

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

*Work supported in part by the National Science Foundation.

†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

(Received 16 October 1975)

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.

It is well known that molecular-field theory for a pure ferromagnet becomes exact in the thermodynamic limit for a constant infinite-ranged exchange interaction provided that the interaction is appropriately scaled with the number of spins in the system.⁸ In this Letter we define and solve the analogous infinite-ranged problem for a disordered system. We obtain a spin-glass solution characterized by the EA order parameter in the appropriate regime of temperature and the strength of the exchange fluctuations. A simple interpretation of this order parameter is given. The various thermodynamic quantities and the competition with ferromagnetic long-range order are explored in some detail.

We consider N Ising spins interacting through infinite-ranged exchange interactions which are independently distributed with a Gaussian proba-

bility density. The Hamiltonian is

$$\mathcal{H} = -\frac{1}{2} \sum_{i \neq j} J_{ij} S_i S_j, \quad S_i = \pm 1, \quad (1)$$

with the J_{ij} distributed according to

$$p(J_{ij}) = [(2\pi)^{1/2} J]^{-1} \exp[-(J_{ij} - J_0)^2 / 2J^2], \quad (2)$$

and J_0 and J scaled by

$$J_0 = \bar{J}_0 / N, \quad J = \bar{J} / N^{1/2}, \quad (3)$$

so that \bar{J}_0 and \bar{J} are both intensive. Following the usual procedure, we calculate the averaged free energy. (Averaging the free energy and not the partition function corresponds to treating a "quenched" rather than an "annealed" system.)

With use of the identity

$$\ln x = \lim_{n \rightarrow 0} (x^n - 1) / n, \quad (4)$$

the averaged free energy F may be expressed as

$$\begin{aligned} F &= -kT \lim_{n \rightarrow 0} n^{-1} \left\{ \int \prod_{(ij)} [p(J_{ij}) dJ_{ij}] \text{Tr}_n \exp \left(\sum_{\alpha=1, \dots, n} \sum_{i \neq j} J_{ij} S_i^\alpha S_j^\alpha / 2kT \right) - 1 \right\} \\ &= -kT \lim_{n \rightarrow 0} n^{-1} \left\{ \text{Tr}_n \exp \left(\sum_{i \neq j} \left[\sum_{\alpha} S_i^\alpha S_j^\alpha J_0 / 2kT + \sum_{\alpha, \beta} S_i^\alpha S_j^\alpha S_i^\beta S_j^\beta J^2 / 4(kT)^2 \right] \right) - 1 \right\}, \end{aligned} \quad (5)$$

where α and β label n dummy replicas. Reordering and dropping terms which vanish in the thermodynamic limit yields

$$F = -kT \lim_{n \rightarrow 0} n^{-1} \left\{ \exp[J^2 N^2 n / 4(kT)^2] \text{Tr}_n \exp \left[\sum_{(\alpha\beta)} \left(\sum_i S_i^\alpha S_i^\beta \right)^2 J^2 / 2(kT)^2 + \sum_{\alpha} \left(\sum_i S_i^\alpha \right)^2 J_0 / 2kT \right] - 1 \right\}, \quad (6)$$

where $(\alpha\beta)$ refers to combinations of α and β with $\alpha \neq \beta$. Using the identity

$$\exp(\lambda a^2) = (2\pi)^{-1/2} \int dx \exp[-x^2/2 + (2\lambda)^{1/2} ax], \quad (7)$$

we rewrite (6) as

$$\begin{aligned} F &= -kT \lim_{n \rightarrow 0} n^{-1} \left\{ \exp[\bar{J}^2 N n / 4(kT)^2] \int \left[\prod_{(\alpha\beta)} (N/2\pi)^{1/2} dy^{(\alpha\beta)} \right] \left[\prod_{\alpha} (N/2\pi)^{1/2} dx^{\alpha} \right] \right. \\ &\quad \times \exp \left[-N \sum_{(\alpha\beta)} (y^{(\alpha\beta)})^2 / 2 - N \sum_{\alpha} (x^{\alpha})^2 / 2 \right. \\ &\quad \left. \left. + N \ln \text{Tr} \exp \left((\bar{J}/kT) \sum_{(\alpha\beta)} y^{(\alpha\beta)} S^{\alpha} S^{\beta} + (\bar{J}_0/kT)^{1/2} \sum_{\alpha} x^{\alpha} S^{\alpha} \right) \right] - 1 \right\}, \end{aligned} \quad (8)$$

where the trace is now over n replicas at a single spin site.

It is assumed that the limit $n \rightarrow 0$ and the thermodynamic limit $N \rightarrow \infty$ can be interchanged. For integral $n \geq 2$, the integrals may be done by steepest descents. Since the replicas are indistinguishable, we consider only the extremum of the exponential for which all the $y^{(\alpha\beta)}$ are equal, as are all the x^{α} . We denote their values by y and x . This permits the replacement $\sum y^{(\alpha\beta)} S^{\alpha} S^{\beta} \rightarrow y[(\sum_{\alpha} S^{\alpha})^2 - n]$, and $(\sum_{\alpha} S^{\alpha})^2$ may be absorbed by the introduction of a random field.³ Continuation to arbitrary n , extraction of the terms linear in n as $n \rightarrow 0$, and the substitutions $y \rightarrow q(\bar{J}/kT)$ and $x \rightarrow m(\bar{J}_0/kT)^{1/2}$ then yield

$$F = NkT \left\{ -\bar{J}^2 (1-q)^2 / (2kT)^2 + \bar{J}_0 m^2 / 2kT - (2\pi)^{-1/2} \int dz \exp(-z^2/2) \ln [2 \cosh(\bar{J} q^{1/2} z / kT + \bar{J}_0 m / kT)] \right\}, \quad (9)$$

where q and m satisfy the simultaneous equations

$$q = 1 - (2\pi)^{-1/2} \int dz \exp(-z^2/2) \text{sech}^2[\bar{J} q^{1/2} / kT z + \bar{J}_0 m / kT], \quad (10a)$$

$$m = (2\pi)^{-1/2} \int dz \exp(-z^2/2) \tanh[(\bar{J} q^{1/2} / kT) z + \bar{J}_0 m / kT]. \quad (10b)$$

To show the physical significance of m and q we note that the thermal average of the spin at site i , $\langle S_i \rangle$, and its square may be written

$$\langle S_i \rangle = (\partial/\partial h) \ln \text{Tr} \exp(\sum_{j \neq i} J_{ij} S_i^\alpha S_j^\alpha / 2kT + h S_i^\alpha)_{h=0}, \quad (11a)$$

$$\langle S_i \rangle^2 = (\partial/\partial h') \ln \text{Tr} \exp[\sum_{j \neq i} J_{ij} (S_i^\alpha S_j^\alpha + S_i^\beta S_j^\beta) / 2kT + h' S_i^\alpha S_i^\beta]_{h'=0}, \quad (11b)$$

where $\alpha \neq \beta$ are dummy labels. Averaging over the J_{ij} distribution, which we denote by $\langle \rangle_J$, we see that $\langle \langle S_i \rangle \rangle_J$ and $\langle \langle S_i \rangle^2 \rangle_J$ are given by taking the $n \rightarrow 0$ limits respectively of $\langle S_i^\alpha \rangle$ and $\langle S_i^\alpha \times S_i^\beta \rangle_{\alpha \neq \beta}$ evaluated for a system characterized by the J -averaged n -ensemble partition function. This result is valid for finite-ranged interactions as well as infinite-ranged ones. Thus⁹

$$m \equiv \langle \langle S_i \rangle \rangle_J, \quad (12a)$$

$$q \equiv \langle \langle S_i \rangle^2 \rangle_J, \quad (12b)$$

independent of i . A nonzero q indicates magnetic order, while nonzero m (in addition to q) indicates that that order is ferromagnetic. When $m = 0$ but q is nonzero, we shall call the state a "spin-glass."

Equations (10) indicate that magnetic order sets in as kT is reduced below the greater of \tilde{J}_0 or \tilde{J} . If $\tilde{J}_0 > \tilde{J}$, the phase that is reached is ferromagnetic, but when the converse is true, spin-glass order ensues, and m remains zero for $kT < \tilde{J}$. The full phase diagram is plotted in Fig. 1, in terms of the dimensionless combinations \tilde{J}_0/\tilde{J} and kT/\tilde{J} , and may easily be rescaled to describe models in which \tilde{J}_0 and \tilde{J} are known functions of external parameters (see, e.g., Ref. 4).

For $\tilde{J}_0/\tilde{J} \gg 1$ the effects of fluctuations are weak, and one can show from (10a) and (10b) that $q \sim m^2$, in accord with the physical interpretation (12b) of q as the square of the modulus of the frozen mo-

ment per site. The zero-temperature magnetization is diminished by weak fluctuations as

$$m \sim 1 - (2/\pi)^{1/2} (\tilde{J}/\tilde{J}_0) \exp(-\tilde{J}_0^2/2\tilde{J}^2), \quad (13a)$$

and vanishes continuously at the spin-glass phase boundary as

$$m \sim (18\pi)^{1/4} (\tilde{J}_0/\tilde{J})^2 [(2/\pi)^{1/2} - \tilde{J}/\tilde{J}_0]^{1/2}. \quad (13b)$$

Values of $m(T)$ and $q^{1/2}$ obtained by numerical solution of (10a) and (10b) are plotted in Fig. 2 for various values of \tilde{J}_0/\tilde{J} . We note that the effect of fluctuations is strongest at low temperatures, causing the decrease in the magnetization as $T \rightarrow 0$ in Fig. 2, and a line of second-order transitions from ferromagnet to spin-glass in the phase diagram of Fig. 1.

The frozen moment, $q^{1/2}(T)$, as is shown in Fig. 2 and as can be derived from (10a) and (10b), is proportional to $(T_c - T)^{1/2}$ just below T_c , tends to unity as $T \rightarrow 0$, and is always greater than $m(T)$ at the same temperature. The linear low-temperature dependence of q and $q^{1/2}$,

$$1 - q(T) \sim (2/\pi)^{1/2} (kT/\tilde{J}) \exp(-\tilde{J}_0^2 m^2 / 2\tilde{J}^2), \quad (14)$$

as $T \rightarrow 0$, contrasts with that of $m(T)$ in a uniform Ising magnet, for which all temperature derivatives vanish at $T = 0$, since excitations from the ferromagnetic ground state require a

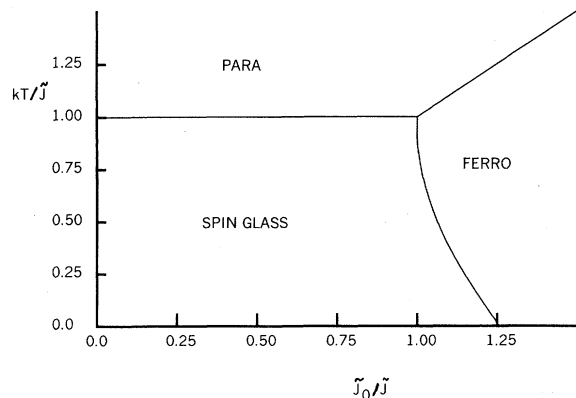


FIG. 1. Phase diagram of spin-glass ferromagnet.

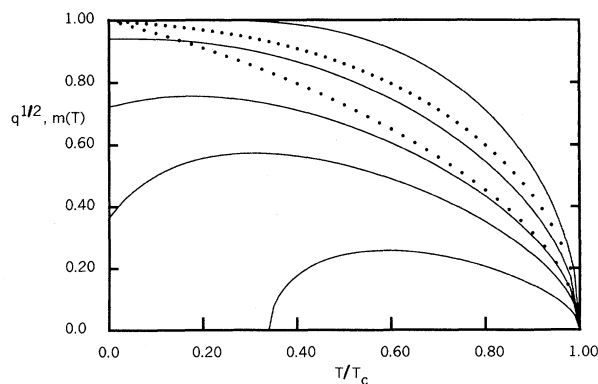


FIG. 2. Solid lines denote $m(T)$ for ratios \tilde{J}_0/\tilde{J} of (top to bottom) ∞ , 2.0, 1.5, 1.3, and 1.1. Dotted lines show $q^{1/2}(T)$ for $\tilde{J}_0/\tilde{J} = 2.0$ (upper line) and 0.0 (lower line).

finite energy.

The differential susceptibility, χ , may be obtained by repeating the steps leading to (9) and (10) with an external field term, $\sum_i HS_i$, in the Hamiltonian (1). This simply adds an extra contribution, H/kT , to the arguments of sech and tanh in (10a) and (10b). Differentiating (10b) with respect to H , and taking the limit $\hbar \rightarrow 0$, we then obtain

$$\begin{aligned}\chi(T) &= [1 - q(T)] / \{kT - \tilde{J}_0[1 - q(T)]\} \\ &= \chi^{(0)} / (1 - \tilde{J}_0 \chi^{(0)}),\end{aligned}\quad (15)$$

where $\chi^{(0)}$ is the result for $\tilde{J}_0 = 0$. Above the ordering temperature, where $q = 0$, this is just a Curie-Weiss law. In the spin-glass phase, the fluctuations decrease χ , while \tilde{J}_0 enhances it. Two examples are plotted in Fig. 3. The dotted lines in Fig. 3 show the effect of a finite field, $H = 0.1\tilde{J}$, on the differential susceptibility in each case.

From (9), we obtain the internal energy, U :

$$U = -N[m^2\tilde{J}_0/2 + \tilde{J}^2(1 - q^2)/2kT]. \quad (16)$$

In the spin-glass phase the leading term in the specific heat at low temperatures is

$$C \sim Nk(kT/\tilde{J})(2/\pi)^{1/2}[(\pi^2/12) - 1/2\pi]. \quad (17)$$

At the spin-glass ordering temperature C has a cusp. For all \tilde{J}_0 , C equals $Nk\tilde{J}^2/2(kT)^2$ above the ordering temperature,¹⁰ in contrast to the corresponding pure systems for which it vanishes. The linear temperature dependences seen in C , m , and $q^{1/2}$ suggest that the system possesses excitations from the ground state whose density remains finite down to zero energy. The entropy S equals $Nk[\ln 2 - \tilde{J}^2/(2kT)^2]$ above the spin-glass ordering temperature, but goes to a negative limit, $-Nk/2\pi$, at $T = 0$. We speculate that this unphysical behavior has its origin in the interchange of limits $N \rightarrow \infty$ and $n \rightarrow 0$, but that the consequences are confined to low temperatures.

When an Ising system described by (1) and (2) with nearest-neighbor interactions is treated with mean-field theory (of the EA type), equations identical to (10) are obtained, with $z\tilde{J}_0$ and $z^{1/2}\tilde{J}$ replacing \tilde{J}_0 and \tilde{J} , where z is the average number of neighbors.¹¹ For interactions which are on the average antiferromagnetic or which include second-neighbor terms, analogous equations result in which m is replaced by the appropriate sublattice magnetization.

For the finite-ranged interactions occurring in real systems, the results presented here have at

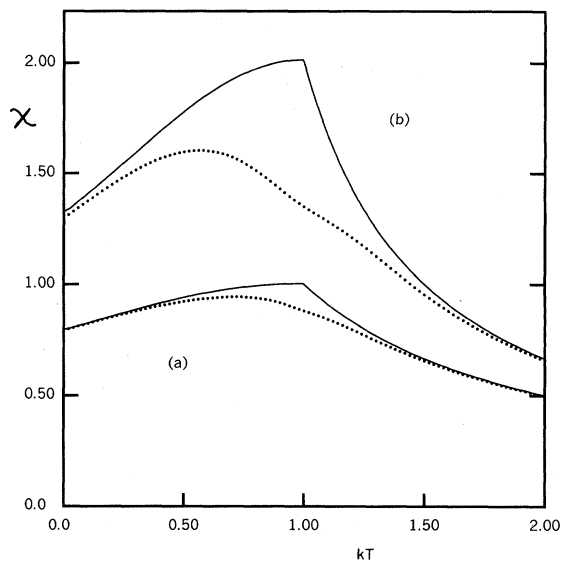


FIG. 3. Differential susceptibility without external field (solid lines) and with a field $H = 0.1\tilde{J}$ (dotted lines) for $\tilde{J}_0/\tilde{J} = 0$, curves *a*, and $\tilde{J}_0/\tilde{J} = 0.5$, curves *b*.

best mean-field significance, and thus cannot treat critical phenomena correctly. However, it is evident that any more sophisticated treatment of critical properties in the presence of random competing exchange interactions should allow for the possibility of order parameters $\langle S_i \rangle^n$, with $n > 1$, such as q discussed above.

*On sabbatical leave from Department of Physics, Imperial College, London SW7 2BZ, England.

¹J. A. Mydosh, in *Magnetism and Magnetic Materials*—1974, edited by C. D. Graham, Jr., G. H. Lander, and J. J. Rhyne, AIP Conference Proceedings No. 24 (American Institute of Physics, New York, 1975), p. 131.

²D. E. Murnick, A. T. Fiory, and W. J. Kossler, to be published; J. M. D. Coey and R. W. Readman, *Nature* (London) **246**, 476 (1973).

³S. F. Edwards and P. W. Anderson, *J. Phys. F: Met. Phys.* **5**, 965 (1975).

⁴D. Sherrington and B. W. Southern, *J. Phys. F: Met. Phys.* **5**, L49 (1975).

⁵K. H. Fischer, *Phys. Rev. Lett.* **34**, 1438 (1975).

⁶V. J. Emery, *Phys. Rev. B* **11**, 239 (1975); G. Grinstein, Ph.D. thesis, Harvard University, 1974 (unpublished); G. Grinstein and A. H. Luther, to be published.

⁷A. Aharony, *Phys. Rev. Lett.* **34**, 590 (1975).

⁸See, e.g., H. E. Stanley, *Phase Transitions and Critical Phenomena* (Oxford Univ. Press, New York, 1971) p. 91.

⁹The identification (12b) of q has also been pointed out by Fischer in Ref. 5.

¹⁰This result can also be obtained from high-temperature expansions.

¹¹R. Harris and D. Zobin (private communication) have

investigated analogous mean-field equations for the Heisenberg spin-glass model of Ref. 4. They find a phase diagram similar to Fig. 1.

Electronic Structure of Polymeric Sulfur Nitride, $(\text{SN})_x$, from X-Ray-Photoelectron Spectroscopy

Lothar Ley

Max-Planck-Institut für Festkörperforschung, Stuttgart, Federal Republic of Germany

(Received 14 July 1975)

An overview of the valence-band region of $(\text{SN})_x$ by means of photoelectron spectroscopy is presented. The spectrum gives, in general, an excellent account of the density of occupied states compared with band-structure calculations. Deviations between theory and experiment in the region of the conduction band are taken as strong evidence for interchain coupling. The interchain matrix element is estimated to be 0.6 times the value of the intrachain matrix element. The consequences of this result are discussed.

Polysulfur nitride, $(\text{SN})_x$, is a quasi one-dimensional inorganic polymer with a metallic ground state.¹ It maintains in contrast to other one-dimensional systems such as $\text{K}_2[\text{Pt}(\text{CN})_4]\text{Cl}_{0.3} \cdot 3\text{H}_2\text{O}$ and tetrathiafulvalene-tetracyanoquinodimethane its metallic conductivity down to very low temperatures² and becomes even superconducting at $T_c \approx 0.26^\circ\text{K}$.³ Experimental information about the electronic structure of this important new material is as yet scarce and—with the exception of one optical absorption measurement⁴—limited to effective masses of the conduction electrons and the density of states at the Fermi energy.²

I report in this Letter the first overall density of occupied states of $(\text{SN})_x$ as measured by x-ray-photoelectron spectroscopy (XPS). The result indicates appreciable interaction of electrons on neighboring chains.

Samples of $(\text{SN})_x$ were prepared following the method developed by Douillard⁵ as films on glass and fused silica substrates.⁶ The films have the characteristic brassy luster and showed good conductivity.

The XPS spectra with a resolution of 0.6 eV were taken in a Hewlett-Packard electron spectrometer utilizing monochromatized x rays ($\text{Al } K\alpha$, 1486 eV). Initial oxygen- and carbon-containing surface contaminations could almost completely be removed by wiping the film surface several times in a dry nitrogen atmosphere just prior to insertion of the sample into the spectrometer vacuum of 1×10^{-9} Torr. No signal from any contamination apart from 3% carbon could be detected after this procedure.⁷

In spite of an average film thickness of several thousand angstroms the films were not found to be completely opaque: The spectrum showed some emission from the substrate.⁸ This emission could easily be corrected for, by removing the $(\text{SN})_x$ film and running a spectrum of the glass substrate alone. Position and intensity of strong core levels common to both spectra allowed a very accurate correction of the original spectra.

The valence-band region of the photoelectron spectrum extending from the Fermi energy, E_F , to 30 eV below E_F is shown in the upper part of Fig. 1. The dots represent the raw data and the continuous line the spectrum corrected for the contribution of the substrate. It is apparent that the corrections are insignificant for most of the spectrum except for a region close to the bottom of the band. Corrected spectra, $I(E)$, identical to the one shown in Fig. 1 were obtained for three different samples with varying substrate contributions. Energies are referred to the Fermi level (E_F) as determined from an Au mask in electrical contact with the film surface.

Five main pieces of structure can be distinguished within the total bandwidth of 24.4 ± 0.7 eV: four peaks labeled 1 to 4 in Fig. 1 centered at 21.0, 15.2, 7.4, and 3.6 eV, respectively, and a shoulder ("5") at 0.7 eV below E_F . The density of states at E_F is small, but finite, thus reaffirming the metallic character of $(\text{SN})_x$.

These features are in excellent agreement with those in the density of states, $N(E)$, calculated by Parry and Thomas(PT),⁹ as shown in Fig. 1. The agreement is further emphasized if the observed lifetime broadening in $N(E)$ is included