JOURNAL OF SOLID STATE CHEMISTRY **10**, 151–166 (1974)

Linear-Chain Antiferromagnetism in the Compounds $M^{II}(N_2H_5)_2(SO_4)_2$ with M = Mn, Fe, Co, Ni, and Cu*

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Received June 4, 1973

Powder-susceptibility measurements in the temperature region 2–80° K on the chain compounds $M^{II}(N_2H_5)_2(SO_4)_2$, with M = Mn, Fe, Co, Ni, and Cu, show that the magnetic properties of these compounds can be interpreted in terms of antiferromagnetic linear-chain systems. The experimental results provide information on the magnitude of the intrachain interactions. In addition, ESR linewidth experiments were used for a determination of the intrachain interaction in $Mn(N_2H_5)_2(SO_4)_2$. For the interpretation of the data on $Fe(N_2H_5)_2(SO_4)_2$, the parallel susceptibility of Ising chains with $S = 2$ is calculated theoretically. An estimate for the ratio between the intra- and interchain coupling is given. Use is made of preliminary results of specific heat measurements on these compounds for the interpretation of the magnetic data.

I. Introduction

As part of a research program on the magnetic properties of compounds having chain structures, which may be expected to behave as one-dimensional magnetic systems, susceptibility and specific heat measurements on polycrystalline samples of the compounds $M(N_2H_5)_2(SO_4)_2$, with M = Mn, Fe, Co, Ni, and Cu (*catena*-bis(hydrazinium)-bis(sulfato)-metal(II) compounds), have been carried out at low temperatures (2–80°K). In this paper the results of the susceptibility measurements and some preliminary results of the specific heat measurements (carried out by F. W. Klaaijsen at the Kamerlingh Onnes Laboratory at Leyden and to be published in detail elsewhere (*1*)) on these compounds are discussed.

A single-crystal structure determination presented by Prout and Powell (*2*) has shown that the Zn ions in the triclinic compound $Zn(N_2H_5)_2(SO_4)_2$ are coordinated by four oxygens belonging to four different, bridging SO_4 groups and by two monodentate N_2H_5 groups, together forming a distorted octahedral coordination around the metal ion. The SO_4 groups are bridging between two adjacent Zn ions, forming chains of metal ions along the *b*-axis.

Additional structure, magnetic, and spectroscopic studies by Hand and Prout (*3*) and Nieuwpoort and Reedijk (*4*) on similar compounds with M = Cr, Mn, Fe, Co, Ni, Cu, and Cd have shown that all these compounds possess the same geometrical arrangement and that most of the measurements (*4*) can be interpreted on the basis of a tetragonal, compressed octahedral geometry with an additional rhombic distortion. The suscepti-

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* Abstracted in part from the Ph.D. Thesis of H. T. Witteveen, Leyden, 1973.

bility and ESR measurements (*4*) on some of these compounds showed the presence of a small magnetic interaction between the metal ions.

The metal–metal distances in the chains are about 5.3 Å. This large distance is prohibitive for the occurrence of direct magnetic interaction between the metal atoms. If intrachain interaction is present, it would be mainly due to a superexchange mechanism via the path M-O-S-O-M. The chains are linked to each other via terminal nitrogen atoms of the N_2H_5 groups, which form hydrogen bonds with SO_4 groups of neighboring chains. It can, therefore, be expected that the magnetic interaction between the chains (interchain interaction) is weaker than the intrachain interaction, although the distance between the metal atoms along the *c*-axis (5.8 Å) is roughly equal to the distance within the chains (along *b*-axis, 5.3 Å).

In Section III it is shown that the susceptibility measurements can be interpreted in terms of the one-dimensional linear-chain model, indicating that, as expected, the intrachain interaction is relatively much stronger than the interchain interaction.

II. Experimental

The compounds $M^{2+}(N_2H_5)_2(SO_4)_2$, with M = Mn, Fe, Co, Ni, Cu, were prepared by adding aqueous solutions of MSO_4 to an aqueous solution of $N_2H_6SO_4$, as described previously (*4*).

The compounds were checked for purity by complexometric metal analysis (accuracy 0.5%, carried out at the Organic Chemical Institute TNO, Utrecht, The Netherlands) and by infrared spectroscopy. The results of the elemental analysis are listed in Table I.

TABLE I

METAL ANALYSES OF THE COMPOUNDS $M(N_2H_5)_2(SO_4)_2$

Compound	% M calculated	% M found
$Mn(N_2H_5)_2(SO_4)_2$	17.5	17.9
$Fe(N_2H_5)_2(SO_4)_2$	18.0	18.2
$Co(N_2H_5)_2(SO_4)_2$	18.6	17.9
$Ni(N_2H_5)_2(SO_4)_2$	18.5	19.0
$Cu(N_2H_5)_2(SO_4)_2$	19.7	19.7

The apparatus used for the specific heat measurements in the temperature region 1.2–80° K will be described in detail elsewhere (*1*).

The susceptibility measurements were carried out in the temperature region 2–80°K by means of a PAR Vibrating Sample Magnetometer Model 150. The temperature was measured with a calibrated GaAs-diode against a Cryocel Ge resistance thermometer (2–90°K) at the Department of Thermometry of the Kamerlingh Onnes Laboratory. Uncertainties in *T* are 0.1°K (at the lowest temperatures) to 0.5°K (in the high-temperature region). The calibration of the magnetometer was carried out by measurement of the room-temperature magnetization of a pure Ni sample (accuracy 1%). The magnetic field strength was determined by measurements of the current in the superconducting coil that supplies the magnetic field necessary for the susceptibility measurements.

The molar susceptibility χ_m of all compounds has been corrected for diamagnetism according to the tables of Selwood (*5*).

Computer calculations were carried out by means of the IBM 360/65 computer at the Computer Centre of Leyden University.

III. Results and Discussion

(*a*) *Theoretical Introduction*

The interpretation of experimental results of magnetic systems is greatly facilitated by the utilization of theoretical models that give a simplified description of the magnetic interactions in these systems. The basic properties of the models can be understood from the spin interaction Hamiltonian

$$\mathscr{H} = -2J \sum_{ij} [aS_i^z \cdot S_j^z + b(S_i^x \cdot S_j^x + S_i^y \cdot S_j^y)], \qquad [1]$$

where J is the exchange parameter between nearest neighbors, $\sum_{ij}$ is the summation over all pairs of ions i and j, and S^x, S^y, S^z are the components of spin S; the ratio a/b is an anisotropy parameter. For $a = 1$ and $b = 0$, the so-called Ising model is obtained, describing the case of extreme anisotropy in the magnetic interactions. If $a = b = 1$, the Hamiltonian denotes the Heisenberg model, in which the magnetic interaction is isotropic. The case $a = 0$ and $b = 1$ is called the XY model or planar Heisenberg model if one requires that the spins lie within the XY-plane. For $0 < a < 1$ and $0 < b < 1$, cases intermediate between the three models mentioned are described.

The magnetic properties of many compounds can be described adequately by the Heisenberg or Ising model, whereas only a few experimental examples are known of the XY model (*23*). The former model gives a good description of magnetic systems with *S*-state ions (e.g., Mn^{2+}), because for these ions single-ion anisotropy and anisotropy in the exchange mechanism are usually very small. The Heisenberg model is also successful for many Cu^{2+} and Ni^{2+} compounds. Many Co^{2+} compounds show strongly anisotropic properties that can be approximately described by the Ising model. The properties of Fe^{2+} compounds are very often intermediate between those expected for a Heisenberg and an Ising system. More details about the models applied to the description of the compounds discussed in this paper are given below for each compound individually.

The so-called Dzialoshinsky–Moriya term $D \cdot S_i \times S_j$ that describes the antisymmetrical part of the superexchange interaction is not included in the discussion above. Obviously, this is allowed if the exchange is isotropic, but in case of anisotropic exchange this term can influence the magnetic behavior. Due to the low crystal symmetry of the compounds $M(N_2H_5)_2(SO_4)_2$, it is quite well possible that, in particular in the cases M = Fe and Co, the Dzialoshinsky–Moriya term influences the magnetic behavior. However, from our powder-susceptibility measurements, no reliable impression about this influence can be obtained. Therefore, this term is not taken into account in the discussion of the results.

(*b*) $Ni(N_2H_5)_2(SO_4)_2$

In Fig. 1a the molar powder-susceptibility χ_m and inverse molar susceptibility $1/\chi_m$ of $Ni(N_2H_5)_2(SO_4)_2$ as a function of temperature are shown. As can be seen in Fig. 1b, the magnetization at 2.2°K is linearly dependent upon the magnetic field strength up to about 25 kOe. Above 25 kOe, the curve shows a deviation from this behavior, which

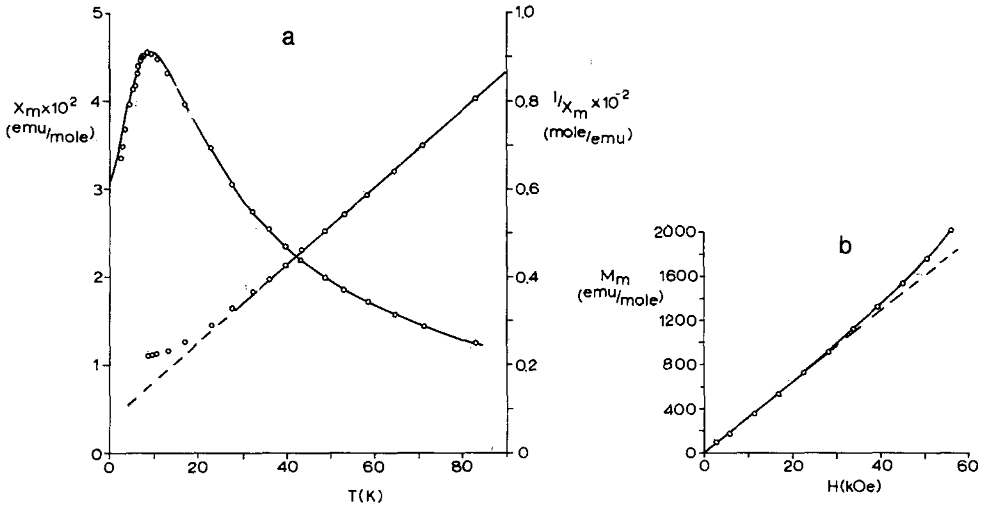

FIG. 1. (a) Molar susceptibility χ_m and inverse molar susceptibility $1/\chi_m$ of $Ni(N_2H_5)_2(SO_4)_2$ as a function of temperature; ○ = experimental points. The full curve represents the theoretical fit for $J/k = -3.35$°K according to Weng's results. The straight line through the $1/\chi_m$ data represents the Curie–Weiss law. (b) Magnetization curve of $Ni(N_2H_5)_2(SO_4)_2$ at 2.2° K.

TABLE II

EXPERIMENTAL VALUES OF SUSCEPTIBILITY MEASUREMENTS

Compound	θ(°K)[a]	$\chi_{max} \times 10^2$ (emu/mole)	T_{max}(°K)
$Ni(N_2H_5)_2(SO_4)_2$	−9.5(5)	4.51(5)	8.7(2)
$Mn(N_2H_5)_2(SO_4)_2$	−5.5(5)	24.50(25)	4.8(2)
$Cu(N_2H_5)_2(SO_4)_2$	−3(1)	5.95(5)	2.1(2)
$Fe(N_2H_5)_2(SO_4)_2$	−13(1)	9.65(10)	15.3(3)
$Co(N_2H_5)_2(SO_4)_2$	−22(1)	9.10(10)	5.7(2)

[a] Uncertainties in the last digit are indicated in parentheses in this table and in Table III.

was found to be a common feature of the other $M(N_2H_5)_2(SO_4)_2$ compounds described below. The susceptibility was measured at a magnetic field of about 5.5 kOe. Preliminary results of these measurements were mentioned in a previous communication (*6*).

The $1/\chi_m$ curve obeys the Curie–Weiss law down to about 35°K with an asymptotic Curie temperature $\theta = -9.5$°K (Table II). The broad maximum that is found in the χ curve at low temperatures (Fig. 1a) is indicative for antiferromagnetic dimers, linear-chain, and two-dimensional systems. On the basis of the crystal structure, it therefore seems reasonable to interpret the magnetic properties of the compound in terms of an antiferromagnetic linear-chain system that, as has been remarked above, can probably be described by the Heisenberg model. In this case, $a = b = 1$ in the Hamiltonian [1], where J indicates now the exchange between nearest neighbors in the chains and has negative sign for antiferromagnetic coupling. The interchain interaction and the single-ion anisotropy of the Ni^{2+} ions are neglected at this stage of the analysis. It can be inferred from the specific heat measurements (*1*) and from a corresponding entropy determination that, as usual for Ni^{2+} compounds, the magnitude of the spin is $S = 1$. In 1968 Weng published in his thesis (*7*) numerical results for antiferromagnetic Heisenberg linear chains of 3 to 7 spins $S = 1$. By extrapolation of his results to an infinite number of spins, he obtained the susceptibility and specific heat as a function of temperature for antiferromagnetic Heisenberg chains with $S = 1$ (*7*).

By fitting our susceptibility results to Weng's theoretical susceptibility curve, one obtains a value for the intrachain interaction. With the variable parameters J/k and g, the high-temperature part of the experimental curve (Fig. 1a) is fitted well to the theoretical curve for $J/k = -3.35$°K (Table III) and $g = 2.17$. The g-value is in good agreement with the value of about 2.2 that is usually found for the spectroscopic splitting factor of Ni^{2+} compounds.

From the experimentally determined values of the maximum in the susceptibility (χ_{max}) and of the temperature ($T_{max}(\chi)$) at which χ_{max} occurs (Table II), values for J/k are also obtained by means of the following relations, derived by Weng:

$$kT_{max}(\chi)/|J| = 2.7 \qquad [2]$$

$$|J|\chi_{max}/Ng^2\beta^2 = 0.0872 \qquad [3]$$

where N = Avogadro's number and β = Bohr magneton. Using the g-value from the high-temperature fit, the J/k-values are calculated (Table III).

The differences between the three obtained J/k-values fall within experimental error. It is seen in Fig. 1a that, if the high-temperature fit is extended to the lower-temperature region, agreement between experiment and theory remains good. Thus, we can describe our susceptibility data very well by Weng's theory, assuming $J/k = -(3.3 \pm 0.1)$°K.

Applying Weng's theoretical results to fit the high-temperature part of the experimental specific heat curve (corrected for the lattice contribution), the value $J/k = -2.7$°K is obtained. From the temperature $T_{max}(C) = 3.7$°K (C = specific heat) and Weng's theoretical relation for $T_{max}(C)$: $kT_{max}(C)/|J| = 1.8$, it is found that $J/k = -2.0$°K. Not only is a large difference observed between the two J/k-values as obtained from the specific heat data, but also between these two values and the J/k-value, calculated from the susceptibility.

This discrepancy cannot be explained at

TABLE III

LISTING OF J/k VALUES AND J'/J FOR COMPOUNDS $M(N_2H_5)_2(SO_4)_2$ OBTAINED FROM SEVERAL METHODS

		Susceptibility results			Specific heat results				
Compound	Theoretical model	J/k from $T_{max}(\chi)$ (°K)	J/k from χ_{max} (°K)	J/k from best fit (°K)	J/k from $T_{max}(C)$ (°K)	J/k from best fit (°K)	J/k from ESR linewidth	Estimated value of J/k (°K)	$\lvert J'/J \rvert$
$Ni(N_2H_5)_2(SO_4)_2$	Heisenberg model	−3.2(1)	−3.4(1)	−3.35(5)	−2.0(1)	−2.7(1)	—	≈ −3.3	$<1 \times 10^{-2}$
$Mn(N_2H_5)_2(SO_4)_2$	Interpolation scheme	−0.49(1)	−0.585(5)	−0.590(5)	−0.45(5)	—	—		
	Scaling method	−0.59(1)	−0.620(5)	−0.615(5)	—	—	—	−0.55(5)	3×10^{-2}
	10/3 effect	—	—	—	—	—	0.52(8)		
$Cu(N_2H_5)_2(SO_4)_2$	Heisenberg model	−1.65(5)	−2.10(5)	−2.00(5)	−1.87	—	—	−1.9(1)	$<1.5 \times 10^{-1}$
$Fe(N_2H_5)_2(SO_4)_2$	Interpolation scheme	−2.22(4)	—	≈ −2.2	−2.90	—			
	Scaling method	−2.59(5)	—	—	—	—	—	≈ −2.5	3×10^{-2}
	Ising model	−2.04(4)	—	—	—	−3.28			
$Co(N_2H_5)_2(SO_4)_2$	XY model	−8.9(3)	—	—	−6.7	—			
	Heisenberg model	−4.5(1)	−5.40(5)	—	−4.47	—	—	≈ −7	1×10^{-2}
	Ising model	−11.5(3)	—	—	−10.3	—			

present, but the disagreement may be due to the occurrence of single-ion zero-field splitting. Because of the strongly distorted octahedral coordination of the Ni ion, it is possible that the zero-field splitting parameter D cannot be neglected and may even be of the same order of magnitude as J.

As far as known, no theory is available which describes antiferromagnetic Heisenberg chains including zero-field splitting of the $S = 1$ state, so that even a qualitative study of the influence of D on the susceptibility and specific heat is not feasible. However, from a recently published theory for $S = 1$ dimers, including zero-field splitting, it is seen that neglection of D does not influence the susceptibility of the dimers very much (*8*). For the magnetic specific heat curve, it is expected that the broad maximum in this curve originates from the contribution of the broad maximum of a Schottky anomaly, caused by the zero-field splitting (*9*), and the broad maximum due to the antiferromagnetic dimer interaction. By extension to linear chains, it is understandable that the magnetic specific heat curve cannot be fitted with Weng's results, whereas a good fit is found for the susceptibility curve.

Other antiferromagnetic linear-chain Ni^{2+} compounds, $RbNiCl_3$ and $CsNiCl_3$, have much larger J/k values (*10*, *11*) and are less distorted from cubic symmetry so that $D \ll J$. The experimental susceptibility of these compounds can be fitted well using Weng's theory (*11*). A comparison with specific heat results is not possible, because only a few specific heat data are known for $CsNiCl_3$ (*12*).

Compounds having linear-chain properties practically always show a magnetic transition, where 3-dimensional, long-range order sets in, due to the interchain interaction. The specific heat measurements did not indicate such a transition point down to 1.5°K, indicating that the interchain interaction is much weaker than the intrachain interaction.

A last remark about $Ni(N_2H_5)_2(SO_4)_2$ concerns the "anomalous" behavior of the magnetization curve (Fig. 1b). Such behavior is predicted by several theoretical investigations on antiferromagnetic Heisenberg and Ising linear-chain models with spin $S = 1/2$ and 1 (*7*, *13–16*) and has been measured experimentally for, for example, the linear-chain compounds $Cu(NH_3)_4SO_4 \cdot H_2O$ (*17*) and $CuCl_2 \cdot 2NC_5H_5$ (*18*). For the other compounds described below, similar magnetization curves are found.

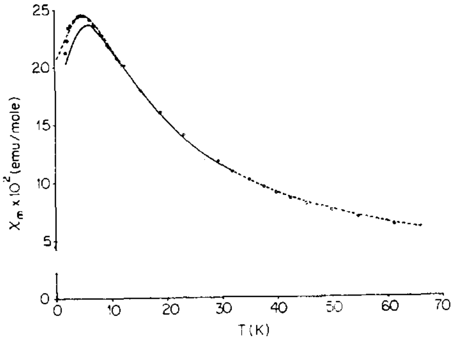

FIG. 2. Molar susceptibility χ_m of $Mn(N_2H_5)_2(SO_4)_2$ as a function of temperature. ○ = experimental points. The full curve is the best fit obtained using Weng's interpolation scheme for $J/k = -0.59$°K and $g = 2.01$. The dashed curve is the best fit obtained using the scaling method for $J/k = -0.615$°K and $g = 2.01$.

(*c*) $Mn(N_2H_5)_2(SO_4)_2$

The observed susceptibility of

$$Mn(N_2H_5)_2(SO_4)_2$$

is shown in Fig. 2. The susceptibility was field independent up to about 10 kOe. The measurements were carried out at a field strength of about 2.7 kOe. The curve shows the broad maximum that, on the basis of the crystal structure, is typical for an antiferromagnetic linear-chain system. The asymptotic Curie temperature $\theta = -5.5$°K (Table II).

The magnetic system of Mn^{2+} compounds can be described by the Heisenberg model. ESR measurements revealed (*4*) that the single-ion anisotropy of $Mn(N_2H_5)_2(SO_4)_2$ is very small ($D = 0.025 \pm 0.005\ cm^{-1}$), so that it can be neglected.

Within the Heisenberg model, one knows two theoretical approximations for the description of antiferromagnetic linear chains with $S = 5/2$. By scaling at high temperatures, the exact results of Fisher (*19*) for an antiferromagnetic linear chain with $S = \infty$ to the series expansion results of Rushbrooke and Wood (*20*) and Wagner and Friedberg

(*21*) obtained Eq. [4] for the molar susceptibility:

$$\chi_m = \frac{Ng^2 \beta^2 S(S+1)}{3\,kT} \cdot \frac{1+u(K)}{1-u(K)}, \qquad [4]$$

where $u(K) = \coth K - 1/K$ and $K = 2JS((S+1)/kT)$. The sign of J is again negative. In this approximation χ_{max} and $T_{max}(\chi)$ for $S = 5/2$ are related to J by:

$$|J|\chi_{max}/Ng^2\beta^2 = 0.1004 \qquad [5]$$

and

$$kT_{max}(\chi)/|J| = 8.2. \qquad [6]$$

The other approximation method is an interpolation scheme for arbitrary spin S, introduced by Weng (*7*). For this scheme he uses the Hamiltonian

$$\mathscr{H} = -2J\frac{\sum\limits_{ij} \mathbf{S}_i \cdot \mathbf{S}_j}{2S(S+1)}$$

with general spin S. On the basis of this Hamiltonian, the results for $S = \infty$ are the same as given by Fisher (*19*) for $S = \infty$ and the results for different S-values agree at infinite temperature. Weng assumes now that an arbitrary thermodynamic quantity $Y(S,T)$, depending on temperature T and spin S, obeys the relation

$$Y(S,T) = \frac{a(T)\,S + b(T)}{c(T)\,S + d(T)} = \frac{a'(T)\,S + b'(T)}{S + d'(T)}, \qquad [7]$$

where $a'(T)$, $b'(T)$, and $d'(T)$ depend on temperature but are independent of S. Tabulating the known numerical results (*13*) for antiferromagnetic Heisenberg linear chains with $S = 1/2$, the numerical results (*7*) for $S = 1$ and the exact results (*19*) for $S = \infty$ on a reduced temperature scale $kT/2|J|S(S+1)$, the unknown constants $a'(T)$, $b'(T)$, and $d'(T)$ can be calculated for each value of $kT/2|J|S(S+1)$. In this way, the susceptibility and specific heat curves for arbitrary spin value are obtained. By means of this interpolation scheme, it is found that for $S = 5/2$:

$$|J|\chi_{max}/Ng^2\beta^2 = 0.0949 \qquad [8]$$

and

$$kT_{max}(\chi)/|J| = 9.8 \qquad [9]$$

Using Eqs. [5, 6, 8, 9], the experimental values for χ_{max} and $T_{max}(\chi)$ (Table II), and the value $g = 2.01$, as found by Nieuwpoort and Reedijk (*4*), the J/k-values in Table III are derived. Also in this table are given the J/k-values obtained from the fits to the high-temperature part of the susceptibility curve (Fig. 2 with $g = 2.01$ and J/k as variable parameter. It is noticed that the best result is found by means of the scaling method of Wagner and Friedberg (*21*).

This is in contradiction with Smith and Friedberg's conclusion (*22*), drawn from their results on the antiferromagnetic Heisenberg linear-chain compound $CsMnCl_3 \cdot 2H_2O$, that Weng's interpolation scheme seems the better approximation method. The conclusion of Smith and Friedberg is supported by de Jongh and Miedema in an extensive review on compounds with one-dimensional magnetic properties (*23*).

It is not possible at present to give an explanation for these conflicting results, but a few remarks are appropriate.

First, if a small paramagnetic impurity is present in the sample of $Mn(N_2H_5)_2(SO_4)_2$, this would tend to increase χ_{max} and to shift $T_{max}(\chi)$ to a lower temperature. This impurity would not influence the susceptibility in the high-temperature region. This is precisely what is observed when the experimental results are compared with the interpolation scheme. Taking into account the results of the chemical analysis of the $Mn(N_2H_5)_2(SO_4)_2$ sample (Table I), it is clear that paramagnetic impurities cannot amount to more than a few percent. Impurities can possibly be the compounds $MnSO_4 \cdot (H_2O)_x (x = 0, 1, 4, 5)$. As far as susceptibility data of these compounds exist for the low-temperature region (*24–27*), we conclude that the presence of a few percent of some of these compounds can cause the deviations of about 1×10^{-2} emu/mole between the experimental curve and the theoretical curve derived from the interpolation scheme in the region around $T_{max}(\chi)$. It is also concluded from these data that at higher temperatures, the experimental susceptibility curve can hardly have been influenced by the impurities.

In the second place, the presence of anisotropy in the magnetic system would also cause a shift of $\chi_{\max}$ to lower temperatures and to higher values (*7*, *13*). But, as has already been remarked, the anisotropy is very small and can at most have a minor influence on the susceptibility curve.

Further, it is noticed that $Mn(N_2H_5)_2(SO_4)_2$ is not equally good an example of a one-dimensional system as $CsMnCl_3 \cdot 2H_2O$. Whereas in the latter compound (*22*, *28*) $T_{\max}(\chi)/T_N = 6.3$, for $Mn(N_2H_5)_2(SO_4)_2$ it is found, by means of specific heat measurements (*1*), that $T_N = 2.09°K$, hence $T_{\max}(\chi)/T_N = 2.3$. This indicates that in this compound the interchain interaction is much stronger than in $CsMnCl_3 \cdot 2H_2O$. Neutron scattering experiments on some antiferromagnetic linear-chain compounds demonstrate that up to temperatures of about $2T_N$ to $4T_N$, the effect of interchain interaction is noticeable (*28*, *29*), in other words, 3-dimensional correlations are found between the chains. Because of this phenomenon and the fact that the theoretical approximation holds for pure 1-dimensional systems only, it can be expected that in linear-chain compounds, where $T_{\max}(\chi)$ is about 2–3 times T_N (hence with a relatively large interchain interaction), the susceptibility shows deviations from the theoretical picture in the region below and at $T_{\max}(\chi)$. It is possible that the 3-dimensional correlations in linear-chain systems above T_N cause an increase of the susceptibility above T_N, compared to the susceptibility of an ideal 1-dimensional system.

Probably one or a combination of more of the phenomena described above explains the difference between the conclusion of Smith and Friedberg (*22*) and our results for $Mn(N_2H_5)_2(SO_4)_2$.

From the specific heat data $T_{\max}(C) = (2.5 \pm 0.3)°K$ is determined. The uncertainty in this value is rather large due to overlap of the strong peak, caused by the 3-dimensional ordering at $T_N = 2.09°K$, with the broad maximum in the specific heat curve. By means of the relation $kT_{\max}(C)/|J| = 5.6$, obtained with the interpolation scheme (Eq. [7]), the value $J/k = -(0.45 \pm 0.05)°K$ is calculated (Table III). This value is in agreement with the one obtained from $T_{\max}(\chi)$.

It has also been possible to determine J/k by means of a paramagnetic linewidth study, in particular, the so-called "10/3 effect". The great advantage of this method is that, if some special conditions are fulfilled, the magnetic exchange can be calculated from the ratio between the linewidths of two ESR signals recorded at two different frequencies (e.g., in X- and Q-band) at room temperature. The special conditions are that only dipolar interaction and isotropic magnetic exchange are present and that the latter is stronger than the former. Kubo and Tomita (*30*) have derived the following expression for the linewidth ΔH of the ESR signal as a function of the measuring frequency f_0:

$$\Delta H = \frac{H_d^2}{H_e}[1 + (5/3)\exp\{-\tfrac{1}{2}(f_o/f_e)^2\} + (2/3)\exp\{-2(f_o/f_e)^2\}], \qquad [10]$$

where H_d = dipolar field and the range of f_0 should be comparable to the frequency f_e that is correlated to the exchange field

$$H_e(f_e = g\beta H_e/h).$$

In the limit $H_e \gg H_0(f_0 = g\beta H_0/h)$, ΔH is 10/3 as large as in the limit $H_0 \gg H_e$.

Pleau and Kokoszka (*31*) employed Eq. [10] to calculate the ratio of linewidths at two frequencies in terms of the magnetic field H_e. To relate H_e to J, they used the expression

$$(g\beta H_e/h)^2 = (8/3)zS(S+1)J^2 \qquad [11]$$

given by Moriya (*32*). Here z = number of magnetic nearest neighbors.

Because the compound $Mn(N_2H_5)_2(SO_4)_2$ fulfills the conditions required for the application of the "10/3 effect", the ESR signals of this compound were recorded at room temperature at the frequencies 9.5 GHz (X-band) and 35.5 GHz (Q-band)[1]. The spectra were recorded as the derivative of the absorption curve with a Varian V-4502/3-10/A spectrometer of which details have been published elsewhere (*33*). The measured linewidths were 241 ± 4 and 212 ± 4 Oe at X- and Q-band frequencies respectively, resulting in a linewidth ratio 0.88 ± 0.03 and an intrachain interaction $J/k = -0.52 \pm 0.08°K$, calculated by means of Eqs. [10] and [11] (Table III). Within experimental uncertainty, this value

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[1] These measurements were carried out by B. Nieuwenhuijse and P. G. van den Akker at the Technological University of Twente, The Netherlands.

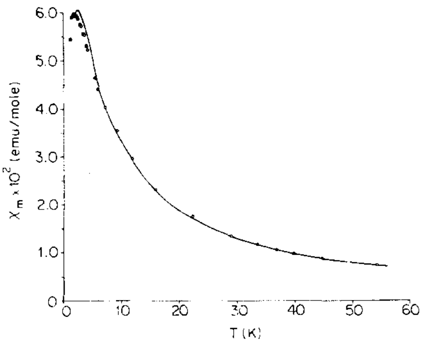

FIG. 3. Molar susceptibility χ_m of $Cu(N_2H_5)_2(SO_4)_2$ as a function of temperature. ○ = experimental points; ■ = experimental points obtained from zero-field susceptibility measurements. The full curve is the best theoretical fit for $J/k = -2.00$°K and $g = 2.12$.

is in agreement with the J/k-values obtained via susceptibility and specific heat measurements.

(*d*) $Cu(N_2H_5)_2(SO_4)_2$

In Fig. 3 the χ_m curve of $Cu(N_2H_5)_2(SO_4)_2$ is depicted. The susceptibility at 2.1°K was field independent up to about 35 kOe. The plotted data refer to measurements at about 10 kOe.

The susceptibility curve (as measured with our apparatus down to 2.1°K) did not exhibit the broad maximum as found for the Ni and Mn compound (Figs. 1a and 2). From the reciprocal susceptibility versus temperature curve, it was determined that $\theta = -3 \pm 1$°K (Table II). By analogy with the Ni and Mn compound, one would expect an antiferromagnetic intrachain interaction. Probably the intrachain interaction is so small that the expected broad maximum only occurs below or in the neighborhood of 2.1°K. To obtain experimental data in the temperature region below 2.1°K, zero-field susceptibility measurements were performed with a twin-T-bridge at a frequency of about 300 kHz.[2] A detailed description of this apparatus will be published elsewhere (*34*). With this bridge, the real part χ' and the imaginary part χ'' of the complex susceptibility $\chi = \chi' - i\chi''$ are measured simultaneously. The measurements on $Cu(N_2H_5)_2(SO_4)_2$ suggested that (at the measuring frequency) χ'' was practically zero. The measurements were carried out in the liquid-helium temperature region (1.2–4.2°K).

Scaling the relative zero-field susceptibility measurements to some of our susceptibility data in the region around 4°K, the results, shown in Fig. 3 and listed in Table II, are obtained.

As remarked above, Cu^{2+} compounds can often be described by the Heisenberg model. Within this model, Bonner and Fisher (*13*) have determined the theoretical susceptibility curve for antiferromagnetic chains with $S = \frac{1}{2}$, in which curve the following relations hold for $T_{max}(\chi)$ and χ_{max}:

$$kT_{max}(\chi)/|J| = 1.282 \qquad [12]$$

and

$$|J|\chi_{max}/Ng^2\beta^2 = 0.07346 \qquad [13]$$

The best fit of the high-temperature part of the χ curve is found for $J/k = -2.00 \pm 0.05$°K and $g = 2.12 \pm 0.02$ (Fig. 3). The g-value is in reasonable agreement with the averaged g-value, defined as $g_{av} = \{\frac{1}{3}[(g_1{}^2 + g_2{}^2 + g_3{}^2)]\}^{1/2} = 2.16$, where $g_1 = 2.05$, $g_2 = 2.10$, $g_3 = 2.34$ were taken from the measurements by Nieuwpoort and Reedijk (*4*). Using the experimental values of $T_{max}(\chi)$ and χ_{max} (Table II), the g-value from the high-temperature fit, and Eqs. [12] and [13], the intrachain coupling is calculated to be $J/k = -1.65$°K and $J/k = -2.10$°K, respectively (Table III).

It is noticed that the theoretical fit and the experimental curve agree well except in the region around $T_{max}(\chi)$, where a small discrepancy appears. This discrepancy might well be related to the small anisotropy in the magnetic system, which is suggested by the presence of small differences between the g-values (*4*). Another explanation could be found in the presence of interactions other than those arising from nearest neighbors.

The value $C_{max}(\exp)/R = 0.34$, obtained from the specific heat measurements, agrees very well with the theoretically expected value (*13*) for an antiferromagnetic Heisenberg linear-chain system with $S = 1/2$: $C_{max}(\text{theor})/R = 0.35$.

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[2] These measurements were carried out by S. Hillaert at the Kamerlingh Onnes Laboratory, Leyden (The Netherlands).

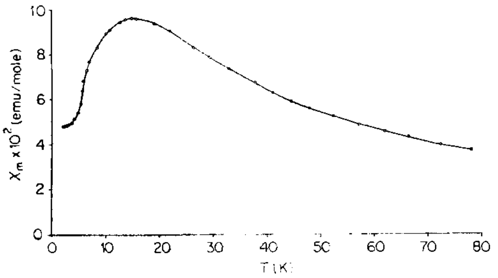

FIG. 4. Molar susceptibility χ_m of $Fe(N_2H_5)_2(SO_4)_2$ as a function of temperature; ○ = experimental points. A smooth curve is drawn through the experimental points.

With the experimental value $T_{max}(C) = 1.8°K$ and the theoretical relation (*13*) $kT_{max}(C)/|J| = 0.962$, the intrachain interaction is calculated to be $J/k = -1.87°K$ (Table III). This value is in good agreement with the value obtained from the best fit of the susceptibility curve.

(*e*) $Fe(N_2H_5)_2(SO_4)_2$

The experimental susceptibility of $Fe(N_2H_5)_2(SO_4)_2$ is shown in Fig. 4. At 2.0°K, the susceptibility was independent of the magnetic field strength up to about 20 kOe. The susceptibility was measured as a function of temperature at about 5 kOe. In Fig. 4 again a broad maximum is noticed. The high-temperature part of the reciprocal susceptibility curve obeys the Curie–Weiss law with an asymptotic Curie temperature $\theta = -13 \pm 1°K$ (Table II).

The theoretical interpretation of the susceptibility gives rise to serious problems. As already remarked, it is usually not possible to describe the magnetic properties of Fe^{2+} compounds by means of either the pure Heisenberg or Ising model, due to the fact that in these compounds the crystalline field anisotropy and the magnetic interaction are often of the same order of magnitude. Another complication due to the crystalline field anisotropy is that the effective spin quantum number is temperature dependent.

The total entropy of the spin system of $Fe(N_2H_5)_2(SO_4)_2$ up to about 80°K, as determined by means of the specific heat data (*1*), agrees with spin $S = 2$. This spin quantum number can be understood in the following way.

In a cubic octahedral field, the ^5D state, which is the ground state of the free Fe^{2+} ion, splits into a lower orbital triplet and a higher orbital doublet. The splitting of the orbital triplet, caused by the simultaneous action of an axial crystal field and spin-orbit coupling, has been calculated by Inomata and Oguchi (*35*) and Griffith (*36*). From their energy level diagram, it can be concluded that, if the effective spin value at low temperatures is $S = 2$, the ratio δ/λ (δ = ground state splitting and λ = spin-orbit coupling parameter) is fairly large and positive: $\delta/\lambda \approx 10$. This conclusion is in accordance with the results, obtained from magnetic and Mössbauer measurements by Nieuwpoort and Reedijk (*4*), that the octahedral coordination of the Fe ion is deformed into a compressed, tetragonal structure with four spectrochemically weak oxygen ligands in the equatorial plane and two spectrochemically strong nitrogen ligands in the axial direction. This deformation leads to a zero-field splitting parameter D.

We will first try to describe the magnetic properties of $Fe(N_2H_5)_2(SO_4)_2$ within the Heisenberg model applied to antiferromagnetic chains with $S = 2$ (in this model D is neglected). By means of the interpolation scheme of Weng (*7*), described in Section IIIc, theoretical susceptibility and specific heat curves for such chains are calculated. For χ_{max} and $T_{max}(\chi)$, the relations

$$kT_{max}(\chi)/|J| = 6.9 \qquad [14]$$

and

$$|J|\chi_{max}/Ng^2\beta^2 = 0.0937 \qquad [15]$$

are derived.

Theoretical susceptibility curves are also obtained by applying Eq. [14] of the scaling method, also described in Section IIIc, to the case $S = 2$. This method yields

$$kT_{max}(\chi)/|J| = 5.9 \qquad [16]$$

and

$$|J|/\chi_{max}/Ng^2\beta^2 = 0.1004 \qquad [17]$$

Because the latter approximation method becomes poorer for small spin values, Eqs.

[14] and [15] are probably more reliable than Eqs. [16] and [17].

With Eqs. [14] and [16] and the experimental value of $T_{\max}(\chi)$ (Table II), the values $J/k = -2.22 \pm 0.04$°K and $J/k = -2.59 \pm 0.05$°K are calculated respectively (Table III). The spectroscopic splitting factor g of $Fe(N_2H_5)_2(SO_4)_2$ is not known, but is usually anisotropic for Fe^{2+} compounds. Hence Eqs. [15] and [17] cannot be used. For these relations another problem also arises because the van Vleck paramagnetism probably cannot be neglected for the Fe compound. With our data it is not possible to determine the contribution of this effect to the total susceptibility. It is clear, however, that, corrected for the van Vleck term, the value of $\chi_{\max}$ will become smaller. Neglecting the van Vleck contribution and trying to fit the high-temperature part of the experimental susceptibility curve by means of the interpolation scheme, only very poor fits are found for J/k in the range $-(2.2\text{–}2.3)$°K and g in the range 3.1–3.2.

The magnetic anisotropy of the Fe compound motivates the use of the Ising model. For the interpretation of the experimental data one can consider, therefore, the following Hamiltonian:

$$\mathscr{H} = -2J \sum_{ij} S_i^z S_j^z + D \sum_i (S_i^z)^2,$$

where D is the crystal-field splitting parameter. In the case that the magnitude of D is comparable to J, the mathematics of the model become intractable. To obtain an estimate of J, we have neglected, therefore, the crystal-field splitting and apply the Ising model with $S = 2$. Within the Ising model no results were known for the parallel susceptibility $\chi_{\parallel}$ of linear chains with $S = 2$ (magnetic field parallel to the axis of anisotropy). Therefore, $\chi_{\parallel}$ is calculated by means of a matrix described in the literature (*37*) and used before by Wagner and Friedberg (*21*) for the case $S = 5/2$.[3]

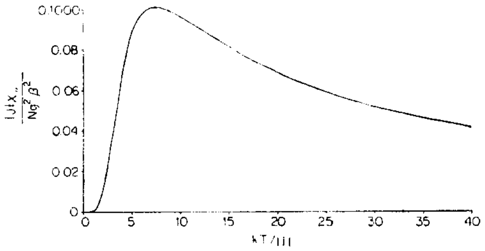

FIG. 5. $|J|\chi_{\parallel}/Ng^2\beta^2$ as a function of $kT/|J|$ for an antiferromagnetic Ising linear-chain system with $S = 2$.

The partition function of an Ising chain with n spins is given by $Z = \text{Tr}(P)^n$ where P is the symmetric matrix:

$$PS_zS_z' = \exp\left[2\frac{J}{kT}S_zS_z' - \frac{g\beta H}{kT}(S_z + S_z')\right].$$

In approximation the partition function is given by $Z = [\lambda(P)]^n$ with $\lambda(P)$ = largest eigen value of matrix P. For any case with specific S, J/k, and g values, χ can be obtained numerically by computer calculations of $\lambda(P)$ and $\partial[\lambda(P)]/\partial H$, using the relation

$$\chi = \lim_{H\to 0} \frac{kT\partial(\ln Z)}{H\partial H}.$$

From the numerical results obtained for $S = 2$ and a set values of J/k and g, the theoretical curve in which the dimensionless magnitude $|J|\chi_{\parallel}/Ng^2\beta^2$ is given as a function of the dimensionless magnitude $kT/|J|$, is composed (fig. 5). In this curve

$$kT_{\max}(\chi)/|J| = 7.5 \qquad [18]$$

and

$$|J|\chi_{\max}/Ng^2\beta^2 = 0.1009 \qquad [19]$$

The validity of this method is supported by the very good agreement between the $\chi_{\parallel}$ curves for $S = 1$ and $3/2$, obtained in the way described above, and the curves obtained by Suzuki *et al.* (*38*) for Ising chains with the same spin values.

Describing now the linear chains in $Fe(N_2H_5)_2(SO_4)_2$ with the Ising model, the value $J/k = -2.04 \pm 0.04$°K is found by means of Eq. [18] (Table III). But if J/k is calculated in this way, an error is introduced because the powder-susceptibility curve is made up of $\chi_{\parallel}$ and $\chi_{\perp}$ (magnetic field perpendicular to the direction of anisotropy). Unfortunately, for

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[3] The computer calculations necessary for this method have been carried out by J. A. R. van Veen and W. Vermin at the Department of Solid State Chemistry of the Gorlaeus Laboratories.

$\chi_\perp$ of Ising chains, a theoretical result (*39*) is known only for spin $S = 1/2$. For $S = 2$, nothing definite can be said about the influence of $\chi_\perp$ on the behavior of the susceptibility curve. Again, relation [19] cannot be used because the *g*-value and the van Vleck paramagnetism are unknown.

The specific heat measurements (*1*) give the experimental values $T_{\max}(C) = 12.3$°K and $C_{\max}/R = 0.96$. From the specific heat data, no indications are found that D is much larger than J. Therefore, the possibility that the magnetic system of the compound can be described by the Ising model with effective spin $S = 1/2$ can probably be excluded. For the antiferromagnetic Heisenberg linear-chain system with $S = 2$, the interpolation scheme yields the relations $C_{\max}/R = 0.67$ and $kT_{\max}(C)/|J| = 4.25$. For antiferromagnetic Ising chains with $S = 2$, it is known (*40*) that $C_{\max}/R = 1.48$ and $kT_{\max}(C)/|J| = 3.75$. So the experimental value of $C_{\max}/R$ lies between the theoretical values of the Heisenberg and Ising model, which is probably an indication that the character of the chain system in

$$\mathrm{Fe(N_2H_5)_2(SO_4)_2}$$

is intermediate between the two models. The experimental value of $T_{\max}(C)$ gives $J/k = -2.90$°K and $J/k = 3.28$°K for the Heisenberg and Ising models, respectively.

Summarizing all results obtained for J/k in the different theoretical models, it seems reasonable to estimate the value $J/k = -2.5 \pm 0.5$°K for the intrachain coupling. Without more experimental data and more sophisticated theoretical approximation methods, it is not possible to calculate a more precise result.

For $\mathrm{Fe(N_2H_5)_2(SO_4)_2}$, a reasonably trustworthy value of the transition temperature T_N at which 3-dimensional ordering sets in can be obtained from the susceptibility data, because for linear-chain compounds, there are reasons to believe (*11*, *41*) that in the powder-susceptibility curve T_N occurs at the maximum value of $\delta\chi/\delta T$. In Fig. 4, this maximum is located at $T_N = 5.5 \pm 0.5$°K. This value is confirmed by the specific heat measurements that revealed a transition temperature $T_N = 5.9$°K.

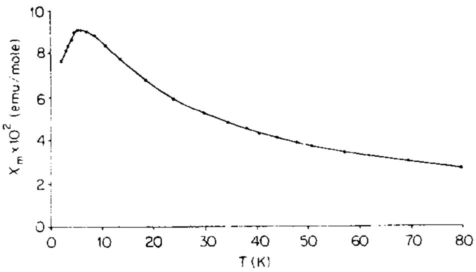

FIG. 6. Molar susceptibility χ_m of $\mathrm{Co(N_2H_5)_2(SO_4)_2}$ as a function of temperature; ○ = experimental points. A smooth curve is drawn through the experimental points.

(*f*) $\mathrm{Co(N_2H_5)_2(SO_4)_2}$

The experimental susceptibility curve of $\mathrm{Co(N_2H_5)_2(SO_4)_2}$ is depicted in Fig. 6. The susceptibility appeared to be field independent up to about 10 kOe. The results quoted refer to measurements at about 3 kOe. The broad maximum is noticed again and the high-temperature part of the reciprocal susceptibility curve obeys the Curie–Weiss law with $\theta = -22 \pm 1$°K.

In a cubic octahedral field the ^4F orbital state of the free $\mathrm{Co^{2+}}$ ion splits into three levels of which the lowest level ^4T is triply degenerate. Under the action of an axial or rhombic distortion of the crystal field in combination with spin-orbit coupling, the ^4T level splits into six Kramers doublets (*42*), causing the ground state of the $\mathrm{Co^{2+}}$ ion to be a doublet. Usually, the splitting between the lowest lying doublets is so large that at low temperatures an effective spin $S = 1/2$ can be used for the description of the spin system of $\mathrm{Co^{2+}}$ compounds with the Co ions in a distorted octahedral coordination, as is also the case for $\mathrm{Co(N_2H_5)_2(SO_4)_2}$. From the entropy at low temperatures, determined by the specific heat measurements, an effective spin $S = 1/2$ is indeed found. Furthermore, from the specific heat measurements, one derives that the splitting between the two lowest lying doublets is about 180°K, so that the contribution of the van Vleck term to the susceptibility cannot be neglected.

Due to the pronounced anisotropic character of many $\mathrm{Co^{2+}}$ compounds the Ising model is often used to describe the magnetic properties (*23*). However, the results of the specific heat measurements of $Co(N_2H_5)_2(SO_4)_2$ indicate that for this compound the Heisenberg and XY model (see Section IIIa) cannot be excluded in the first instance in the theoretical description (*vide infra*).

From theoretical calculations, it has been found that $C_{max}/R = 0.326$, 0.350, and 0.445 for the XY, Heisenberg, and Ising models of linear chains with $S = 1/2$, respectively (*13*, *14*, *38*, *40*). Experimentally, it is found that $C_{max}/R = 0.325$, which value is in good agreement with the XY and the Heisenberg models, but not at all in agreement with the Ising model.

Using the experimental values of $T_{max}(C) = 4.3°K$ and $T_{max}(\chi) = 5.7°K$ (Table II), it is calculated that $T_{max}(\chi)/T_{max}(C) = 1.33$, which value is in very good agreement with the theoretical value in the Heisenberg model (*13*). But this may be fortuitous in view of the fact that the powder-susceptibility curve of $Co(N_2H_5)_2(SO_4)_2$ is composed of $\chi_\perp$ and $\chi_\parallel$. The Ising model predicts (*14*, *38*, *39*):

$$T_{max}(\chi_\parallel)/T_{max}(C) = 2.40$$

and

$$T_{max}(\chi_\perp)/T_{max}(C) = 1.00$$

It is possible, therefore, that a mixture of both ratios gives a value for $T_{max}(\chi)_{powder}/T_{max}(C)$ that is in accordance with the value obtained from the Heisenberg model.

ESR measurements carried out at liquid hydrogen temperature[4] on a sample of the compound $Zn(N_2H_5)_2(SO_4)_2$ doped with about 1% Co^{2+} revealed the following values of the *g*-components:

$$g_1 = 2.20 \pm 0.01;$$
$$g_2 = 4.40 \pm 0.02;$$
$$g_3 = 5.45 \pm 0.02,$$

which values will probably not differ very much from the *g*-values of the undiluted compound $Co(N_2H_5)_2(SO_4)_2$. From the difference in magnitudes of the *g*-values, it is obvious that a considerable anisotropy is present. It may be noted that one *g*-value is relatively small and the other two *g*-values are much larger. This fact, in combination with the experimental value of C_{max}/R (see above), indicates that the XY model could be the appropriate model to describe the magnetic properties of $Co(N_2H_5)_2(SO_4)_2$. Besides this model also the Heisenberg and Ising model will be used for the interpretation.

XY Model

Calculations on basis of this model (*14*, *23*) give

$$kT_{max}(\chi_\perp)/|J| = 0.64 \qquad [20]$$

and

$$|J|\chi_{max}(\perp)/Ng^2\beta^2 = 0.174. \qquad [21]$$

Combining the experimental value of $T_{max}(\chi)$ with Eq. [20] yields $J/k = -8.9 \pm 0.3°K$ (Table III), but in this way the contribution of $\chi_\parallel$ to χ_{powder} is neglected. However, for $\chi_\parallel$ no theoretical results are known. By using Eq. [21] problems arise due to the lack of knowledge about the van Vleck contribution. Another complication concerns the fact that the *g*-values obtained by the ESR measurements are identified with the axes of the distorted octahedra and these axes do not coincide with the crystal axes. From the relation (*14*) $kT_{max}(C)/|J| \approx 0.64$ and the experimental value $T_{max}(C) = 4.3°K$, it is calculated that $J/k = -6.7°K$ (Table III).

Heisenberg Model

Within the Heisenberg model, the relations [12] and [13] (Section IIId) are valid (*13*) for antiferromagnetic chains with $S = 1/2$. With Eq. [11] and the experimental $T_{max}(\chi)$, it is calculated that $J/k = -4.5 \pm 0.1°K$ (Table III). The application of Eq. [13] gives rise to problems, due to the anisotropic *g*-values and the van Vleck term. Neglecting the van Vleck term and using the experimental value of χ_{max} (Table II) and the *g*-value $g_{av} = [\frac{1}{3}(g_1^2 + g_2^2 + g_3^2)]^{1/2} = 4.23$, the intrachain interaction is calculated to be $J/k = -5.40°K$. If the χ curve were corrected for the van Vleck contribution, χ_{max}(exp.) would be lower and $|J/k|$, therefore, higher.

A theoretical fit with the experimental curve was not found within the Heisenberg model.

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[4] These measurements were carried out by J. van Dijk at the Department of Chemistry, Technological University, Delft (The Netherlands), by means of a Varian E 3-instrument.

From the experimental $T_{\max}(C)$ and the relation (*13*) $kT_{\max}(C)/J = 0.962$, the value $J/k = -4.47$°K is obtained (Table III).

Ising Model

If we want to describe the powder-susceptibility curve with the Ising model, $\chi_\parallel$ as well as $\chi_\perp$ have to be taken into account. For $\chi_\parallel$ it is calculated theoretically that

$$kT_{\max}(\chi_\parallel)/|J| = 1 \qquad [22]$$

and

$$|J|\chi_{\max}(\perp)/Ng^2\beta^2 = 0.09197. \qquad [23]$$

For $\chi_\perp$ one knows that (*39*)

$$kT_{\max}(\chi_\perp)/|J| = 0.4186 \qquad [24]$$

and

$$|J|\chi_{\max}(\perp)/Ng^2\beta^2 = 0.2999. \qquad [25]$$

From relations [22] and [24], the values $J/k = -5.7$°K and $J/k = -13.6$°K are obtained. In a powder-susceptibility curve, $T_{\max}$(exp.) will lie between $T_{\max}$(exp.) of $\chi_\perp$ and $T_{\max}$(exp.) of $\chi_\parallel$, so that the real value of J/k would lie between −5.7 and −13.6°K. The averaged value $J/k = -9.7$°K of these two results provides a rough estimate of the exchange interaction. Due to reasons mentioned above, the use of Eqs. [23] and [25] gives rise to problems again.

By means of the results (*13*, *39*) for $\chi_\parallel$ and $\chi_\perp$, as calculated in the Ising model with $S = 1/2$:

$$\chi_\parallel = (Ng^2\beta^2/4kT)\exp(-|J|/kT), \qquad [26]$$

$$\chi_\perp = (Ng^2\beta^2/4|J|)(\tanh(|J|/2kT) + (|J|/2kT)\,\mathrm{sech}|J|/2kT), \qquad [27]$$

and the formula

$$\chi_{\text{powder}} = \tfrac{1}{3}\chi_\parallel + \tfrac{2}{3}\chi_\perp, \qquad [28]$$

we have tried to find a best fit with the experimental susceptibility curve. However, this was not feasible. Of course, the van Vleck contribution plays a role here. Also, the discrepancy between the real magnetic system and the Ising model may be too large to justify the use of the pure Ising system. But it was possible with Eqs. [26–28] to obtain agreement between the theoretical value of $T_{\max}(\chi)$ and the experimental value (Table II) for $J/k \approx -11.5$°K (Table III) and $g \approx 3.5$.

By means of the experimental value of $T_{\max}(C)$ and the relation $kT_{\max}(C)/|J| = 0.416$ as found for the Ising model (*14*, *39*, *40*), we derive $J/k = -10.3$°K (Table III).

Summarizing, we believe, particularly from the specific heat and ESR measurements, that the XY model gives the best approximation for the magnetic system in $Co(N_2H_5)_2(SO_4)_2$ and that, therefore, $J/k \approx -7$ to -8°K (Table III). But our measurements do not give sufficient information to put this assumption on sound footing.

Finally, it may be mentioned that the specific heat measurements on

$$Co(N_2H_5)_2(SO_4)_2$$

showed a magnetic transition point at 1.57°K, indicating that the interchain coupling is much weaker than the intrachain coupling.

IV Intra- and Interchain Interaction

Summarizing all results obtained on the various $M(N_2H_5)_2(SO_4)_2$ compounds, it is concluded that for the Mn and Cu compounds reliable values for the intrachain interaction are obtained. For the Ni compound, the results of susceptibility and specific heat measurements show large differences that possibly can be explained by the presence of a single-ion anisotropy of the same order of magnitude as J. The J/k-value calculated from the susceptibility data seems to give a reasonable estimate. For the Fe and Co compound, no precise values of J/k can be derived because both compounds are probably examples of magnetic systems intermediate between the Heisenberg and Ising models and between the Heisenberg and XY models, respectively. Estimates about the order of magnitude of J/k are given in Table III, together with the J/k-values of the other compounds.

The question arises, what is the origin of the relatively strong intrachain coupling, in spite of the presence of three intervening nonmagnetic ligands in the most probable superexchange path in the chains: M-O-S-O-M? Usually such a number of intervening ligands allows only a very weak interaction.

This long-range superexchange mechanism is probably of the same nature as is found in $LiMnPO_4$ (*43*) (superexchange path Mn–O–P–O–Mn), $LiCuVO_4$ (*44*) (superexchange path Cu–O–V–O–Cu), and in a number of other compounds which have been reviewed by Blasse (*45*). It can be explained by assuming strongly covalent S–O bonds, due to the high electron affinity of the S^{6+} ion in the $(SO_4)^{2-}$ group.

The specific heat and susceptibility data indicate that the interchain coupling is much weaker than the intrachain coupling. This is probably due to the weak hydrogen bonds that form the links between the N_2H_5 groups and SO_4 groups of neighboring chains. About the ratio between the interchain coupling J' and the intrachain coupling J, the following can be remarked.

Oguchi has calculated (*46*) by means of Green function techniques an approximate, numerical relation between the transition point T_N of an antiferromagnetic Heisenberg linear-chain system (with general spin S and interchain coupling J') and the ratio $|J'/J|$ for a tetragonal lattice structure. By means of these results, information about the magnitude of the ratio $|J'/J|$ is obtained, using the experimentally determined T_N-values. This method can only give an order of magnitude estimate in our case since the crystal structure of the $M(N_2H_5)_2(SO_4)_2$ compounds is triclinic and several of the compounds cannot be described by the Heisenberg model. Another complication is that the interchain interactions along the *a*- and *c*-axes are probably not equal, due to the difference between the lengths of these axes (ratio between the lengths ≈ 0.8).

Using (a) the experimentally determined T_N-values for the Mn, Fe, and Co compounds, (b) the fact that for the Ni and Cu compounds no transition point is detected down to 1.5°K, and (c) the J/k-values, which are estimated for the different compounds (Table III), the ratios $|J'/J|$, given in Table III, are obtained. It is seen clearly that $|J'| \ll |J|$.

The main conclusion to be drawn from these numbers is that J' is very much smaller than J, so that the analysis in terms of linear-chain models is very appropriate for these compounds.

Acknowledgments

The present investigations have been carried out partly under the auspices of the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

The authors are indebted to Prof. W. J. Huiskamp and Dr. W. J. A. Maaskant for many valuable discussions. The aid with the ESR measurements, zero-field susceptibility measurements, and synthesis of the compounds by Dr. B. Nieuwenhuijse (Twente University of Technology), Dr. J. van Dijk (Delft University of Technology), Dr. S. Hillaert (Kamerlingh Onnes Laboratory), and Mr J. A. Smit (Department of Coordination Chemistry, Leyden) respectively is gratefully acknowledged.

Dr. F. W. Klaaijsen is thanked for making available specific heat results prior to publication.

References

1. F. W. KLAAIJSEN AND F. DOKOUPIL, to be published.
2. C. K. PROUT AND H. M. POWELL, *J. Chem. Soc.* **1961**, 4177 (1961).
3. D. W. HAND AND C. K. PROUT, *J. Chem. Soc.* **A1966**, 168 (1966).
4. A. NIEUWPOORT AND J. REEDIJK, *Inorg. Chim. Acta*, **7**, 323 (1973).
5. P. W. SELWOOD, "Magnetochemistry," Interscience Publishers, Inc., New York (1956).
6. H. T. WITTEVEEN AND J. REEDIJK, *Solid State Commun.*, **12**, 1121 (1973).
7. C. WENG, Thesis, Carnegie-Mellon University (1968).
8. A. P. GINSBERG, R. L. MARTIN, AND R. C. SHERWOOD, *Inorg. Chem.* **11**, 2884 (1972).
9. F. W. KLAAIJSEN, J. REEDIJK, AND H. T. WITTEVEEN, *Z. Naturforsch.* **27a**, 1532 (1972).
10. N. ACHIWA, *J. Phys. Soc. Japan* **27**, 561 (1969).
11. H. T. WITTEVEEN AND J. A. R. VAN VEEN, *J. Phys. Chem. Solids*, in press.
12. M. MEKATA, K. ADACHI, H. TAKAKI, AND N. ACHIWA, Proc. 12th Int. Conf. Low Temp., Kyoto, p. 801 (1970).
13. J. C. BONNER AND M. E. FISHER, *Phys. Rev.* **135**, A640 (1964).
14. S. KATSURA, *Phys. Rev.* **127**, 1508 (1962).
15. S. INAWASHIRO AND S. KATSURA, *Phys. Rev.* **140**, 892 (1965).
16. R. B. GRIFFITHS, *Phys. Rev.* **133**, A768 (1964).
17. T. HASEDA AND H. KOBAYASHI, *J. Phys. Soc. Japan* **19**, 1260 (1964).

18. M. MATSUURA, *Phys. Letters*, **34A**, 274 (1971).
19. M. E. FISHER, *Amer. J. Phys.* **32**, 343 (1964).
20. G. S. RUSHBROOKE AND P. J. WOOD, *Mol. Phys.* **1**, 257 (1958).
21. G. R. WAGNER AND S. A. FRIEDBERG, *Phys. Letters* **9**, 11 (1964).
22. F. SMITH AND S. A. FRIEDBERG, *Phys. Rev.* **176**, 660 (1968).
23. L. J. DE JONGH AND A. R. MIEDEMA, *Advanc. Phys.* in press.
24. L. C. JACKSON, *Proc. Roy. Soc. (London)* **A140**, 695 (1933).
25. L. C. JACKSON AND H. KAMERLINGH ONNES, *Proc. Roy. Soc. (London)* **A104**, 671 (1923).
26. M. DATE, *J. Phys. Soc. Jap.* **12**, 1314 (1957).
27. M. LECONTE, J. DE GUNZBOURG, M. FEYRAL, A. MEEDAN-GROS, AND G. ALLAIN, *Solid State Commun.* **10**, 235 (1972).
28. J. SKALYO, JR., AND G. SHIRANE, *Phys. Rev.* **B2**, 4632 (1970).
29. V. J. MINCKIEWICZ, D. E. COX, AND G. SHIRANE, *Solid State Commun.* **8**, 1001 (1970).
30. R. KUBO AND K. TOMITA, *J. Phys. Soc. Japan* **9**, 888 (1954).
31. E. J. PLEAU AND G. F. KOKOSZKA, *Inorg. Nucl. Chem. Letters* **8**, 779 (1972).
32. T. MORIYA, *Progr. Theor. Phys.* **16**, 23 (1956).
33. R. D. DOWSING, B. NIEUWENHUIJSE, AND J. REEDIJK, *Inorg. Chim. Acta* **5**, 301 (1971).
34. S. HILLAERT, Ph.D. thesis, Leyden, 1973.
35. K. INOMATA AND T. OGUCHI, *J. Phys. Soc. Japan* **23**, 765 (1967).
36. J. S. GRIFFITH, "The theory of Transition-Metal Ions," p. 357, Cambridge University Press (1961).
37. G. F. NEWELL AND E. W. MONTROLL, *Rev. Mod. Phys.* **26**, 353 (1953).
38. M. SUZUKI, B. TSUJIYAMA, AND S. KATSURA, *J. Math. Phys.* **8**, 124 (1967).
39. M. E. FISHER, *J. Math. Phys.* **4**, 124 (1963).
40. T. OBAKATA AND T. OGUCHI, *J. Phys. Soc. Japan* **25**, 322 (1968).
41. L. J. DE JONGH, private communication.
42. A. ABRAGHAM AND M. H. L. PRYCE, *Proc. Royal Soc. (London)* **A206**, 173 (1951).
43. J. M. MAYS, *Phys. Rev.* **131**, 38 (1963).
44. H. SAJI, *J. Phys. Soc. Japan* **33**, 671 (1972).
45. G. BLASSE, *Philips Res. Reports* **20**, 327 (1965).
46. T. OGUCHI, *Phys. Rev.* **133**, A1098 (1964).