

- ⁵R. Jullien, M. T. Beal-Monod, and B. Coqblin, *Phys. Rev. B* **9**, 1441 (1974).
- ⁶M. B. Brodsky, *Phys. Rev. B* **9**, 1381 (1974).
- ⁷A. H. Thompson, K. R. Pisharody, and R. F. Koehler, Jr., *Phys. Rev. Lett.* **29**, 163 (1972).
- ⁸A. H. Thompson, F. R. Gamble, and C. R. Symon, *Mater. Res. Bull.* **10**, 915 (1975).
- ⁹D. A. Winn and B. C. H. Steele, in *The Electrochemical Society: Extended Abstracts. Spring Meeting, Toronto, Canada, 12-16 May 1975* (The Electrochemical Society, Princeton, N. J., 1975), Vol. 75-1, p. 51.
- ¹⁰J. A. Benda, *Phys. Rev. B* **10**, 1409 (1974).
- ¹¹F. R. Shepherd and P. M. Williams, *J. Phys. C: Solid State Phys.* **7**, 4416 (1974).
- ¹²H. W. Myron and A. J. Freeman, *Phys. Rev. B* **9**, 481 (1974).
- ¹³For example, see R. A. Smith, *Wave Mechanics of Crystalline Solids* (Chapman and Hall, Ltd., London, 1961).
- ¹⁴S. Takeuchi and H. Katsuda, *J. Jpn. Inst. Met.* **34**, 758 (1970).
- ¹⁵C. Herring, in *Magnetism: A Treatise on Modern Theory and Materials*, edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. 4, p. 36.
- ¹⁶M. H. Cohen and E. I. Blount, *Philos. Mag.* **5**, 115 (1960).
- ¹⁷For a tabulation of transitions, see A. H. Thompson, *Phys. Rev. Lett.* **34**, 520 (1975).
- ¹⁸F. Bloch, *Z. Phys.* **59**, 208 (1930).
- ¹⁹E. H. Sondheimer, *Proc. Phys. Soc., London, Sect. A* **65**, 561 (1952).
- ²⁰A. W. Overhauser, *Phys. Rev.* **167**, 691 (1968).
- ²¹P. M. Williams, G. S. Parry, and C. B. Scruby, *Philos. Mag.* **29**, 695 (1974).
- ²²J. A. Wilson, F. J. DiSalvo, and S. Mahajan, *Phys. Rev. Lett.* **32**, 882 (1974).
- ²³A. H. Thompson and B. G. Silbernagel, to be published.
- ²⁴P. M. Williams, private communication.

Resistivity and Mössbauer Measurements for Solid Xe-Fe Mixtures*

Z. Shanfield, P. A. Montano,† and P. H. Barrett

Department of Physics, University of California, Santa Barbara, California 93106

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Resistivity measurements of frozen mixtures of Xe and Fe versus concentration and temperature exhibit various conduction regions including a nonconducting-to-conducting transition at ~ 30 at. % Fe. Mössbauer-effect measurements reveal no changes in isomer shift or hyperfine magnetic field with concentration above ~ 14 at. % Fe. However, the change in shape of the Mössbauer spectra suggests that a transition from a paramagnetic relaxing phase to a magnetically ordered phase occurs at ~ 30 at. % Fe.

Since Mott¹ proposed the occurrence of metal-nonmetal transitions, a number of these transitions have been investigated.² Recently transitions have been observed in frozen mixtures of rare gases and metals.³⁻⁶ Sharp, discontinuous transitions of resistivity as a function of concentration have been reported for Ar-Na³ and Ar-Cu.⁴ Also a sharp transition was suggested by the optical measurements on Xe-Hg.⁵ By contrast, Kr-Rb and Xe-Cs systems⁶ did not show sudden changes in their optical properties, while resistivity measurements indicated gradual metal-nonmetal transitions.

We report a study of a system in which the metallic constituent is a magnetic transition metal. In this study we monitor the resistivity and ⁵⁷Fe Mössbauer-effect parameters of Xe-Fe as a function of iron concentration. A gradual transition from a nonconducting to a conducting phase was observed around 30 at. % Fe. Neither the Mössbauer isomer shift nor the hyperfine

field of ⁵⁷Fe (H_i) showed an observable change on passing through the transition.

Samples were prepared in a vacuum of better than 10^{-7} Torr by allowing Fe vapor and Xe gas to condense on the 7-K surface of either a sapphire or beryllium substrate. Iron was evaporated from an alumina crucible held in a tantalum heater that was temperature regulated to better than $\pm 2^\circ\text{C}$. By weighing the crucible before and after an evaporation, and by using the furnace efficiency (the ratio of Fe deposited on the substrate to Fe evaporated), the amount of Fe in the sample could be determined. The furnace efficiency was determined in a separate experiment by weighing the Fe deposited on a substrate held at room temperature. It was assumed that the sticking coefficient for Fe was the same at 7 K as at 300 K. From the amount of Fe deposited and from the attenuation of the 14.4-keV γ ray of ⁵⁷Co, the amount of Xe deposited was determined. The error in the amount of iron in

each sample was $\pm 3\%$ as a result of the uncertainty in the furnace efficiency. This was the main source of error in the concentration. The thickness of the sample was determined from the γ -ray attenuation. The final thicknesses of the samples were of the order of a micron. The linear attenuation coefficient is the product of the mass attenuation coefficient and the effective density.⁷ The effective density was estimated from the concentration. Errors produced by this estimate were within the experimental uncertainty of the resistance measurements.

The experimental arrangement and the details of the sample preparation have been reported earlier.⁸ Substrates were clamped to a copper cold finger suspended beneath a liquid-helium cryostat. For resistance measurements, a sapphire substrate was used to which a Au-0.07%-Fe versus Chromel-P thermocouple was attached. Resistance was measured using a two-probe parallel-electrode configuration. The temperature of the sample could be varied by a heater attached to the substrate. The resistance was monitored during the deposition; the resistivity was determined from a plot of conductivity versus thickness. Mössbauer-effect measurements were made on samples deposited on a Be substrate kept at 4.2 K.

In Fig. 1 the results of the resistivity measurements are plotted. Below 30 at.% Fe only a leakage resistance was measurable; therefore a lower limit of $10^7 \Omega \text{ cm}$ is given for the resistivity. Above this concentration the measured resistivity decreased to less than $1.6 \times 10^{-3} \Omega \text{ cm}$ (the lower limit of resistivity measurable with our two-probe system) for the 100-at.%-Fe sample. Published values for resistivity of amorphous Fe films are $\sim 150 \mu\Omega \text{ cm}$.⁹ For samples with concentrations greater than 30 at.% Fe, resistivities decreased with increasing temperature. For the 100-at.%-Fe sample, the change was irreversible up to the highest temperature measured, 100 K. For other concentrations there existed both a reversible and a small irreversible decrease. This later change is probably caused by matrix annealing. Near the transition (~ 32 at.% Fe) and near pure Fe, a temperature change from 7 to 40 K produced a reversible decrease in the resistivity of 2 or 3%. However, for the 77-at.%-Fe sample, the same temperature variation decreased the resistivity by 25%.

Previous studies⁴⁻⁶ of frozen mixtures of rare gases and metals have used percolation models

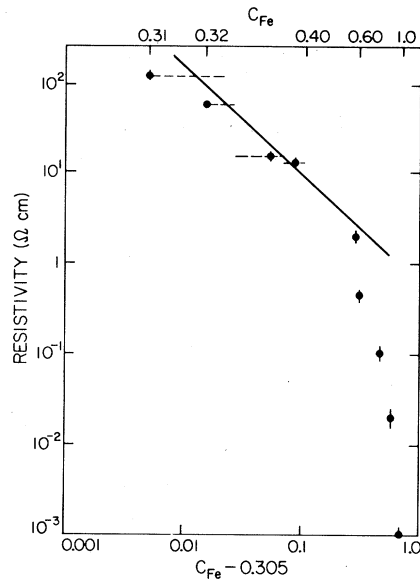


FIG. 1. Log-log plot of resistivity of Xe-Fe versus concentration of Fe. Note that the lower abscissa scale is logarithmic while the upper nonlogarithmic scale indicates the relative positions of the various concentrations.

to describe the resistivity transitions. With use of the suggestion of Scher and Zallen¹⁰ that the critical volume fraction of conducting material is 0.15 in three dimensions, and use of a hard-sphere model⁴ for the constituents, the critical percolation concentration has been calculated. For the hard-sphere radii, we used the Van der Waals radius of Xe (2.2 \AA) and the atomic radius of Fe (1.26 \AA).¹¹ For variation of the packing fraction between the value for liquid metals (0.45)¹² and the value for hard-sphere models (0.65),¹³ the calculated critical concentration varied between 65 and 54 at.% Fe; this was to be compared with the measured value of 30.5 ± 2.0 at.% Fe. This discrepancy could arise from either the oversimplification of the percolation hard-sphere model or the inappropriateness of the atomic radii used above.

Kirkpatrick has made Monte Carlo calculations¹⁴ for a bond-percolation problem in which resistors are randomly distributed on a simple cubic lattice. He found that the resistivity (ρ) versus concentration (c) had the functional form $\rho \propto (c - c_0)^{-\gamma}$, where c_0 is the critical percolation concentration, and $\gamma = 1.6$ in the critical region, while above this region the dependence was linear. Figure 1 is a log-log plot of resistivity versus $c - c_0$. The data can be fitted by the above

equation in the region between $c=0.3$ and 0.6 with $\gamma=1.2\pm 0.5$. In the region beyond $c=0.6$ a fit by $\gamma\sim 9$ or by an exponential function is possible. Between $c=0.3$ and 0.6 Kirkpatrick's model is appropriate; however, above $c=0.6$ this model fails to describe our results.

The theoretical models that have been applied by Mott² and Cohen and Jortner¹⁵ to other disordered materials will be used to explain the various functional dependences of resistivity upon concentration observed in Fig. 1. For the region near pure disordered Fe the electronic transport is characterized by propagation of electrons between scattering events in which the effective mean free path (L) is greater than the interatomic distance (a). A lower limit for the extent of this *propagation* regime¹⁵ can be obtained by using the nearly-free-electron formula for resistivity¹⁶ and the resistivity of amorphous Fe films⁹ to calculate L . Using the bulk Fe values¹⁶ of electron density, effective mass, and Fermi velocity, we found an L of order 100 \AA . Therefore, of the 4-order-of-magnitude variation of resistivity between $c=1$ and 0.6 only 2 orders can be accounted for by variation of scattering in the propagation regime. To extend this regime further requires a decrease in the effective electron density² caused by increasing disorder or dilution of the metallic constituent.¹⁶ When $L\sim a$ electronic transport is characterized by *diffusion*.² Between 80 and 30 at.% Fe fits of the resistivity versus inverse temperature by an exponential function gave energy barriers¹⁷ that increased with decreasing Fe concentration. However, between approximately 80 and 60 at.% Fe (possibly the diffusion regime), the change in the barrier was insufficient to account for the change of resistivity with concentration. Below 60 at.% Fe the data can be described by the model of Kirkpatrick¹⁴; therefore, we associate this region with a *percolation* regime and the transition at 30.5 ± 2.0 at.% Fe with a critical percolation probability. It should be pointed out that the conductivity just above the metal-nonmetal transition [$\sim 10^{-2} (\Omega \text{ cm})^{-1}$] is considerably lower than the "minimum metallic conductivity" [$200\text{--}500 (\Omega \text{ cm})^{-1}$] proposed by Mott.^{1,2} Below the transition, conduction probably occurs by means of a localized hopping mechanism.² At 7 K such a mechanism should allow very little conduction; therefore, it was not surprising that the conductivity was below our sensitivity.

The Mössbauer spectra for various concentrations are displayed in Fig. 2. The Mössbauer

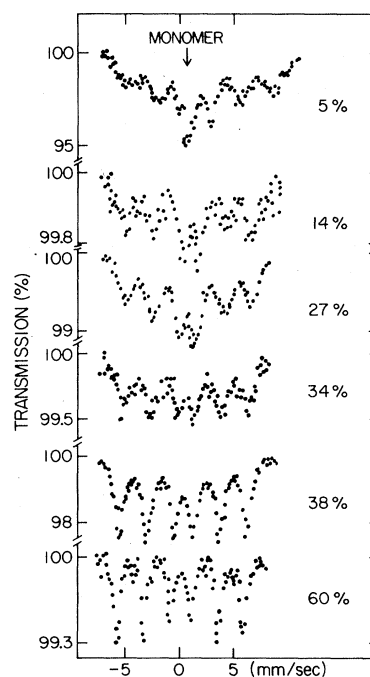


FIG. 2. Mössbauer-effect spectra of Xe-Fe samples at various concentrations of Fe.

spectra taken below 30 at.% Fe were typical of a paramagnetic system with slow spin relaxation time¹⁸ and/or inhomogeneous internal fields. The enhanced amplitude in the center of the spectra below 30 at.% Fe suggests that some of the Fe atoms are in clusters which have fast ($< 10^{-7}$ sec) electronic relaxation times. The spectrum at 34 at.% Fe was as expected for an ordered system in which a distribution of local environments has caused line broadening. As the concentration of Fe was raised, a decrease in disorder reduced the linewidths. At 60 at.% Fe the spectrum was similar to bulk Fe. There is no evidence of an abrupt change in the Mössbauer spectra between the conducting and nonconducting regions except for the change in shape of the Mössbauer spectra which suggests a transition from a paramagnetic relaxing phase to a magnetically ordered phase as discussed above.

The isomer shift (IS), which is proportional to the electron density at the nucleus, is a function of electronic configuration.¹⁹ The IS was obtained from the difference of the "center of gravity" of the spectrum and the zero of velocity. The zero of velocity is with reference to an Fe absorber at room temperature. H_i , which is also a function of electronic configuration, is the sum of orbital, dipolar, and core-polarization

contributions.²⁰ For Fe metal, H_i is predominantly produced by core polarization.²¹ From the spectra in Fig. 2 H_i was determined from the splitting of the two outermost lines of the spectrum.¹⁹ For concentrations above approximately 14 at.% Fe, the IS and H_i were independent of concentration, within the experimental uncertainty, and equal to that of bulk Fe metal at 4 K (IS equals 0.116 ± 0.003 mm/sec with respect to Fe metal at 300 K, and $H_i = 338 \pm 3$ kOe).²² Therefore, any change in electronic structure with concentration was undetectable using the Mössbauer effect. This was also true of the optical measurements of Phelps, Avei, and Flynn.⁶

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†Present address: Department of Physics, West Virginia University, Morgantown, W. Va. 26506.

¹N. F. Mott, Proc. Phys. Soc., London, Sec. A **62**, 416 (1949).

²N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, England, 1971).

³R. C. Cate, J. G. Wright, and N. E. Cusak, Phys. Lett. **32A**, 467 (1972).

⁴H. Endo, A. I. Eatah, J. G. Wright, and N. E. Cusak, J. Phys. Soc. Jpn. **34**, 666 (1972).

⁵B. Raz, A. Gedanken, U. Even, and J. Jortner, Phys. Rev. Lett. **28**, 1643 (1972).

⁶D. J. Phelps, R. Avei, and C. P. Flynn, Phys. Rev.

Lett. **34**, 23 (1975).

⁷J. H. Hubbel, *Photon Cross Sections, Attenuation Coefficients, and Energy Absorption Coefficients from 10 keV to 100 GeV*, U. S. National Bureau of Standards, National Standards Reference Data Series—29 (U.S. GPO, Washington, D.C., 1969).

⁸T. K. McNab and P. H. Barrett, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum, Oxford, England, 1971), Vol. 7.

⁹P. K. Leung and J. G. Wright, Philos. Mag. **30**, 995 (1974).

¹⁰H. Scher and R. Zallen, J. Chem. Phys. **53**, 3759 (1970).

¹¹R. C. Evers, *An Introduction to Crystal Chemistry* (Cambridge Univ. Press, Cambridge, England, 1966).

¹²N. W. Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966).

¹³G. D. Scott, Nature (London) **188**, 908 (1960).

¹⁴S. Kirkpatrick, Phys. Rev. Lett. **27**, 1722 (1971).

¹⁵M. H. Cohen and J. Jortner, Phys. Rev. Lett. **30**, 699 (1973).

¹⁶N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover, New York, 1958).

¹⁷C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1967).

¹⁸H. H. Wickman, M. P. Klein, and D. A. Shirley, Phys. Rev. **152**, 345 (1966).

¹⁹G. K. Wertheim, *Mössbauer Effect* (Academic, New York, 1964).

²⁰*Chemical Applications of Mössbauer Spectroscopy*, edited by V. I. Goldanskii and R. H. Herber (Academic, New York, 1968).

²¹M. B. Stearns, Phys. Rev. B **9**, 2311 (1974).

²²R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. **128**, 2207 (1962).

Solvable Model of a Spin-Glass

David Sherrington* and Scott Kirkpatrick

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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We consider an Ising model in which the spins are coupled by infinite-ranged random interactions independently distributed with a Gaussian probability density. Both "spin-glass" and ferromagnetic phases occur. The competition between the phases and the type of order present in each are studied.

Compelling experimental^{1,2} and theoretical³⁻⁵ evidence has accumulated in recent years suggesting that a new magnetic phase may occur in spatially random systems with competing exchange interactions. In this "spin-glass" phase, moments are frozen into equilibrium orientations, but there is no long-range order. Edwards and Anderson (EA) have demonstrated³ that such a phase occurs within a novel form of molecular-field theory, and they propose that spin correla-

tions between Gibbs-like replicas of the random system play the role of a spin-glass order parameter.

A closely related replica formalism has been employed in several recent papers^{6,7} applying renormalization-group methods to random magnetic systems. The possibility of an EA-type⁴ order parameter was not considered in that work, although some of the models studied⁷ appear likely to exhibit spin-glass phases.