sub> (К)	M(0) (emu/g)	$10^{5}B$ (K <sup>-3/2</sup> )	
A	$23.6 \pm 1.0$	$550 \pm 30$	$94 \pm 4$	$3.8 \pm 0.2$	
В	22.0	$620 \pm 30$	$97 \pm 4$	$2.7 \pm 0.2$	
С	20.3	$720 \pm 30$	$114 \pm 5$	$2.6 \pm 0.2$	
D	19.0	$750 \pm 30$	$108 \pm 5$	$2.2 \pm 0.2$	
G	21	• • •	$97 \pm 4$	$3.0 \pm 0.2$	
Со	• • •	1393 <sup>a</sup>	164 <sup>a</sup>	$0.25^{b}$	
Ni	•••	631 <sup>a</sup>	58 <sup>a</sup>	$0.75 \pm 0.2^{\circ}$	
<sup>a</sup> Ref.	16.	<sup>c</sup> Ref. 18.			

<sup>b</sup>Ref. 19.



FIG. 1. M(T)/M(0) versus  $T/T_C$  for four amorphous CoP alloys and crystalline Ni using a low-field ac loop tracer.

magnetization at 4.2 K remains essentially unchanged up to 55 kOe.<sup>3</sup>

The ac loop measurements were made at a number of temperatures from 77 to 700 K. The lower-temperature data were extrapolated to T=0, giving M(0). At high temperatures,  $T_0$  for sample B turned out to be quite close to the Curie temperature  $T_{\rm C}$ , which was estimated as  $T_{\rm C}$ =  $620 \pm 30$  K. This value was used to calculate  $T_{\rm C}$  for the remaining alloys by requiring that the reduced magnetization for all the samples coincide at m(T) = 0.5 for the same value of t. The  $T_{\rm C}$  values so obtained are listed in Table I. The data for samples A to D are summarized in Fig. 1, which plots m versus t and shows that the amorphous CoP alloys obey a correspondingstates law. Also shown in Fig. 1 is a similar plot for polycrystalline Ni from data obtained in this apparatus. Nickel provides a relevant comparison with CoP because it is a close-packed ferromagnet (as in Co) with  $T_{\rm C}$  = 631 K<sup>16</sup> and can be saturated at relatively low fields. Moreover, on a reduced plot, the m-t curve for Ni is identical to that for Co.<sup>16</sup> In agreement with other transition-metal systems, amorphous CoP demagnetizes at a rate which is significantly faster at the low-temperature end than the comparable crystalline system. Near the transition temperature, the amorphous m-t slope is correspondingly smaller although uncertainties in the  $T_{\rm C}$  values are reflected directly in its magnitude.

Subsequently, the VSM was used to obtain highresolution (~2 parts in  $10^4$ ) data below room temperature in constant fields.<sup>17</sup> Figure 2(a) shows the demagnetization for all five samples plotted



FIG. 2. (a)  $\Delta M/M(0)$  versus  $T^{3/2}$  for five amorphous CoP alloys. (b) Data from (a) replotted as a function of  $(T/T_{\rm C})^{3/2}$ .

as  $\Delta M/M(0)$  against  $T^{3/2}$  in low applied fields (0.5-0.9 kOe). The  $T^{3/2}$  demagnetization coefficients are given in Table I along with the corresponding values for Ni and Co. Significantly, the CoP parameters are a factor of 3 to 6 times that of Ni<sup>18</sup> and 8 to 16 times that of Co.<sup>19</sup> Figure 2(b) shows the data replotted as  $\Delta m$  versus  $t^{3/2}$  using the Curie temperatures previously determined. The small deviations from the dashed curve can be accounted for by the error limits quoted on  $T_{c}$ . Hence, Fig. 2(b) confirms the corresponding-states law illustrated in Fig. 1 and establishes the temperature dependence at low temperatures as  $t^{3/2}$ . Moreover, the range of this simple  $t^{3/2}$  variation extends beyond t = 0.2and is appreciably greater than is observed for Ni.18

For crystalline ferromagnets a low-temperature,  $T^{3/2}$  demagnetization arises from the excitation of spin waves for which the low-energy density of states has a square-root energy dependence,<sup>20</sup>

$$n(E) \propto (E - E_0)^{1/2}$$
. (1)

Furthermore, the effect of a magnetic field is included by setting  $E_0 = g\mu_B H$ , the Zeeman energy of a spin wave in the internal field. For  $g\mu_B H$ < kT the  $T^{3/2}$  spin-wave magnetization is then modified by the factor<sup>18</sup>

$$G(H, T) = 1 - 1.36 (g \mu_{B} H/kT)^{1/2} + 0.56 (g \mu_{B} H/kT).$$
(2)

As shown in Fig. 3, the field dependence of the reduced magnetization of amorphous CoP (sam-



FIG. 3.  $\Delta M/M(0)$  for sample G: line a, H=15 kOe versus  $T^{3/2}$ ; line b, H=0.5 kOe versus  $T^{3/2}$ ; line c, both H=15 and H=0.5 kOe versus  $T^{3/2}G(H,T)$ .

ple G) is also described by the same factor, G(H, T). When taken together, the temperature and field behavior lead us to conclude that amorphous CoP demagnetizes by the thermal excitation of spin waves. This conclusion has a direct bearing on the analysis of the correspondingstates curve shown in Fig. 1. The difference between crystalline Co or Ni and amorphous CoPin the low-temperature regime does *not* result from a random molecular field, but originates in the effect of atomic disorder on the *collective excitations*.

Finally, it is interesting to note that those theories<sup>13-15</sup> that explicitly examine the behavior of the collective modes in random systems exhibit a common feature: The introduction of disorder into crystalline ferromagnets leads consistently to an increase in the density of states of the low-energy excitations. This feature correlates qualitatively with the relative ease with which spin waves are excited in the amorphous CoP alloys.

We are indebted to Professor R. Alben, Professor M. F. Thorpe, Professor D. Weaire, and Professor M. J. Zuckermann for helpful discussions, and to Professor R. Harris for his criti-

## cal reading of the manuscript.

\*Work supported in part by the National Research Council of Canada and the National Science Foundation.

<sup>1</sup>C. C. Tsuei, in *Amorphous Magnetism*, edited by H. O. Hooper and A. M. de Graaf (Plenum, New York, 1973), p. 299.

<sup>2</sup>G. S. Cargill, III, and R. W. Cochrane, in *Amorphous Magnetism*, edited by H. O. Hooper and A. M. de Graaf (Plenum, New York, 1973), p. 313.

 $^{3}$ G. S. Cargill, III, and R. W. Cochrane, in Proceedings of the Conference on Disordered Metallic Systems, Strasbourg, France, 1973 (to be published).

<sup>4</sup>G. S. Cargill, III, J. Appl. Phys. 41, 2248 (1970).

<sup>5</sup>J. L. Finney, Proc. Roy. Soc., Ser. A <u>319</u>, 497 (1970).

<sup>6</sup>D. E. Polk, Acta. Met. <u>20</u>, 485 (1972).

<sup>7</sup>J. F. Sadoc, J. Dixmier, and A. Guinier, J. Non-Cryst. Solids 12, 46 (1973).

<sup>8</sup>A. W. Simpson and D. R. Brambley, Phys. Status Solidi (b) 49, 685 (1972).

<sup>9</sup>C. C. Tsuei, G. Longworth, and S. C. H. Lin, Phys. Rev. <u>170</u>, 603 (1968).

<sup>10</sup>A. Sinha, J. Appl. Phys. 42, 338 (1971).

<sup>11</sup>K. Handrich, Phys. Status Solidi <u>32</u>, K55 (1969).

<sup>12</sup>S. Kobe, Phys. Status Solidi <u>41</u>, K13 (1970).

<sup>13</sup>C. G. Montgomery, J. I. Krugler, and R. M. Stubbs, Phys. Rev. Lett. 25, 669 (1970).

<sup>14</sup>R. A. Tahir-Kheli, Phys. Rev. B <u>6</u>, 2808, 2838 (1972).

<sup>15</sup>T. Oguchi, I. Ono, and T. Ishikawa, in Proceedings of the International Conference on Magnetism, Moscow, U.S.S.R., 1973 (to be published).

<sup>16</sup>A. H. Morrish, *The Physical Principles of Magnetism* (Wiley, New York, 1965).

<sup>17</sup>The applied field was limited to 15 kOe for these measurements because of small irreproducible fieldand temperature-dependent signals from the addenda.

<sup>18</sup>B. E. Argyle, S. H. Charap, and E. M. Pugh, Phys. Rev. <u>132</u>, 2051 (1963).

<sup>19</sup>The  $T^{3/2}$  magnetization coefficient for Co has been calculated from the dispersion coefficient measured by S. J. Pickart, H. A. Alperin, V. J. Minkiewicz, R. Nathans, G. Shirane, and O. Steinsvoll, Phys. Rev. <u>156</u>, 623 (1967).

<sup>20</sup>The low-energy spin-wave spectrum is usually described in terms of the wave-vector dispersion relation,  $E(q) = Dq^2$ . Such a formulation cannot be strictly applicable, except for very small q, because of the absence of translational symmetry for the amorphous structure.