Contribution from the
Department of Inorganic Chemistry University
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The Metal-Metal Interaction in Coordination Compounds. Magnetic Properties. III. The $d^n d^n$ and $d^n d^m$ Electron Systems with Positive Exchange Integral.

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Assuming that the exchange integral takes positive values, the magnetic susceptibilities within the range 10 to 300°K were calculated for the Me-Me system with the following electron structures: $d^1 d^1$, $d^2 d^2$, $d^3 d^3$, $d^4 d^4$, $d^5 d^5$, $d^2 d^1$, $d^3 d^1$, $d^4 d^1$, $d^5 d^1$, $d^3 d^2$, $d^4 d^2$, $d^5 d^2$, $d^4 d^3$, $d^5 d^3$, $d^5 d^4$. The magnetic moment of this system was shown to change with the increase of the exchange integral J from $\mu = \sqrt{2}\{\sqrt{S_1(S_1+1)} + \sqrt{S_2(S_2+1)}\}\mu_B$ to $\mu = 2\sqrt{S(S+1)}\mu_B$, where $S = |S_1+S_2|$.

Introduction

In papers [1] and [2] the equations are given and the theoretical magnetic susceptibility curves are plotted for the system Me-Me with the following electron structures: $d^1 d^1$, $d^2 d^2$, $d^3 d^3$, $d^4 d^4$, $d^5 d^5$, $d^2 d^1$, $d^3 d^1$, $d^4 d^1$, $d^5 d^1$, $d^3 d^2$, $d^4 d^2$, $d^5 d^2$, $d^4 d^3$, $d^5 d^3$, $d^5 d^4$.

The calculations have been made for various negative values of the exchange integral J.

In order to obtain a full view of magnetic properties of the Me-Me system, similar calculations have been made for the above electron structures of this system with the exchange integral J taking positive values.

Calculations

In order to calculate the magnetic susceptibility of the Me-Me system, the magnetic susceptibility equations for this system in various electron structures were used; these were given in papers [1] and [2]. The calculations have been made for the following values of J, 0, +50, +100, +150, ... +500 cm^{-1}, and at temperatures T lying in the range: 10, 20, 30, ... 300°K for each value of J.

Some results of these calculations are given in Figures 1-15. In these figures the values of the exchange integral J are given in cm^{-1}.

The numerical values of the magnetic susceptibility were calculated in an ELLIOTT-803 computer in the Department of Numerical Methods, University of Wroclaw.

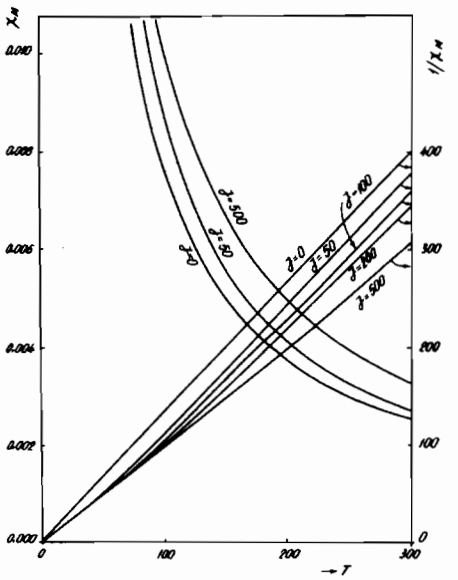

Figure 1. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^1 d^1$ electronic structure of the Me-Me system.

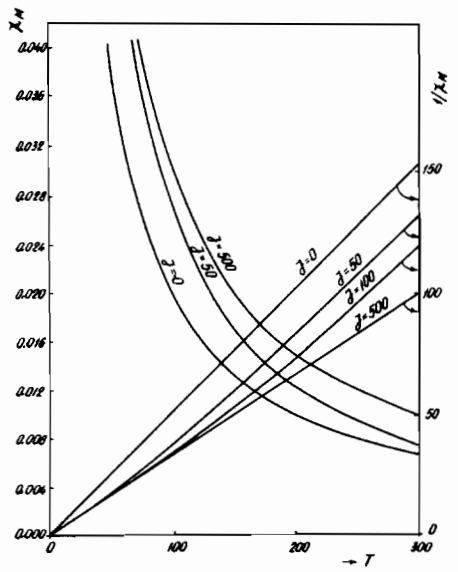

Figure 2. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^2 d^2$ electronic structure of the Me-Me system.

(1) W. Wojciechowski, *Inorg. Chim. Acta*, *1*, 319(1967).
(2) W. Wojciechowski, *Inorg. Chim. Acta*, *1*, 324(1967).

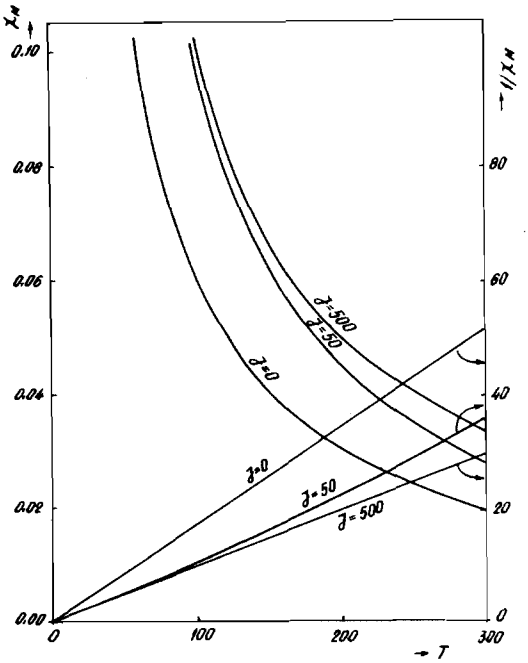

Figure 3. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^3\,d^3$ electronic structure of the Me-Me system.

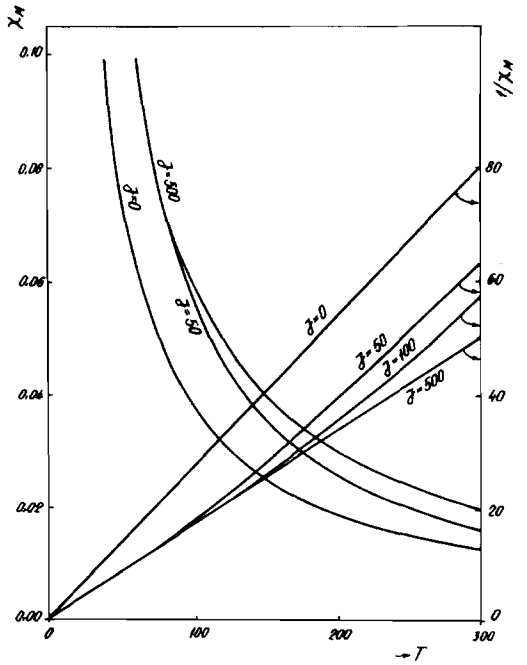

Figure 4. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^4\,d^4$ electronic structure of the Me-Me system.

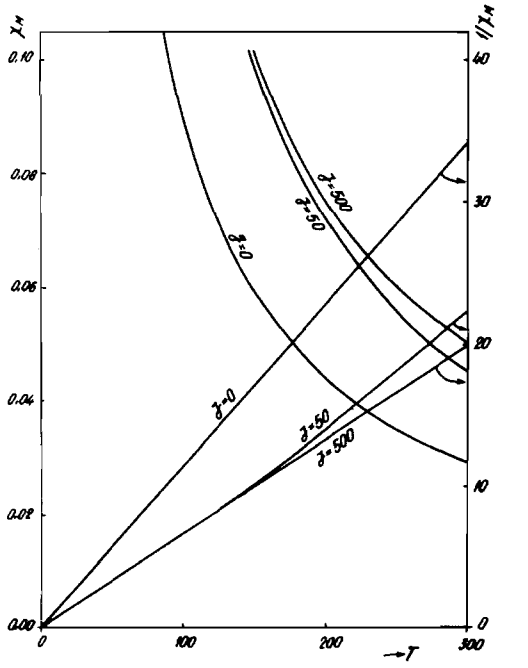

Figure 5. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^5\,d^5$ electronic structure of the Me-Me system.

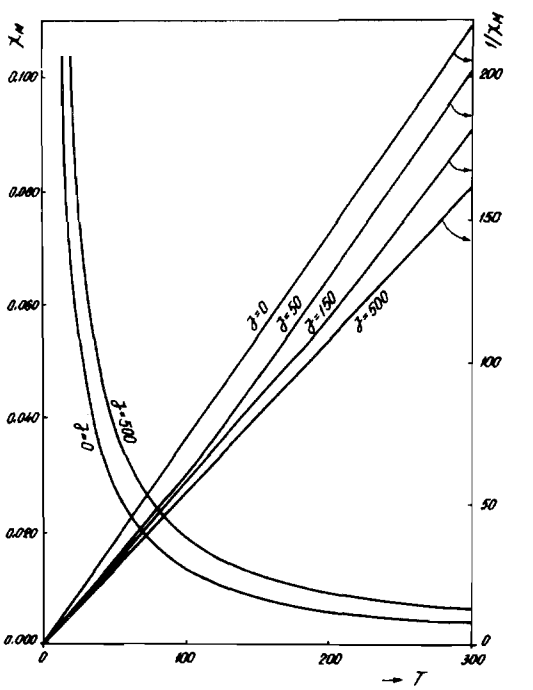

Figure 6. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^2\,d^1$ electronic structure of the Me-Me system.

Discussion

In the case of the positive of the exchange integral J the magnetic moment computed on the basis of the Curie law, is increasing for all examined systems (Table I).

The values of the magnetic moments μ_1 and μ_2 given in Table I were calculated under assumption that the contribution of each electron to magnetic susceptibility of the Me-Me system is the same.

For the exchange integral J = 500 cm^{-1}, in all cases, the reciprocal value of the magnetic susceptibility, plotted against the temperature takes the linear form with Weiss constant equal to zero. For indirect

Table I. The magnetic moments for the Me-Me system (in μ_B)

No	Electronic structure	J (in cm^{-1})	$\mu_{Me\text{-}Me}/\sqrt{2}$	$\mu_{Me\text{-}Me}$	μ_1	μ_2	$(\mu_1+\mu_2)/2$
1	$d^1\,d^1$	0	1.73	2.44	1.73	1.73	1.73
		500	2.00	2.83	2.00	2.00	2.00
2	$d^2\,d^2$	0	2.84	4.01	2.84	2.84	2.84
		500	3.48	4.92	3.48	3.48	3.48
3	$d^3\,d^3$	0	3.87	5.47	3.87	3.87	3.87
		500	4.92	6.96	4.92	4.92	4.92
4	$d^4\,d^4$	0	4.90	6.92	4.90	4.90	4.90
		500	6.35	8.99	6.35	6.35	6.35
5	$d^5\,d^5$	0	5.90	8.34	5.90	5.90	5.90
		500	7.80	11.01	7.80	7.80	7.80
6	$d^2\,d^1$	0	2.36	3.34	2.73	1.93	2.33
		500	2.73	3.87	3.15	2.23	2.69
7	$d^3\,d^1$	0	3.01	4.26	3.96	2.13	2.91
		500	3.48	4.92	4.25	2.46	3.35
8	$d^4\,d^1$	0	3.68	5.21	4.67	2.33	3.50
		500	4.21	5.95	5.31	2.65	3.98
9	$d^5\,d^1$	0	4.39	6.20	5.67	2.52	4.09
		500	4.92	6.95	6.34	2.84	4.59
10	$d^3\,d^2$	0	3.26	4.62	3.58	2.92	3.25
		500	4.21	5.95	4.61	3.75	4.18
11	$d^1\,d^2$	0	4.04	5.71	4.65	3.28	3.97
		500	4.93	6.96	5.71	4.03	4.87
12	$d^5\,d^2$	0	4.64	6.55	5.53	3.49	4.51
		500	5.64	7.97	6.73	4.26	5.49
13	$d^4\,d^3$	0	4.44	6.27	4.74	4.10	4.41
		500	5.64	7.97	6.02	5.21	5.61
14	$d^5\,d^3$	0	4.93	6.96	5.50	4.27	4.88
		500	6.35	8.99	7.10	5.50	6.30
15	$d^5\,d^4$	0	5.39	7.71	5.75	5.13	5.44
		500	7.09	10.00	7.47	6.67	7.04

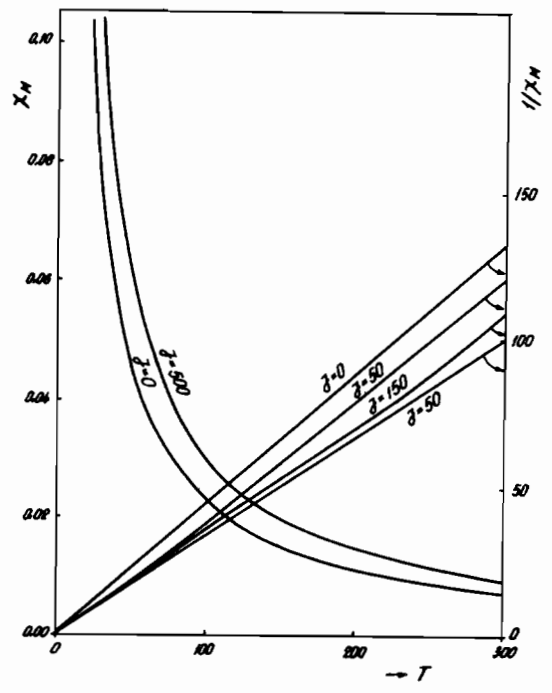

Figure 7. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^3\,d^1$ electronic structure of the Me-Me system.

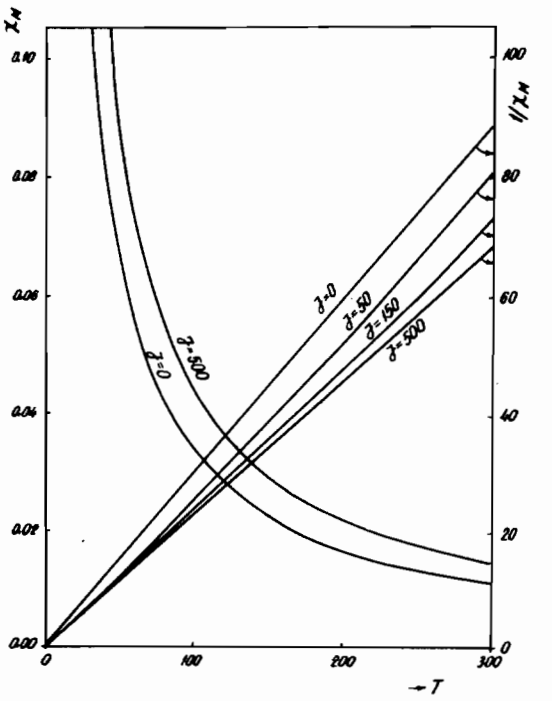

Figure 8. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^4\,d^1$ electronic structure of the Me-Me system.

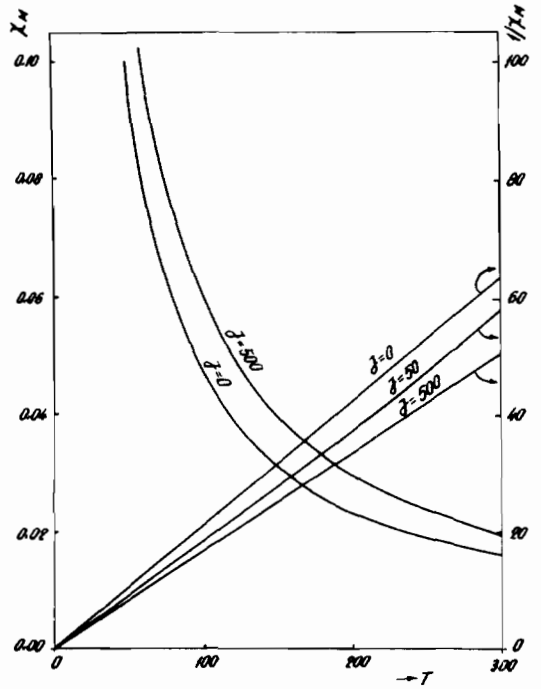

Figure 9. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^5\,d^1$ electronic structure of the Me-Me system.

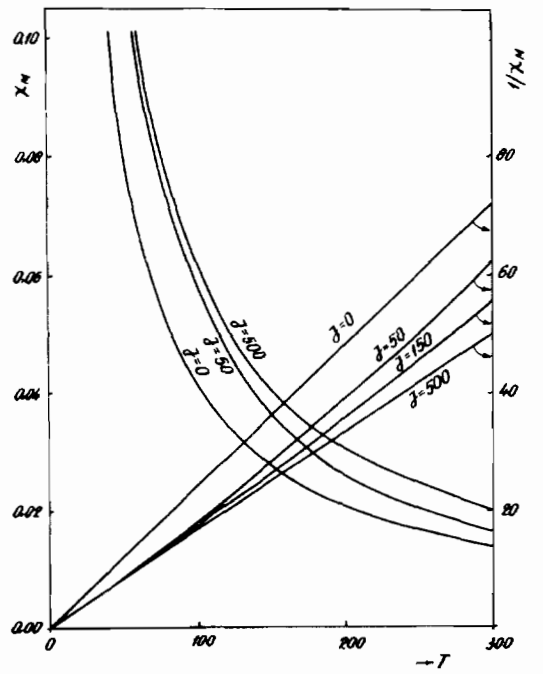

Figure 11. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^4\,d^2$ electronic structure of the Me-Me system.

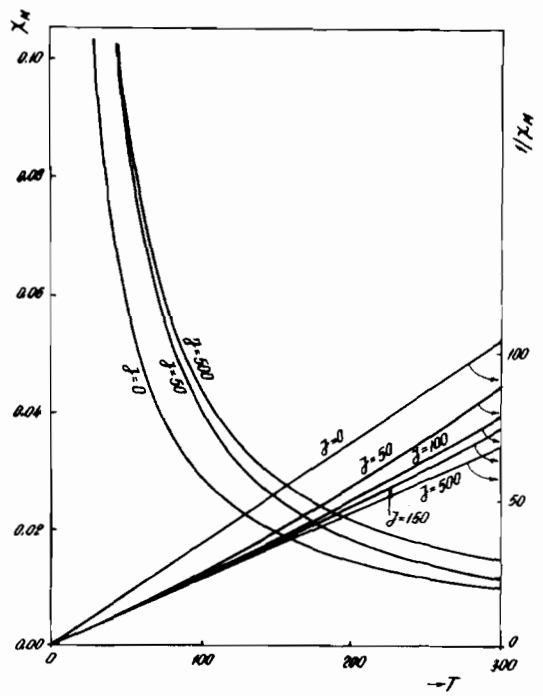

Figure 10. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^3\,d^2$ electronic structure of the Me-Me system.

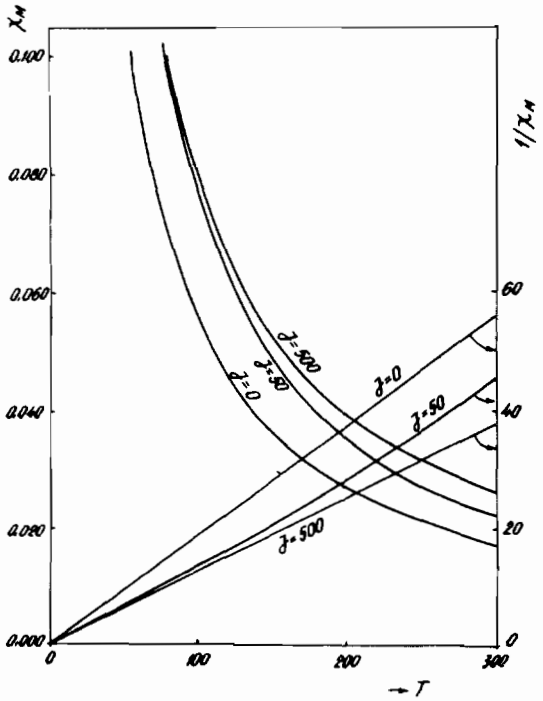

Figure 12. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^5\,d^2$ electronic structure of the Me-Me system.

values of the exchange integral, i.e. from $J = 0$ to $J = 500\ cm^{-1}$ the magnetic susceptibility obeys, in the small range of temperatures, the Curie-Weiss law. In low temperatures the curves $\chi_M^{-1} = f(T, J)$ are convergent to the straigh line given by the dependence $\chi_M^{-1} = f(T, J = 500\ cm^{-1})$ (Figures 1-15).

On the basis of the Figures 1-15, may be assumed, that for the values of $J > 500\ cm^{-1}$, in the considered range of the temperature, the magnetic susceptibility will take the same values as for the value $J = 500\ cm^{-1}$.

Thus the two straight lines, $\chi_M^{-1} = f(T, J=0)$ and $\chi_M^{-1} = f(T, J>500\ cm^{-1})$ limit the ferromagnetic properties of compounds which are exhibiting the Me-Me system.

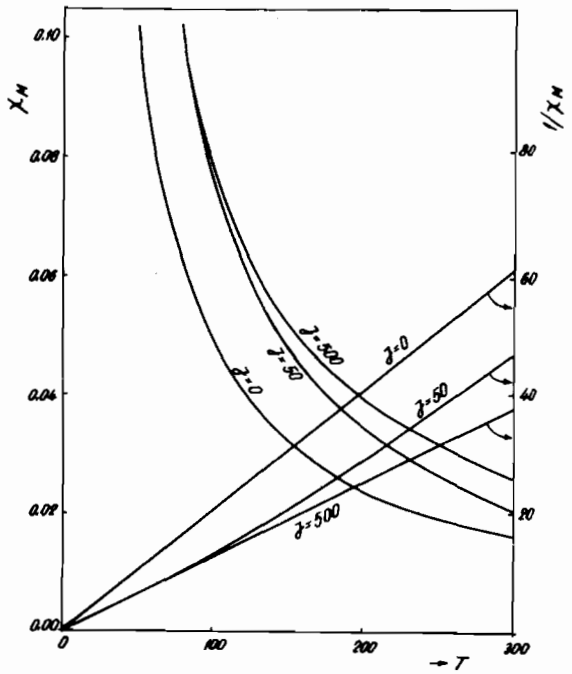

Figure 13. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^4\,d^1$ electronic structure of the Me-Me system.

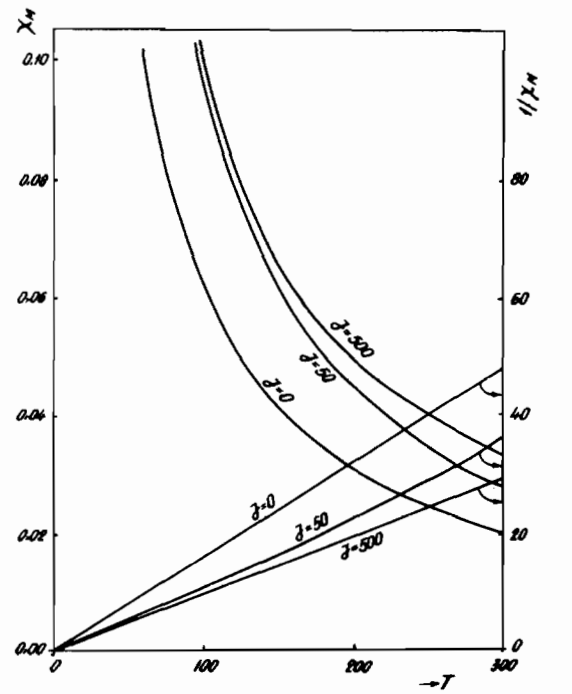

Figure 14. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^5\,d^3$ electronic structure of the Me-Me system.

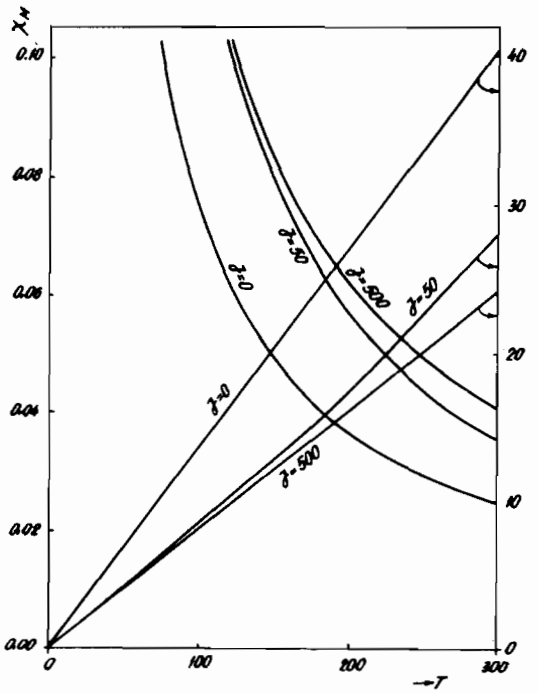

Figure 15. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^5\,d^4$ electronic structure of the Me-Me system.

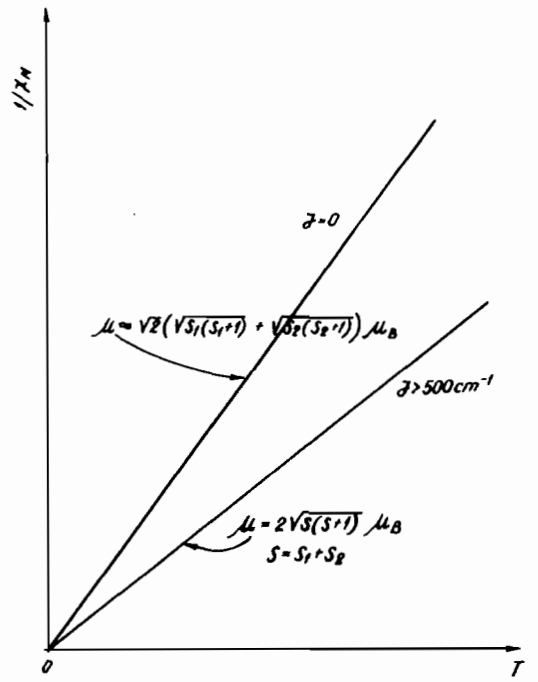

Figure 16. Temperature dependence of the reciprocal magnetic susceptibility for high values of J and for J=0.

It is characteristic that in the case of big values of the exchange integral J the magnetic moments depend only on the number of electrons 2S, of the metal ions interacting with themselves.

The table makes it clear that the magnetic moment of the Me-Me system for big J values is equal to

$$\mu = 2\sqrt{S(S+1)}\mu_B \qquad (1)$$

where $S = S_1 + S_2$. This means that in the case of positive J values the magnetic changes from the value (2):

$$\mu = \sqrt{2}\{\sqrt{S_1(S_1+S_2)} + \sqrt{S_2(S_2+1)}\}\mu_B \qquad (2)$$

Table II. The dependence of the magnetic moments for the Me-Me system on the value of quantum number 2S

$2S=2(S_1+S_2)$	Electronic structure	$\mu_{Me\text{-}Me}$ (for $J=500\ cm^{-1}$) in μ_B	$\mu=2\sqrt{S(S+1)}$ (in μ_B)
2	$d^1\ d^1$	2.84	2.84
3	$d^2\ d^1$	3.86	3.87
4	$d^2\ d^2$ $d^3\ d^1$	4.92 4.92	4.90
5	$d^4\ d^1$ $d^3\ d^2$	5.95 5.95	5.95
6	$d^3\ d^3$ $d^5\ d^1$ $d^4\ d^2$	6.96 6.96 6.96	6.94
7	$d^5\ d^2$ $d^4\ d^3$	7.97 7.97	7.94
8	$d^4\ d^4$ $d^5\ d^3$	8.99 8.99	8.96
9	$d^5\ d^4$	10.00	9.95
10	$d^5\ d^5$	11.01	10.95

to the value

$$\mu = 2\sqrt{S(S+1)}\mu_B, \qquad (3)$$

where $S = S_1+S_2$.

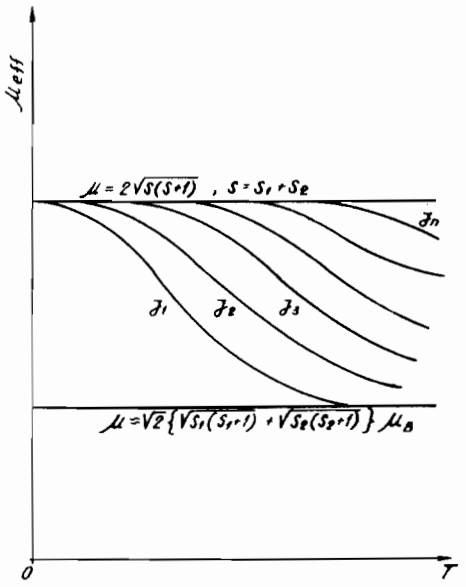

Figure 17. Temperature dependence of the magnetic moment μ_{eff} on the exchange integral J for a $d^n\ d^n$ and $d^n\ d^m$ electronic structure of the Me-Me system.

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