Contribution from the
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The Metal-Metal Interaction in Coordination Compounds. Magnetic Properties. II. The $d^n d^m$ Electron Systems with Negative Exchange Integral.

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The magnetic susceptibility functions of the Me-Me system of a d^n d^m electronic configuration have been derived, where n and m are equal to 1, 2, 3, 4, 5 and for a given electron configuration $n \neq m$. Theoretical magnetic susceptibility curves have been plotted against temperature for these electron configurations at different negative values of the exchange integral J. The applicability of the Curie and Curie-Weiss laws was examined. The magnetic moment of the Me-Me system was shown to be changed with the increase of the (—J) from

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

to $\mu = 2\sqrt{S(S+1)}\mu_B$ *where* $S = |S_1-S_2|$.

Introduction

In the previous work [1] the magnetic susceptibility functions of the Me-Me system of a d^n d^m electronic structure have been derived, where n was equal to 1, 2, 3, 4, 5. The temperature dependence of the magnetic susceptibility was also calculated for these configuration at various magnitudes of the exchange integral J. These calculations enabled to find out a relationship between that integral and the Néel temperature T_N as well as permitted to plot the temperature dependence of the magnetic moment μ_{eff} (calculated from the Curie law) at constant values of the exchange integral J.

The present paper has taken into account the Me-Me interaction for d^n d^m electronic structure, where n and m are equal to 1, 2, 3, 4, 5 and for a given electron configuration n is always different from m. Such calculations have been made for the d^5 d^3 electronic structure of the Me-Me system.[2] The compounds containing the Me-Me systems are known but, however only a few experimental data are available on their magnetic properties.[3-7]

Calculations

The magnetic susceptibility functions of the d^n d^m electronic structure of the Me-Me system have been derived analogically to those of the magnetic susceptibility for the d^n d^n electronic structure.[1] Ten electron configurations of the following spin systems: (1, 1/2), (3/2, 1/2), (2, 1/2), (5/2, 1/2), (3/2, 1), (2, 1), (5/2, 1), (2, 3/2), (5/2, 3/2), (5/, 2) have been discussed. The results are given in Table I.

In Table I g is the spectroscopic splitting factor, β is the Bohr's magneton, k is Boltzmann's constant, T is the temperature.

The numerical values of the magnetic susceptibility for particular spin systems have also been calculated. These calculations were made for the J assuming the values of 0, —10, —20, —30, —40, —50, —100, —150 ..... —500 cm^{-1} and T assuming the values 10, 20, 30, ... 300°K for each value of J. The results were computed in the Department of Numerical Methods of thes Wroclaw University in an ELLIOT-803 computer.

The results are presented in Figures 1 to 10. The value of J in these figures is given in cm^{-1}, and Θ is a constant in the Curie-Weiss equation.

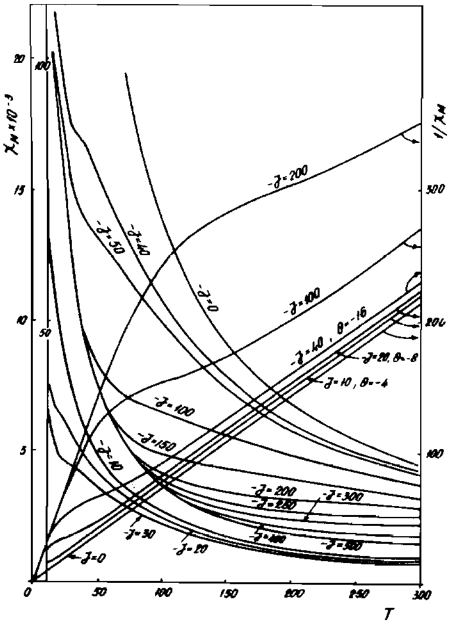

Figure 1. The magnetic susceptibility curves and their reciprocals for various values of J according to the temperature for the d^2 d^1 electronic structure of the Me-Me system.

(1) W. Wojciechowski, *Inorg. Chim. Acta, 1,* 319 (1967).
(2) K. Kambe, *J. Phys. Soc. Japan, 5,* 48 (1950).
(3) R. S. Nyholm, E. Coffey, J. Lewis, Proceedings 7ICCC, Stockholm and Uppsala, p. 66 (1962).
(4) R. C. Thompson, *J. Am. Chem. Soc., 70,* 1045 (1948).
(5) A. K. Battacharya, *J. Indian Chem. Soc., 18,* 71 (1941).
(6) D. Davidson, L. A. Welo, *J. Phys. Chem., 32,* 1191 (1928).
(7) L. A. Welo, *Phil. Mag., 6,* 481 (1928).

Table I. Magnetic susceptibility and energy levels of the Me-Me system with a $d^n d^m$ electronic configuration

Electronic structure	S_1	S_2	S	$-JS_1S_2$: $-1/2\,J[S(S+1)]$	$-JS_1S_2$: $1/2\,J[S_1(S_1+1)+S_2(S_2+1)]$	$\chi = N\dfrac{g^2\beta^2}{kT}\sum_S \sum_{M_s=-S}^{S} M_s^2 \exp\left[-\dfrac{E^\circ(S)}{kT}\right] \Big/ \sum_S \sum_{M_s=-S}^{S} \exp\left[-\dfrac{E^\circ(S)}{kT}\right]$	No
d^2d^1	1	1/2	3/2 1/2	−15/8 J −3/8 J	+11/8 J +11/8 J	$\chi = N\dfrac{g^2\beta^2}{kT}\,\dfrac{(1/2)\exp(-3J/2kT)+5}{2\exp(-3J/2kT)+4}$	(1′)
d^3d^1	3/2	1/2	2 1	−3 J −J	+9/4 J +9/4 J	$\chi = N\dfrac{g^2\beta^2}{kT}\,\dfrac{2\exp(-2J/kT)+10}{3\exp(-2J/kT)+5}$	(2′)
d^4d^1	2	1/2	5/2 3/2	−35/8 J −15/8 J	+27/8 J +27/8 J	$\chi = N\dfrac{g^2\beta^2}{2kT}\,\dfrac{10\exp(-5J/2kT)+35}{4\exp(-5J/2kT)+6}$	(3′)
d^5d^1	5/2	1/2	3 2	−6 J −3 J	+19/4 J +19/4 J	$\chi = N\dfrac{g^2\beta^2}{kT}\,\dfrac{10\exp(-3J/kT)+28}{5\exp(-3J/kT)+7}$	(4′)
d^3d^2	3/2	1	5/2 3/2 1/2	−35/8 J −15/8 J −3/8 J	+23/8 J +23/8 J +23/8 J	$\chi = N\dfrac{g^2\beta^2}{kT}\,\dfrac{(1/2)\exp(-4J/kT)+5\exp(-5J/2kT)+(35/2)}{2\exp(-4J/kT)+4\exp(-5J/2kT)+6}$	(5′)
d^4d^2	2	1	3 2 1	−6 J −3 J −J	+4 J +4 J +4 J	$\chi = N\dfrac{g^2\beta^2}{kT}\,\dfrac{2\exp(-5J/kT)+10\exp(-3J/kT)+28}{3\exp(-5J/kT)+5\exp(-3J/kT)+7}$	(6′)
d^5d^2	5/2	1	7/2 5/2 3/2	−63/8 J −35/8 J −15/8 J	+43/8 J +43/8 J +43/8 J	$\chi = N\dfrac{g^2\beta^2}{kT}\,\dfrac{5\exp(-6J/kT)+(35/2)\exp(-7J/2kT)+42}{4\exp(-6J/kT)+6\exp(-7J/2kT)+8}$	(7′)
d^4d^3	2	3/2	7/2 5/2 3/2 1/2	−63/8 J −35/8 J −15/8 J −3/8 J	+39/8 J +39/8 J +39/8 J +39/8 J	$\chi = N\dfrac{g^2\beta^2}{kT}\,\dfrac{(1/2)\exp(-15J/2kT)+5\exp(-6J/kT)+(35/2)\exp(-7J/2kT)+42}{2\exp(-15J/2kT)+4\exp(-6J/kT)+6\exp(-7J/2kT)+8}$	(8′)
d^5d^3	5/2	3/2	4 3 2 1	−10 J −6 J −3 J −J	+25/4 J +25/4 J +25/4 J +25/4 J	$\chi = N\dfrac{g^2\beta^2}{kT}\,\dfrac{2\exp(-9J/kT)+10\exp(-7J/kT)+28\exp(-4J/kT)+60}{3\exp(-9J/kT)+5\exp(-7J/kT)+7\exp(-4J/kT)+9}$	(9′)
d^5d^4	5/2	2	9/2 7/2 5/2 3/2 1/2	−99/8 J −63/8 J −35/8 J −15/8 J −3/8 J	+59/8 J +59/8 J +59/8 J +59/8 J +59/8 J	$\chi = N\dfrac{g^2\beta^2}{kT}\,\dfrac{(1/2)\exp(-12J/kT)+5\exp(-21J/2kT)+(35/2)\exp(-8J/kT)+42\exp(-9J/2kT)+(165/2)}{2\exp(-12J/kT)+4\exp(-21J/2kT)+6\exp(-8J/kT)+8\exp(-9J/2kT)+10}$	(10′)

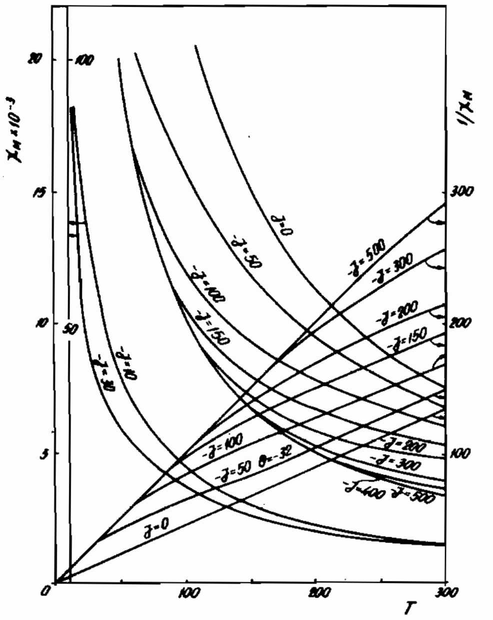

Figure 2. The magnetic susceptibility curves and their reciprocals for various values of J according to the temperature for the d^3d^1 electronic structure of the Me-Me system.

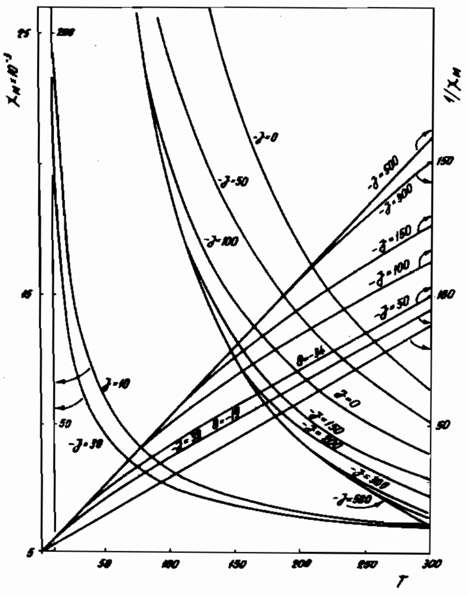

Figure 3. The magnetic susceptibility curves and their reciprocals for various values of J according to the temperature for the d^4d^1 electronic structure of the Me-Me system.

Results and Discussion

The magnetic moments calculated from the Curie-Weiss law for the magnetic susceptibilities at low values of (−J) (such values for which the Curie-Weiss constant may be determined) are equal to the magnetic moments calculated from the Curie law for the magnetic susceptibilities at $J=0$. These moments calculated for two metal ions of the Me-Me system are given in Table II.

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

No.	Electronic structure	$\mu_{Me\text{-}Me}$	$\mu_{Me} = \mu_{Me\text{-}Me}/\sqrt{2}$	$\mu = \sqrt{S_1(S_1+1)} + \sqrt{S_2(S_2+1)}$	$\mu = 2\sqrt{(\lvert S_1-S_2\rvert)(\lvert S_1-S_2\rvert+1)}$	μ_1	μ_2	$(\mu_1+\mu_2)/2$
1	$d^2\,d^1$	3.34	2.36	2.28	1.74	2.73	1.93	2.33
2	$d^3\,d^1$	4.26	3.01	2.80	2.84	3.69	2.13	2.91
3	$d^4\,d^1$	5.21	3.68	3.32	3.87	4.67	2.33	3.50
4	$d^5\,d^1$	6.20	4.39	3.81	4.91	5.67	2.52	4.09
5	$d^3\,d^2$	4.62	3.26	3.35	1.74	3.58	2.92	3.25
6	$d^4\,d^2$	5.71	4.04	3.87	2.84	4.65	3.28	3.97
7	$d^5\,d^2$	6.55	4.64	4.37	3.87	5.53	3.49	4.51
8	$d^4\,d^3$	6.27	4.44	4.39	1.74	4.74	4.10	4.41
9	$d^5\,d^3$	6.96	4.93	4.88	2.84	5.50	4.27	4.88
10	$d^5\,d^4$	7.71	5.39	5.40	1.74	5.75	5.13	5.44

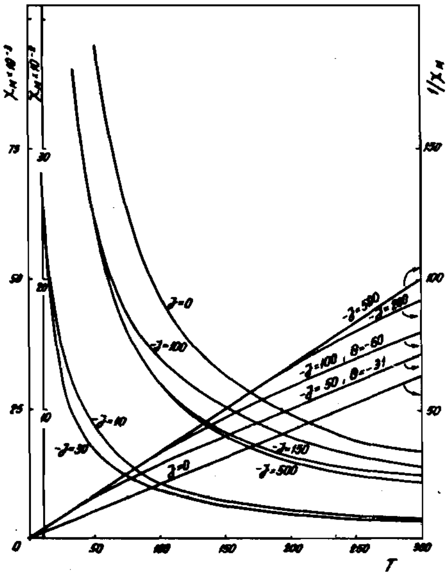

Figure 4. The magnetic susceptibility curves and their reciprocals for various values of J according to the temperature for the $d^5\,d^1$ electronic structure of the Me-Me system.

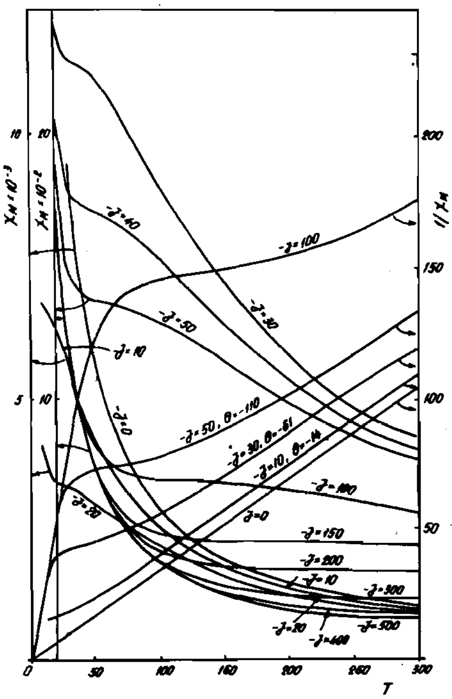

Figure 5. The magnetic susceptibility curves and their reciprocals for various values of J according to the temperature for the $d^3\,d^2$ electronic structure of the Me-Me system.

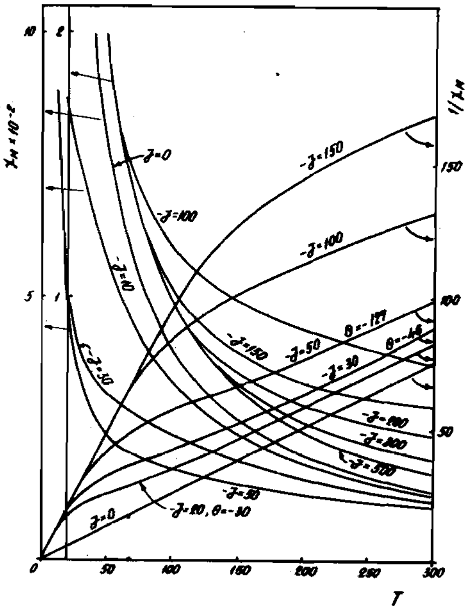

Figure 6. The magnetic susceptibility curves and their reciprocals for various values of J according to the temperature for the $d^4\,d^2$ electronic structure of the Me-Me system.

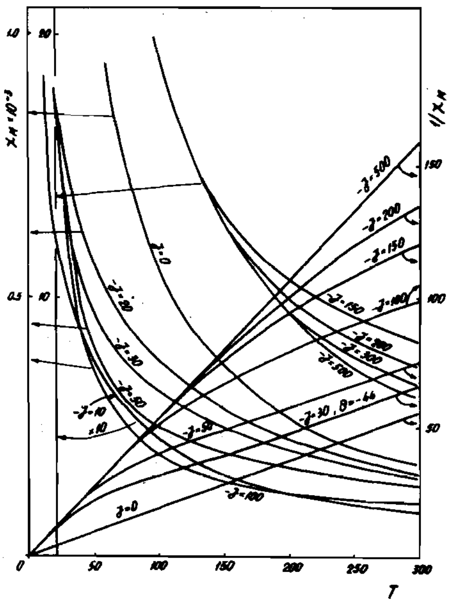

Figure 7. The magnetic susceptibility curves and their reciprocals for various values of J according to the temperature for the $d^5\,d^2$ electronic structure of the Me-Me system.

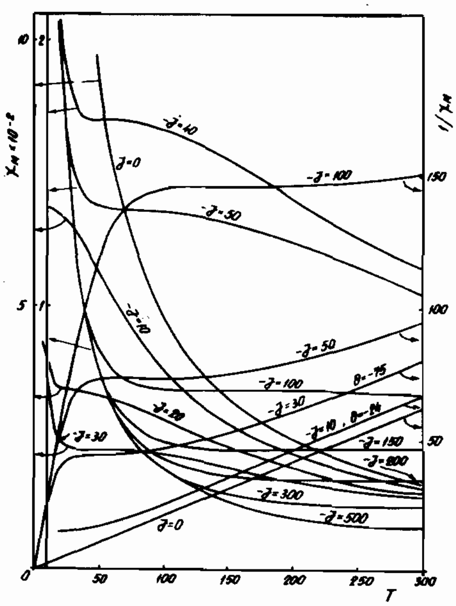

Figure 8. The magnetic susceptibility curves and their reciprocals for various values of J according to the temperature for the $d^4 d^3$ electronic structure of the Me-Me system.

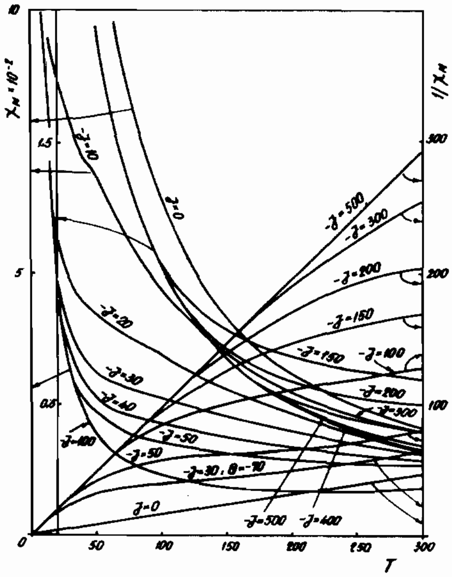

Figure 9. The magnetic susceptibility curves and their reciprocals for various values of J according to the temperature for the $d^5 d^3$ electronic structure of the Me-Me system.

This table gives also the magnetic moments calculated for one metal ion of the Me-Me system from the equation:

$$\mu_{Me} = \mu_{Me\text{-}Me}/\sqrt{2} \qquad (1)$$

It appears that this moment is close to the magnetic moment calculated as an arithmetic mean of the magnetic moments for particular metal ions of the Me-Me system. That is

$$\mu_{Me} \approx \{\sqrt{S_1(S_1+1)} + \sqrt{S_2(S_2+1)}\}\mu_B. \qquad (2)$$

Table II shows that this dipendence is the better obeyed for the $d^n d^m$ electronic structure of the Me-Me system the lower is the difference between n and m. Hence, this relationship is worst obeyed in the $d^5 d^1$ electronic structure.

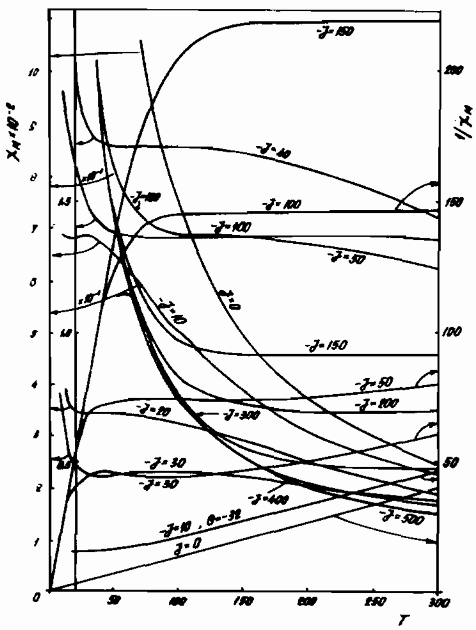

Figure 10. The magnetic susceptibility curves and their reciprocals for various values of J according to the temperature for the $d^5 d^4$ electronic structure of the Me-Me system.

Assuming that the contribution of each electron to the magnetic susceptibility of the Me-Me system is the same, the magnetic moments for particular ions of this system may be calculated. The results are given in Table II. The arithmetic mean of these moment is close to the magnetic moment calculated from the equation (1). The values of μ_{Me} and $(\mu_1+\mu_2)/2$ are very close each to other for the $d^n d^m$ electronic structure of the Me-Me system if $|n-m|=1$. As this difference is increasing the agreement becomes less pronounced.

Table II indicates that the $d^n d^m$ electronic structure of the Me-Me system if $n>m$, has the moment μ_1 (for a d^n electronic structure metal ion) lower than that calculated from the equation

$$\mu_1 = \sqrt{n(n+2)}\mu_B. \qquad (3)$$

The magnetic moment calculated for a d^m electron metal is higher than that calculated from the equation

$$\mu_2 = \sqrt{m(m+2)}\mu_B. \qquad (4)$$

The values of moments μ_1 and μ_2 approach each other as the difference $n-m$ is increasing. This may suggest a certain tendency for equalization of electron spins in the Me-Me system.

The magnetic moment of the total Me-Me system having a $d^n d^m$ electronic structure is defined by the equation:

$$\mu = \sqrt{(|n-m|)(|n-m|+2)}\mu_B = 2\sqrt{(|S_1-S_2|)(|S_1-S_2|+1)}\mu_B \qquad (5)$$

for high values of the (—J).

The magnetic moments μ_1 and μ_2 will not then be completely compensated. Such an incomplete compensation of two different magnetic moments in the anti-parallel orientation is characteristic of the ferrimagnetic compounds.[8]

The temperature dependence of magnetic susceptibility for high values of $(-J)$ obeys the Curie law. This law is satisfied also for the magnetic susceptibilities (calculated for all values of J) at low temperatures. The higher is the value of the $(-J)$, the more extensive is the applicability range of this law.

The range of magnetic properties of the $d^n\, d^m$ electronic structure of the Me-Me system with the negative values of J is limited by the two straight lines representing a reciprocal temperature dependence of the magnetic susceptibility for $J=0$ and $(-J)$ assuming very high values.

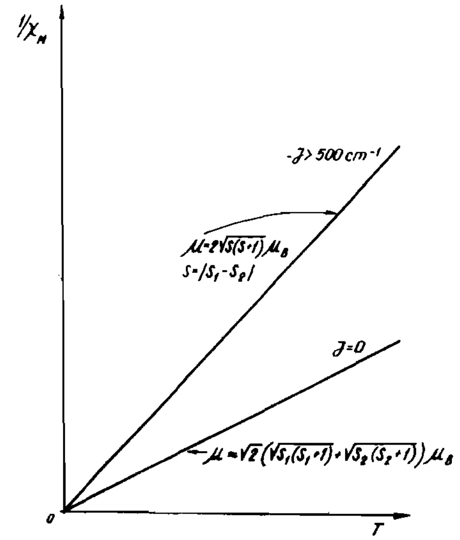

Figure 11. Temperature dependence of the reciprocal magnetic susceptibility for high values of $(-J)$ and for $J=0$.

The magnetic moment μ_{eff} calculated from the Curie law for the magnetic susceptibilities calculated at

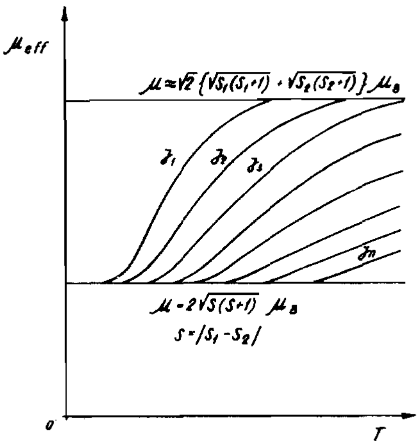

Figure 12. Temperature dependence of the magnetic moment μ_{eff} on the exchange integral J for a $d^n\, d^m$ electronic structure of the Me-Me system.

(8) B. Stalinski, *Magnetochemia*, PWN, Warszawa (1966).

various values of J is changed with temperature from the value

$$\mu = 2\sqrt{(|S_1-S_2|)(|S_1-S_2|+1)}\mu_B \qquad (5)$$

to

$$\mu \approx \sqrt{2}\{\sqrt{S_1(S_1+1)}+\sqrt{S_2(S_2-1)}\}\mu_B \qquad (6)$$

It is clear from Figures 1-10 that the temperature dependence of the magnetic susceptibility for the $d^n\, d^{n+1}$ electronic structure of the Me-Me systems show some inflection points. These inflections disappear as the difference between n and m for a $d^n\, d^m$ electronic structure of the Me-Me system increases.

An interesting temperature dependence of the magnetic susceptibility was obtained for the $d^5\, d^4$ electronic structure of the Me-Me system. There are two temperatures T_{N_1} and T_{N_2} at which the magnetic susceptibility curves possess maxima. These temperatures depend lineary on the $(-J)$.

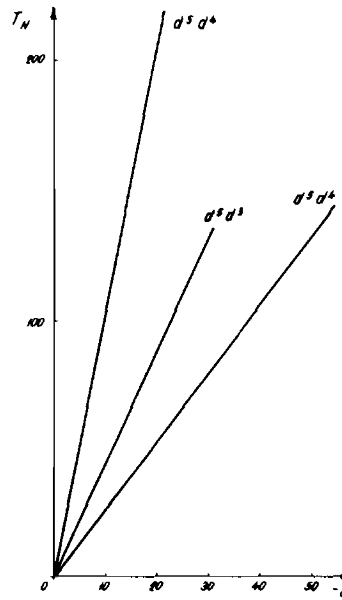

Figure 13. Dependence of the temperature T_N on the exchange integral J for the $d^5\, d^3$ and $d^5\, d^4$ electronic structures of the Me-Me system.

These results,like those obtained for the $d^n\, d^n$ electronic structure [1] of the Me-Me system, are valid for a $d^n\, d^m$ electron configuration in this system where n and m are comprised between 5 and 10. Derived equations are also valid if the crystal field will change the number of unpaired electrons of the metal ions in the Me-Me system. The magnetic susceptibility is then defined by the equation

$$\chi(d^n\, d^m) \qquad (7)$$

where n and m are the numbers of unpaired electrons.

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