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Magnetic properties of poly(metal phosphinates): The effects of structural disorder on one-dimensional antiferromagnetic chains

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The magnetic properties of several materials from the class poly(metal phosphinates) have been measured. In particular ESR spectra and the temperature dependence of the static susceptibility of three poly (chromium phosphinates) imply that these polymers comprise a class of one-dimensional antiferromagnetic chains with $J/k \sim 4$ K and with a varying degree of crystallinity. Structural disorder is found to limit the range of spin correlations and, in the extreme case, prohibits extended short-range order. The data are analyzed in terms of a model of chains of constant exchange but finite length. Comparison is made with an alternative model of infinite chains with Heisenberg exchange J varying randomly about a mean. The width of the distribution of J provides a direct measure of the disorder in each system.

I. INTRODUCTION

The poly(metal phosphinates)[1-4] represent an interesting series of inorganic coordination polymers whose solid-state properties have, up to now, been almost completely ignored. They are versatile materials capable of a variety of structures, crystalline modifications, and physical properties. The polymeric nature of these compounds comes from the ability of the phosphinate anions [see Fig. 1(a)] to bridge between metal centers. The structures and properties of these materials depend on the substituents R, R', etc., the type and oxidation state of the metal species, and the nature of any other ligands which may be present in the system.

Our present interest arises since the metal ion can be of a transition series and therefore a magnetic site in the polymer chain. Since magnetic susceptibility measurements show that the spins are, in general, antiferromagnetically coupled, there is a possibility of varying the strength of this exchange interaction by substituting different R groups in the phosphinate ($-\mathrm{OP}RR'\mathrm{O}-$) bridges.

In addition, the arrangement of the chains themselves can be varied by appropriate choice of metal ion, combination of R groups, and method of preparation. Some materials have separate chains, while others are more or less cross linked. Disorder may be introduced either in the fabric of the chain itself or in its relationship with other chains. Thus, we have the possibility of a magnetic system which is both one dimensional and (in an appropriate sense) amorphous.

The paper is arranged as follows: Sec. II summarizes the chemistry and structure of the polymetal-phosphinates; Sec. III deals with the magnetic properties, focussing primarily on three chromium-based polymers with different degrees of structural disorder; Sec. IV discusses the magnetic data and its correlation with structural disorder.

II. MATERIALS PREPARATION AND CHARACTERIZATION

Details of the chemical preparation of Ni, Co, Mn, Cu, and Cr phosphinates have been given elsewhere.[5] These references contain the main features of the ir spectra. The visible spectra show broad absorption band characteristic of the appropriate metal ion in a moderately strong ligand field (see, for example, Ref. 2).

In this communication, we focus primarily on three chromium-phosphinate polymers which were chosen for their close approximation to one-dimensional behavior and which are, respectively, amorphous (sample A), crystalline (sample C), and intermediate (B). Sample A is poly[hydroxychromium (III) *bis*-methylphenyl-phosphinate], $[\mathrm{Cr(OH)(O_2PCH_3C_6H_5)_2}]_n$,[2] n having an average value of 10^3 and a minimum value of 30. The structure is shown in Fig. 1(b). This material is a powder, totally amorphous with respect to x rays, which displays minimal optical birefringence. Materials B and C nominally have the same formula[3,4] $[\mathrm{Cr(O_2PCH_3C_6H_5)_2(O_2PC_8H_{17})}]_n$ [see Fig. 1(c)]. Viscosity data indicate that B and C have chain lengths at least an order of magnitude greater than A. Both form films, but B is brittle [tensile strength 3000–3500 psi, elongation (3–6)%],

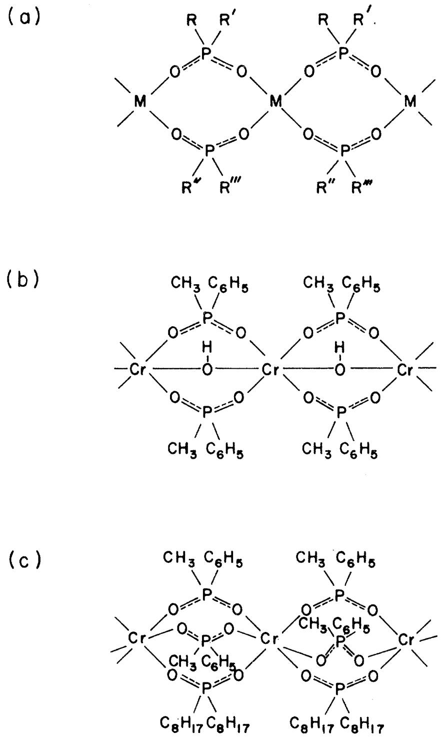

FIG. 1. (a) General structure of poly(metal phosphinates). R, R', R'', R''' are alkyl groups or a phenyl group and may be the same or different. M is a metal, the oxidation state of which determines the number of phosphinate bridges. (b) Most probable bridging structure for sample A (nomenclature is given in the text). (c) Stoichiometric structure of samples B and C.

whereas C is flexible [2000–3000 psi, (17–25)%].[4] Moreover, C is highly birefringent, indicating crystallinity on a scale of thousands of angstroms; B shows slight optical activity. Direct visual comparison of the three samples between crossed polarizers indicates birefringence $C \gg B \gg A$. X-ray patterns of both B and C show diffuse scattering; however, C shows several relatively sharp Bragg peaks, indicating a higher degree of crystallinity. We interpret the diffuse scattering as indicating a disordered arrangement of the $-OP(CH_3)(C_6H_5)O-$ and $-OP(C_8H_{17})_2O-$ bridging groups in the chains, as well as lateral chain-chain displacements. However, both the optical properties and the x-ray studies indicate that, on the average, the chains of C are more regularly aligned, and the flexibility leads to the conclusion that the plasticizing octyl groups are distributed more evenly.[4] In addition, the solubility of the films indicates that there are few cross links and that therefore they are linear polymer chains.

III. MAGNETIC PROPERTIES

The static susceptibility of the samples was measured as a function of temperature between 4 and 300 K using a Faraday balance.[6] The g values, linewidths, and line shapes were measured at 10 and 30 GHz using conventional EPR spectrometers.

The static susceptibility was corrected for core diamagnetism using Pascal's constants.[7] The resulting inverse susceptibility (χ_p^{-1}) is plotted as a function of temperature [Fig. 2(a)] for some typical Co- and Ni-based materials. The high-temperature data for these and several other materials were fitted by a nonlinear least-squares procedure[8] to the form

$$\chi_p = C/(T+\Theta) + \chi_{VV}^{exp}, \tag{1}$$

where $C = g^2 \mu_B^2 S(S+1) N_A / 3k$, Θ is the Curie-Weiss temperature (defined here as positive), and χ_{VV}^{exp} is the temperature-independent Van Vleck contribution to the susceptibility. C, Θ, and χ_{VV}^{exp} were treated as fitting parameters. The results are quoted in Table I.

We note that the three-parameter fit is not unique. For example, in the mean-field approximation, $\Theta = 2zJS(S+1)/3k$ (where z is the number of nearest neighbors, equaling 2 in the case of one dimension), and J may depend in some way on T. Therefore we expect our fit to give only approximate values of the microscopic parameters.[9]

From C is calculated the effective moment per spin $p = g\sqrt{S(S+1)}$. Assuming a value for S on the basis of the number of d electrons, we obtain g (static). This can be compared to the result obtained directly from ESR measurements, which is also given in Table I. In the cases where the ESR spectra have been observed, the values are in excellent agreement.

We omit discussion of the low-temperature data of these materials since they are not sufficiently well characterized at the moment. Note, however, that the behavior is qualitatively similar to that of the three chromium materials [Fig. 2(b)].

In the high-temperature region, samples A, B, and C have the same behavior, that of a paramagnet with antiferromagnetic exchange interaction. At temperatures below 20 K, there is variation; sample A has an inverse susceptibility which appears to be going to zero at 0 K (i.e., the susceptibility diverges).[10] Sample C has a susceptibility with a broad maximum at 7 K, indicative of increasing short-range order in one dimension. Sample B falls between these two; it does not diverge, nor does it show a minimum in χ_p^{-1} (although the curvature is concave upwards).

The high-temperature slopes of the χ_p^{-1} vs T

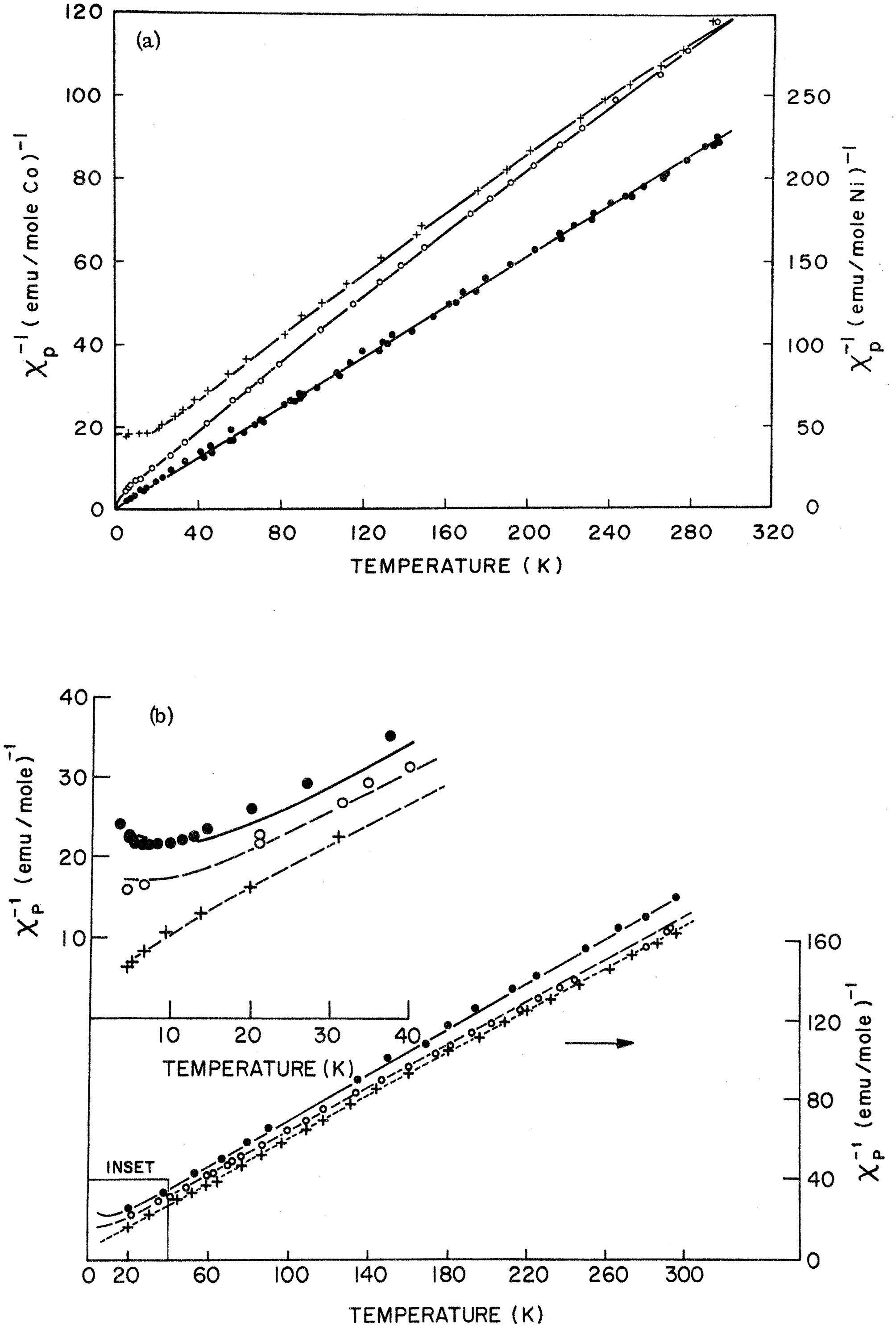

FIG. 2. Inverse susceptibility vs temperature. (a) Poly(nickel dioctylphosphinate) (●) (i.e., M=Ni, $R=R'=R''=R'''=C_8H_{17}$), poly(cobalt di-n-butylphosphinate) (+) (i.e., M=Co, $R=R'=R''=R'''=CH_2CH_2CH_2CH_3$), and poly(cobalt di-$t$-butylphosphinate) (●) [i.e., M=Co, $R=R'=R''=R'''=C(CH_3)_3$]. Ordinate for Co materials is on the left-hand side, for Ni on the right-hand side. Lines are merely a guide for the eye. (b) Samples A (+), B(○), and C(●) (see text); curves are generated from Eq. (2) using the values of the parameters in Table II.

TABLE I. Representative data on several samples of nickel, cobalt, manganese, and copper poly(metal phosphinates).

Metal	Phosphinate bridging groups	Spin S	C (emu K/mole)	Θ (K)	χ_{VV}^{exp} (10^{-3} emu/mole)	Moment p (μ_B)	g (static)	g (ESR)	Linewidth (gauss)
Nickel (II)	*bis*-dioctyl	1	1.37 ± 0.07	0	0 ± 0.3	3.31 ± 0.08	2.35 ± 0.06	Not observed	
	bis-diphenyl	1	1.47 ± 0.07	15.8 ± 2.2	0 ± 0.3	3.43 ± 0.08	2.42 ± 0.06	Not observed	
Cobalt (II)	*bis*-dioctyl	$\frac{3}{2}$	2.69 ± 0.14	19.1 ± 2.6	0.4 ± 0.6	4.64 ± 0.12	2.40 ± 0.06	Not observed	
	bis-diphenyl	$\frac{3}{2}$	2.19 ± 0.06	5.9 ± 1.4	0.7 ± 0.3	4.18 ± 0.06	2.16 ± 0.03	Not observed	
	bis-(methyl phenyl)	$\frac{3}{2}$	2.45 ± 0.07	7.2 ± 1.3	1.0 ± 0.4	4.43 ± 0.07	2.28 ± 0.03	Not observed	
	bis-di-*t*-butyl	$\frac{3}{2}$	2.27 ± 0.04	3.8 ± 0.7	1.0 ± 0.2	4.27 ± 0.03	2.20 ± 0.02	Not observed	
	bis-di-*n*-butyl	$\frac{3}{2}$	2.38 ± 0.06	25.0 ± 1.4	1.0 ± 0.2	4.36 ± 0.05	2.25 ± 0.03	Not observed	
Manganese (II)	*bis*-dioctyl	$\frac{5}{2}$	3.61 ± 0.06	0.8 ± 0.8	2.2 ± 0.3	5.38 ± 0.06	1.82 ± 0.04	2.00 ± 0.01	810
	bis-di-*t*-butyl	$\frac{5}{2}$	3.90 ± 0.12	9.3 ± 1.7	1.0 ± 0.5	5.58 ± 0.08	1.89 ± 0.04	2.00 ± 0.01	135 (30 GHz) 170 (10 GHz)
Copper (II)	*bis*-diphenyl	$\frac{1}{2}$	0.48 ± 0.04	0	0 ± 0.1	1.96 ± 0.08	2.26 ± 0.09	$g_{\parallel}=2.37$ $g_{\perp}=2.07$ $g_{\mathrm{av}}=2.17$	Multiline spectrum

curves of all three samples are consistent with spin $S=\frac{3}{2}$, which is expected for Cr^{3+} (d^3 configuration) in sixfold octahedral coordination, ground term $^4A_{2g}$.[11] The temperature dependence above about 30 K does not follow precisely a Curie-Weiss law. However, the deviation can be attributed to temperature-independent (Van Vleck) paramagnetism $\chi_{\mathrm{VV}}=8N_A\mu_B^2/10Dq$, where N_A is Avogadro's number, μ_B is the Bohr magneton ($N_A\mu_B^2=0.261$ cm^{-1}/mole), and $10Dq$ is the ligand field splitting ($^4A_{2g}-{}^4T_{2g}$), which can be found from the absorption band in the visible spectrum at 15 000 cm^{-1}. Using this crystal-field splitting, we estimate the value $\chi_{\mathrm{VV}}^{\mathrm{calc}}=0.14\times10^{-3}$ emu/mole. The susceptibility was fit in the form of Eq. (1) for the parameters C, Θ, $\chi_{\mathrm{VV}}^{\mathrm{exp}}$. Their values, together with the effective moment $p=g\sqrt{S(S+1)}\,\mu_B$ and the deduced splitting factor g, are given in Table II.

The g values have also been measured by electron paramagnetic resonance where the spectrum is found to consist of a single broad Lorentzian line. The results (see Table II) are in excellent agreement with the static susceptibility data. For Cr^{3+} in a sixfold-coordination octahedral ligand field, we expect a g shift from the free-spin value 2.002 of $\Delta g=-4\lambda k^2/10Dq$, where λ is the spin-orbit coupling parameter in the L-S representation, and k is the covalency correction factor.[11] Setting $k=1$ and using the free-ion value $\lambda=91$ cm^{-1}, we obtain $\Delta g=-0.024$, in excellent agreement with experiment. This value of Δg is too small to use in a meaningful re-evaluation of k.

IV. DISCUSSION

At low temperature, the susceptibility deviates from the Curie-Weiss form as a result of magnetic short-range order limited by the structural disorder. Fisher[12] has given an exact solution for the susceptibility of a chain of classical ($S=\infty$) spins coupled according to Heisenberg exchange of strength J. His Eq. (3.10) contains explicitly the number of spins in the chain, $N+1$. We modify this equation for finite spin after the method of Wagner and Friedberg[13] to obtain the molar susceptibility of a sample consisting of chains of average number of spins $N+1$,

$$\chi_{\mathrm{Fisher}}=\frac{g^2\mu_B^2S(S+1)N_A}{3kT}\left(\frac{N+1}{N}\,\frac{1-u}{1+u}+\frac{2u[1-(-u)^{N+1}]}{N(1+u)^2}\right), \tag{2}$$

where $u=-\coth[2JS(S+1)/kT]+4T/2JS(S+1)$ is the temperature parameter. The susceptibilities were least-squares fitted[10] to $\chi_p=\chi_{\mathrm{Fisher}}+\chi_{\mathrm{VV}}$, with χ_{VV} fixed at the values obtained above, and g, J, N treated as parameters. The best values of g, J, and N are given in Table II, and the fitted curves are drawn on Fig. 2(b). The values of $2JS(S+1)/k$

from the Fisher fit agree well with the Curie-Weiss constant Θ $[2zJS(S+1)/3k$ in mean-field theory].

The numerical results indicate that the value of N increases with the degree of crystallinity from a value of 2 for the most amorphous material to an immeasurably large value for the most crystalline. Although the model is obviously oversimplified, we interpret these results to mean that the coherence length for spin correlation is limited in the amorphous case to next nearest neighbors, whereas in the crystalline case the limit is the polymer chain length. Alternatively, we can view the susceptibility as arising from spins coupled by an exchange interaction which is constant in the crystalline case, but in the amorphous case has fluctuations from bond to bond of the order of J itself such that J has a nonvanishing probability of being zero.

The values of g obtained by this method are somewhat lower than those obtained directly by spin resonance, but considering the simplicity of the model and the approximations inherent in Fisher's solution (infinite spin, neglect of three-dimensional effects) the overall picture is remarkably consistent. The low value of N obtained for material A indicates that the model of an extended chain should be replaced by clusters of a few spins isolated or weakly coupled to each other.

A somewhat more realistic model is to use Fisher's solution for classical spins, but to apply it to a chain in which the exchange J_i varies randomly with the position of the bridge i.[14] If there is no correlation in this variation, i.e., $\langle u(J_i)u(J_k)\rangle = \langle u(J_i)\rangle\langle u(J_k)\rangle = \langle u\rangle^2$ (where the average $\langle\ \rangle$ is over the distribution of J), then we obtain simply

$$\chi = \frac{N_A g^2 \mu_B^2 S(S+1)}{3kT} \frac{1-\langle u\rangle}{1+\langle u\rangle} \tag{3}$$

for an infinite chain. We have computed this function for the distribution

$$p(J_i) = \begin{cases} 1/\lambda, & J - \tfrac{1}{2}\lambda \leq J_i \leq J + \tfrac{1}{2}\lambda & \text{(4a)} \\ 0, & \text{otherwise .} & \text{(4b)} \end{cases}$$

The result is

$$\langle u\rangle = \frac{-kT}{2\lambda S(S+1)} \ln \frac{(2J+\lambda)\sinh[(2J-\lambda)S(S+1)/kT]}{(2J-\lambda)\sinh[(2J+\lambda)S(S+1)/kT]} . \tag{5}$$

This function, which has the correct form in the limit $\lambda - 0$, yields a divergent susceptibility at zero temperature when $\lambda/2J > 1$; i.e., when there exist some interactions which are either zero or ferromagnetic.

The data, corrected for χ_{VV}^{exp} as obtained from the high-temperature analysis, were fitted to

TABLE II. Magnetic parameters of the three samples A, B, and C. Quoted standard deviations arise statistically from the scatter in the data and do not include consistent errors which might arise from the calibration of the susceptometer or the weighing of the samples.

		High-temperature Curie-Weiss fit						Fisher fit		
Material	χ_{VV}^{calc} (10^{-3} emu/mole)	χ_{VV}^{exp} (10^{-3} emu/mole)	Curie-Weiss constant Θ (K)	C (emu K/mole)	Moment p (μ_B)	g (from static susceptibility)	g (from EPR)	g calc	g_{Fisher}	$\Theta_{\text{Fisher}} = 2JS(S+1)$ (K)	N
A	0.14	0.3 ± 0.1	9.3 ± 0.6	1.777 ± 0.022	3.77 ± 0.04	1.95 ± 0.02	1.977 ± 0.002	1.978	1.62 ± 0.1	12.9 ± 0.3	2
B	0.14	0.3 ± 0.1	18.9 ± 0.7	1.814 ± 0.025	3.83 ± 0.06	1.98 ± 0.02	1.974 ± 0.001	1.978	1.89 ± 0.1	18.8 ± 0.4	26
C	0.14	0.2 ± 0.1	24.3 ± 1.0	1.740 ± 0.030	3.73 ± 0.08	1.93 ± 0.04	1.974 ± 0.001	1.978	1.86 ± 0.02	21.2 ± 0.3	$>10^4$ [a]

[a] Fitting procedure would not converge with finite N; N was set equal to ∞ in order to fit the other parameters.

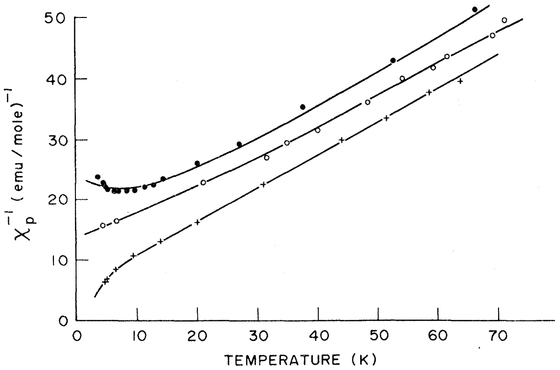

FIG. 3. Curves fitted to the susceptibility data of samples *A* (+), *B* (○), and *C* (●), using Eqs. (3) and (5). Values of the parameters are given in Table III.

Eqs. (3) and (5) for the parameters g, J, and λ. The quality of fit is much better than that using Eq. (2), the mean-square error being reduced by a factor of 3 or more. The fitted curves and the data are shown in Fig. 3, and the values of the expressions g, $2JS(S+1)/k$, and $\lambda/2J$ (the relative width of the square distribution) are given in Table III.

The width of the distribution parameterizes, in a unique manner, the magnetic disorder, which can be seen to relate directly to the structural disorder. Even in the case of the most "crystalline" sample, the value of λ is not negligible. This is as one would expect, since the relatively well-ordered polymer is far from being a good crystal.

TABLE III. Parameters giving best fit to the susceptibility of samples *A*, *B*, and *C*, using Eqs. (3) and (5).

Sample	g	$2JS(S+1)/k$	$\lambda/2J$
A	1.95 ± 0.05	13 ± 1	1.9 ± 0.2
B	1.95 ± 0.05	22 ± 1	0.90 ± 0.08
C	1.89 ± 0.06	25 ± 1	0.66 ± 0.06

V. CONCLUSION

We have concentrated on only a small subset from this class of materials which can be expected to yield many interesting solid-state properties. There are problems inherent in elucidating the structures of polymers, but this initial study shows that the magnetic properties can be understood in traditional terms, and that they can be used (in conjunction with other techniques) as a probe of the molecular properties of these transition-metal polymers.

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