

necessarily mean that the system must order antiferromagnetically (as is the case in the Heisenberg model).

Experimental data have recently been recorded<sup>13</sup> which show a general increase in  $T_c$  with increasing applied magnetic intensity  $H$ . These data cannot be interpreted in terms of a transition from a paramagnetic phase to a spin-flipped antiferromagnetic phase because of the small value of the magnetic dipole anisotropy energy, nor as simply due to free spins partially ordering in the applied field because  $H$  was not large enough to produce the needed entropy changes. If the phase transition is first order, we may use the magnetic Clausius-Clayperon equation

$$dT_c/dH = -\Delta M/\Delta S,$$

where  $\Delta S$  and  $\Delta M$  are respectively the discontinuities in the entropy and magnetization. Since  $\Delta S = S(\text{disordered}) - S(\text{ordered}) > 0$ ,  $\Delta M = M(\text{disordered}) - M(\text{ordered})$  must be opposite in sign to  $dT_c/dH$ . Thus,  $dT_c/dH > 0$  implies ferromagnetism! If the usual second-order ferromagnetic transition occurs, there are no singularities in the thermodynamic variables, but there is still a peak in the specific heat for small  $H$ , whose temperature increases with increasing  $H$ . Of course, we cannot rule out antiferromagnetism from these data for very low fields, but the data are too uncertain at such fields for further speculation.

\*Work supported in part by National Science Founda-

tion Grant No. DMR72-03282-A02.

<sup>1</sup>W. P. Kirk and E. D. Adams, Phys. Rev. Lett. **17**, 392 (1972); J. M. Dunson and J. M. Goodkind, Phys. Rev. Lett. **32**, 1343 (1974); W. P. Halperin, C. N. Archie, F. B. Rasmussen, R. A. Buhrman, and R. C. Richardson, Phys. Rev. Lett. **32**, 927 (1974).

<sup>2</sup>R. A. Guyer, R. C. Richardson, and L. I. Zane, Rev. Mod. Phys. **43**, 532 (1971); A. Landesman, Ann. Phys. (Paris) **8**, 53 (1974); S. B. Trickey, W. P. Kirk, and E. D. Adams, Rev. Mod. Phys. **44**, 668 (1972).

<sup>3</sup>A. Widom and J. B. Sokoloff, to be published.

<sup>4</sup>D. S. Greywall, Phys. Rev. B **11**, 4717 (1975).

<sup>5</sup>J. B. Sokoloff, Phys. Rev. B **4**, 232 (1971).

<sup>6</sup>J. B. Sokoloff, Phys. Rev. B **2**, 3707 (1970), and **3**, 3826 (1971).

<sup>7</sup>W. F. Brinkman and T. M. Rice, Phys. Rev. B **2**, 1324 (1970).

<sup>8</sup>Y. Nagaoka, Phys. Rev. **147**, 392 (1966).

<sup>9</sup>We have been assuming that the vacancies behave as fermions. This is strictly true only in the completely ferromagnetic state. Since the vacancies in the band tails are primarily confined to regions of parallel nuclear spin, however, it should be also correct to treat these vacancies as fermions. Furthermore, the fluctuation rate of the parallel-spin regions ( $\sim kT_c/\hbar$ ) is negligibly slow compared to the vacancy-hopping rate ( $t/\hbar$ ).

<sup>10</sup>I. M. Lifshitz, Adv. Phys. **13**, 483 (1969).

<sup>11</sup>As is the case of most mean-field free energies, our free energy is unstable (i.e., has the wrong convexity). If we transform from an  $m$  to a magnetic-field ensemble, however, thermal stability is recovered. See, for example, T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956), p. 167.

<sup>12</sup>P. B. Visscher, Phys. Rev. B **10**, 943 (1974).

<sup>13</sup>R. B. Kummer, E. D. Adams, W. P. Kirk, A. S. Greenberg, R. M. Mueller, C. V. Britton, and D. M. Lee, Phys. Rev. Lett. **34**, 517 (1975).

## Structural Manifestations in Amorphous Alloys: Resistance Minima\*

R. W. Cochrane, R. Harris, J. O. Ström-Olson, and M. J. Zuckermann

*Eaton Electronics Laboratory, McGill University, Montreal H3C 3G1, Quebec, Canada*

(Received 13 May 1975)

Logarithmic anomalies in the temperature-dependent resistivity of a series of amorphous alloys have been measured and shown to be nonmagnetic in origin. We associate these anomalies with the noncrystalline structure.

Much of the recent interest in amorphous solids has focused on finding properties which are a direct consequence of the noncrystalline structure. Most striking is the low-temperature linear specific heat observed in insulating glasses,<sup>1</sup> which has been explained<sup>2</sup> by the existence of a number of atomic configurations of equivalent energy separated by low energy barriers. In

amorphous metals, on the other hand, no common property has as yet been exclusively associated with the disordered structure, despite the qualitatively similar atomic arrangements.<sup>3</sup>

We report here the observation of resistance anomalies in four amorphous metal alloys of quite different composition produced by three different techniques in three different laborato-

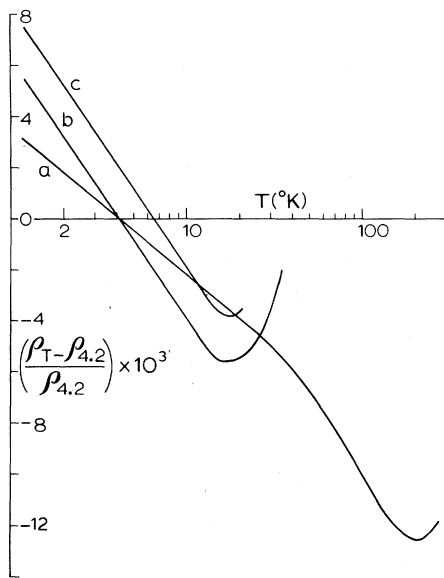


FIG. 1. Resistivity versus  $\ln T$  for (curve *a*) Metglas 2826A at  $H=0$  and  $H=45$  kOe; (curve *b*) NiP at  $H=0$ ; and (curve *c*) NiP at  $H=45$  kOe. For *b* and *c*, scale  $\times 10$ .

ries: Ni<sub>75</sub>P<sub>25</sub>, Co<sub>76</sub>P<sub>24</sub>, Co<sub>92</sub>Sm<sub>8</sub>, and Metglas 2826A (Fe<sub>32</sub>Ni<sub>36</sub>Cr<sub>14</sub>P<sub>12</sub>B<sub>6</sub>). The characteristic behavior is a resistance minimum with a logarithmically increasing resistivity below the minimum. Similar measurements have been reported by Lin,<sup>4</sup> Hasegawa and co-workers,<sup>5-7</sup> and Liang and Tsuei.<sup>8</sup> Although this behavior is also characteristic of the Kondo effect we shall show that in our alloys it cannot be caused by magnetic scattering; we believe that it is a manifestation of the disordered structure.

Figure 1 illustrates the temperature dependence of the resistivity for NiP and Metglas, plotted as  $[\rho(T) - \rho(4.2)] / \rho(4.2)$  against  $\ln T$ . The logarithmic temperature dependence is also evident for the other two alloys, although in CoP the minimum occurs at 7 K restricting the  $\ln T$

range to below 4 K. The resistivity for all alloys is of the order of  $10^{-4}$   $\Omega$  cm and, surprisingly, the slope of the  $\ln T$  behavior is the same for all alloys within a factor of 5, even though there are few similarities in their constituents.

That the magnetic behavior of the samples ranges from ferromagnetic with or without localized moments (CoP, CoSm, Metglas) to nonmagnetic (NiP) leads us to believe that the resistance anomaly cannot be magnetic in origin. The similarity in the magnitude of the  $\ln T$  term lends further support to this hypothesis. Nor is the effect consistent with small amounts of magnetic impurities such as Fe.<sup>9,10</sup> The nonmagnetic origin of the anomaly is confirmed by the behavior in a magnetic field, also illustrated in Fig. 1. In all alloys the *lnT dependence of the resistivity is totally unaltered by a field of 45 kOe*; indeed, the shape of the entire  $\rho$ - $T$  curve is unaffected, the whole being shifted according to whether the magnetoresistance is positive (NiP, CoP), negative (CoSm), or, in the case of Metglas, zero. Table I summarizes the results from all the alloys.

A resistivity varying as  $\ln T$  implies the existence of a low-energy degree of freedom to which the conduction electrons can couple. In Kondo alloys,<sup>11</sup> the degenerate states of the impurity spin provide the necessary degrees of freedom, but as explained above this mechanism cannot be dominant in the amorphous alloys. However, suitable degrees of freedom can arise from the random structure because of the lack of periodicity in the lattice potential. Although the lattice potential wells will have an *average* spacing  $r_0$ , given by the position of the first maximum in the radial distribution function, many of them will be corrugated on a scale of a fraction of  $r_0$  giving rise to an indeterminacy of position for the atom in each well.<sup>12</sup> We now show that it is possible for such configurations to lead to resis-

TABLE I. Sample and resistivity data.

Sample	$\rho(4.2 \text{ K})$ ( $\mu\Omega$ cm)	$T_{\text{min}}$ (K)	Ferromagnetic $T_c$ (K)	$10^3 \frac{\rho(45 \text{ kOe}) - \rho(0)}{\rho(0)} \Big _{4.2 \text{ K}}$	Logarithmic slope, $\rho_3^d$
Ni <sub>75</sub> P <sub>25</sub> <sup>a</sup>	105 $\pm$ 20	17	Nonmagnetic	+0.2	1.0 $\pm$ 0.04
Co <sub>76</sub> P <sub>24</sub> <sup>a</sup>	95	7	550 $\pm$ 30	+0.38	1.5
Co <sub>92</sub> Sm <sub>8</sub> <sup>b</sup>	70	22	>300	-3.9	1.4
Fe <sub>32</sub> Ni <sub>36</sub> Cr <sub>14</sub> P <sub>12</sub> B <sub>6</sub> <sup>c</sup> (Metglas 2826A)	110	210	250 $\pm$ 2	+0.02	5.8

<sup>a</sup>Electrodeposited from solution at 75°C.

<sup>b</sup><sup>c</sup>sputtered onto a room-temperature substrate.

<sup>c</sup>Rapidly quenched from the melt.

<sup>d</sup> $\rho_3 = (-1/\rho_0)(d\rho/d\ln T) \Big|_{T=1.1 \text{ K}} \times 10^3$ .

tance anomalies which are consistent with our data.

Following Anderson, Halpern, and Varma,<sup>2</sup> we consider a well with two minima separated by a distance  $x$  and a barrier  $V_0$ . For simplicity we take the minima to have equal energy so that the eigenstates of the system are the symmetric and antisymmetric tunneling states,  $|\pm\rangle$ , which are split by an energy  $2\Delta = \hbar\omega_0 e^{-\lambda}$ , where  $\hbar\omega_0$  is a zero-point energy<sup>2</sup> ( $\sim 10$  K) and  $\lambda = (MV_0/2\hbar^2)^{1/2}x$ . Because the relaxation time of the electron sea ( $\sim 10^{-13}$  sec) is much smaller than the tunneling time ( $\sim 10^{-10}$  sec) the electrons can distinguish between the environments provided by the two tunneling states. This allows us to label the electron wave functions as  $|k_\pm\rangle$ , where  $k$  is the wave vector and  $\pm$  refers to the tunneling states. For a resistance minimum to arise we shall require that the two electron states,  $|k_\pm\rangle$ , must be largely orthogonal, i.e.,  $\langle k_+ | k_- \rangle \sim 0$ . This sets a lower bound to  $x$  relating it to the degree of localization of the electron wave functions around the atom. If we assume that the electrons, being  $d$ -like, are well represented by Gaussian resonances at the atomic sites, then the degree of orthogonality can be estimated as  $\sim \exp(-4x^2/r_0^2)$  so that a value of  $x \gtrsim 0.3r_0$  would be acceptable.

The Hamiltonian describing the alloy is then

$$H = H_0 + H_1$$

where

$$H_0 = \sum_{\alpha=\pm} (\alpha\Delta) b_\alpha^\dagger b_\alpha + \sum_{k,\alpha=\pm} \epsilon_{k\alpha} a_{k\alpha}^\dagger a_{k\alpha} b_\alpha^\dagger b_\alpha \quad (1)$$

represents the unperturbed system and

$$H_1 = \sum_{\substack{kk' \\ \alpha\alpha'=\pm}} V_{kk'}^{\alpha\alpha'} a_{k\alpha}^\dagger a_{k'\alpha'} b_\alpha^\dagger b_{\alpha'} \quad (2)$$

describes the scattering of the electrons from the tunneling states.  $a^\dagger$ ,  $a$ ,  $b^\dagger$ , and  $b$  are creation and annihilation operators for the electrons and tunneling states, respectively. The diagonal part of  $H_1$  can be absorbed into  $H_0$ . The off-diagonal part contains two terms: The first, having matrix element  $V_c$ , involves electron scattering without change in tunneling state, and the second, having matrix element  $V_c e^{-\lambda}$ , involves a change in tunneling states. Defining pseudospin operators by  $b_\pm^\dagger b_\pm = \frac{1}{2} \pm I_z$  and  $b_\pm^\dagger b_\mp = I_\pm$  and retaining only those terms involving the operators  $I_z$ ,  $I_\pm$ ,

we obtain

$$H_{\text{scat}} = V_c \sum_{kk'} [(a_{k+}^\dagger a_{k'+} - a_{k-}^\dagger a_{k'-}) I_z + e^{-\lambda} (a_{k+}^\dagger a_{k'-} I_+ + a_{k-}^\dagger a_{k'+} I_-)]. \quad (3)$$

If the electron states  $|k_\pm\rangle$  are orthogonal, this term has precisely the form of an anisotropic exchange interaction which, as is well known, leads in third order to a resistivity varying as  $\ln T$ . The functional form of the resistivity for scattering from a single site is

$$\rho_3 = \frac{m}{\hbar e^2 N n} (NV_c)^3 e^{-2\lambda} \ln \left[ \left( \frac{kT}{D} \right)^2 + \left( \frac{\Delta}{D} \right)^2 \right], \quad (4)$$

where  $N$  is the density of electron states at the Fermi energy,  $n$  the number of electrons per unit volume, and  $D$  is the electron bandwidth.

The magnitude of the resistivity,  $10^{-4} \Omega \text{ cm}$ , gives  $NV_c \sim 1$ , where we use  $N \sim 1.0 (\text{eV atom})^{-1}$ , and  $n \sim 10^{22} \text{ cm}^{-3}$ . Summing over the allowed values of  $\lambda$ , the total contribution to the resistivity becomes

$$\rho_3^T \sim -10^{-4} f e^{-2\lambda} \ln(kT^2 + \Delta^2) \Omega \text{ cm}, \quad (5)$$

where  $f$  is the fraction of atoms with  $\lambda$  values in the appropriate range. The crucial negative sign comes from the *attractive* character of the Coulomb interaction. Equation (5) is in agreement with the experimental data if  $f e^{-2\lambda} \gtrsim 10^{-3}$  and if  $\Delta \lesssim 1$  K. We believe that these limits are consistent with the constraints mentioned earlier for  $f$  of order a few percent.<sup>13</sup>

In conclusion we re-emphasize that the resistance anomalies reported here are clearly non-magnetic in character. The model we have constructed incorporates the noncrystalline structure of the amorphous alloys in a direct way to account for this experimental requirement.

We wish to thank G. S. Cargill, III, Yale University; R. P. Allen, Battelle Northwest Laboratories; and G. R. Bretts, Allied Chemical Corporation, for supplying the samples, and to acknowledge helpful discussions with L. J. Sham and A. Zawadowski.

\*Work supported in part by the National Research Council of Canada and the Ministère de l'Éducation de Québec, subvention FCAC.

<sup>1</sup>R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971).

<sup>2</sup>P. W. Anderson, B. I. Halpern, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

- <sup>3</sup>G. S. Cargill, III, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1975), Vol. 30, p. 227.
- <sup>4</sup>S. C. H. Lin, *J. Appl. Phys.* **40**, 2173 (1969).
- <sup>5</sup>R. Hasegawa, *J. Phys. Chem. Solids* **32**, 2487 (1971).
- <sup>6</sup>R. Hasegawa and J. A. Demon, *Phys. Lett.* **42A**, 407 (1973).
- <sup>7</sup>R. Hasegawa and C. C. Tsuei, *Phys. Rev. B* **2**, 1631 (1970), and **3**, 214 (1971).
- <sup>8</sup>V. K. C. Liang and C. C. Tsuei, *Phys. Rev. B* **7**, 3215 (1973).
- <sup>9</sup>The susceptibility of the *NiP* was measured to be less than  $2 \times 10^{-7}$  emu/g at 1.3 K. This sets an upper limit of approximately 10 ppm to the Fe concentration assuming a Curie law for spin 1. Nevertheless the effect in *NiP* is comparable to that found in *Fe(PdSi)*<sub>99</sub> which has 1000 times as much iron.
- <sup>10</sup>A. C. Ehrlich and D. J. Gillespie [*Bull. Am. Phys. Soc.* **20**, 347 (1975)], report a resistivity minimum in amorphous *PdSi* which does not correlate with the Fe

impurity content.

- <sup>11</sup>J. Kondo, *Progr. Theor. Phys.* **32**, 37 (1964).
- <sup>12</sup>Corrugations on a scale close to  $r_0$  will involve relatively large energy barriers, of order the crystallization temperature (500 K), and will play a central role in the macroscopic diffusion and rearrangement which occurs during crystallization.
- <sup>13</sup>The extension of our simple model to include wells with minima at different energies will affect the functional form of our result. However, we argue that at low temperatures the value of  $f$  is essentially constant, and given by that fraction of the corrugated wells where the energy difference is less than the zero-point energy  $\hbar\omega_0$ . At higher temperatures,  $kT > \hbar\omega_0 \sim 10$  K, we might therefore expect to see additional terms of logarithmic character. These seem to be masked by the ordinary phonon scattering in the *NiP*, *CoP*, and *CoSm* alloys, but in the Metglas alloy (curve *a* of Fig. 1) there does seem to be some evidence for additional scattering at temperatures above  $\sim 30$  K.

## Experimental Evidence for a New Interpretation of Local-Moment Resonances in Metals\*

Saul Oseroff,<sup>†</sup> Bruce Gehman,<sup>‡</sup> and Sheldon Schultz  
*University of California, San Diego, La Jolla, California 92037*

and

Carlos Rettori<sup>§</sup>  
*University of California, Los Angeles, Los Angeles, California 90024*  
(Received 30 April 1975)

The transmission and two reflection spin-resonance signals for single-crystal *AgGd* are shown to have the same crystal-field parameter, and hence are attributable to an isolated local moment. This identification illustrates why *S*-state resonance data need re-examination. The ratio of the averages of  $J(k, k')$  appropriate to the exchange field and relaxation rate of the local moment is  $\approx 3$  which may be difficult to interpret within the framework of presently accepted models.

We believe the results reported here, in conjunction with the theoretical analysis of the following paper<sup>1</sup> (II), support the conclusion that electron-spin-resonance data for *S*-state local moments in metals need to be reexamined. To illustrate the nature of this reexamination we present our measurements for dilute *AgGd* alloys which we believe to be the most complete and precise set of such data yet taken for a local-moment-metal system.

The primary data consist of both reflection and transmission electron-spin-resonance (RESR and TESR) spectra, at 9.2 and 35 GHz, for single-crystal *AgGd* samples at cryogenic temperatures. The *Gd* concentrations ranged from 17 to 450 ppm and were determined in conjunction with resistivity-ratio, emission-spectrograph, and dc-suscep-

tibility measurements. We have also made TESR measurements on a single-crystal sample doped with Au, as well as RESR measurements on powder samples doped with Sb. The experimental procedures have been described elsewhere.<sup>2</sup>

Our work was motivated, in part, by a desire to resolve the following paradox. The observed  $g$  values corresponding to the reflection and transmission resonances in *AgGd* were known to be appreciably different, 2.09 versus 2.00, respectively. The depth of the paradox may be appreciated when one considers that this  $g$  difference corresponds to a separation of the lines by more than a full linewidth. How is it that the same sample can respond at two well-separated frequencies, and how is one to interpret these data so as to deduce the intrinsic properties of the local-