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Paramagnetic Behaviours of the Hydrated Salts of Ti^{3+}, V^{3+}, Fe^{2+} and Co^{2+}

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Introduction

In the alums of Ti^{3+}, $(3d^1\ {}^2D)$ and V^{3+}, $(3d^2\ {}^3F)$ the crystalline electric field is trigonally distorted[1) 2)] whereas, it is approximately tetragonally distorted in the Tutton salts of Fe^{2+}, $(3d^6\ {}^5D)$ and Co^{2+}, $(3d^7\ {}^4F)$. Since such an anisotropic field and the spin-orbit coupling can only partially split the basic cubic field triplets Γ_4 or Γ_5 as the case may be, to the extent of 10^{-2} to 10^{-3} cm^{-1}, the second order perturbation effects are quite large and the exact solutions of the secular equations often present great difficulty. Moreover, fairly large covalency overlap often occurs between the $3d$ charge cloud of the paramagnetic ion and s and p clouds of the surrounding water oxygens making the electrostatic model invalid[3) 4)]. The cases of V^{3+}, Fe^{2+} and Co^{2+} can, however, still be treated to a good degree of approximation by the method of Van Vleck[5)], and Abragam and Pryce[6)] introducing an empirical covalency factor, while Ti^{3+} with a single $3d$ electron, though apparently simple, has to be treated by the more general molecular orbital method of Van Vleck[7)] and Stevens[8)]. We have accordingly derived the expressions for the principal susceptibilities of the above ions to a very high degree of approximation and compared these with the existing experimental results.

Discussions

(*a*) V^{3+} *alums*[9)]. On the assumption that the cubic field is not strong enough to break down the $(l\text{-}l)$ coupling altogether, that the 2nd order and 4th order trigonal field coefficients have +ve signs and are comparable in magnitude[2)] and taking into consideration the admixtures from the different upper levels including a ${}^3P$ term (Fig. 1), the mean gm-ionic susceptibility expression using Abragam and Pryce's method, is finally obtained as:

$$K=\frac{8N\beta^2}{3k}\times\frac{(A^2/4T)+(2B^2k/D)[\exp(D/kT)-1]}{2+\exp(D/kT)}+K_c \tag{1}$$

where, the coefficients A, B, D and K_c are

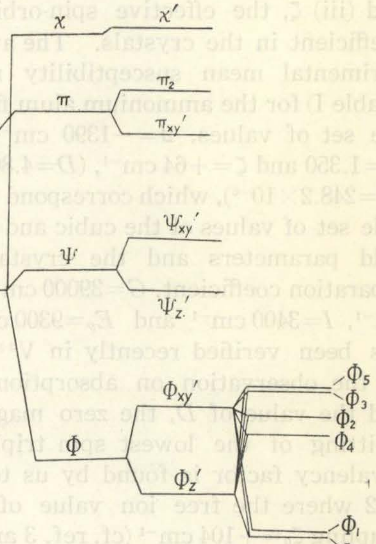

Fig. 1. The energy level diagram for V^{3+} ion under the predominantly cubic with a small trigonal electric field and the effect of $L\text{-}S$ coupling on the lowest φ-orbital states.

Table I. A, B, and g parameters for the different alums. $(p_f{}^2=AT+B)$

	Vanadium alum				Titanium alum
	NH_4	Rb	Cs	Tl	Cs
B	6.949 (6.921)	6.995	7.015	7.136	2.650
$A\times10^4$	11.4 (13.1)	13.1	12.5	8.2	6.6
g	1.864 (1.860)	1.870	1.872	1.888	1.880

The values in the parentheses are from Van den Handel's data.

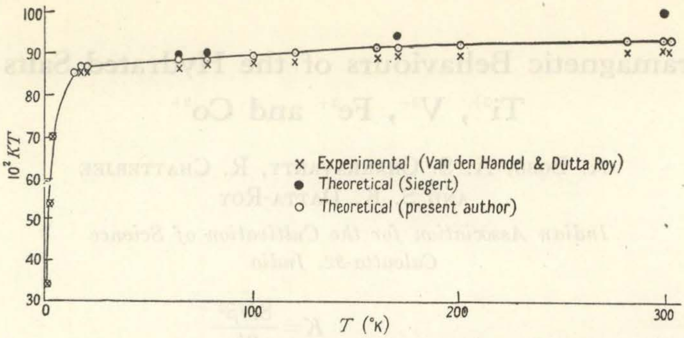

Fig. 2. Variation of $10^2 KT$ with temperature.

complicated functions of (i) α, α' the effective Landé admixture factors for the crystals, along and perpendicular to the trigonal field; (ii) Δ, the trigonal field separation coefficient; and (iii) ζ, the effective spin-orbit coupling coefficient in the crystals. The available experimental mean susceptibility results[10) 11)] (Table I) for the ammonium alum fit well with the set of values, $\Delta=-1390\ \mathrm{cm}^{-1}$, $\alpha=1.105$, $\alpha'=1.350$ and $\zeta=+64\ \mathrm{cm}^{-1}$, ($D=4.800\ \mathrm{cm}^{-1}$ and $K_c=248.2\times10^{-6}$), which correspond to a reasonable set of values of the cubic and anisotropic field parameters and the crystalline term separation coefficient, $G=39000\ \mathrm{cm}^{-1}$, $H=3500\ \mathrm{cm}^{-1}$, $I=3400\ \mathrm{cm}^{-1}$ and $E_p=9300\ \mathrm{cm}^{-1}$. This has been verified recently in V^{3+} corundum by the observation on absorption spectra[12)] and the value of D, the zero magnetic field splitting of the lowest spin triplet[13)]. The covalency factor is found by us to be $\zeta/\zeta_0\approx 0.62$ where the free ion value of spin-orbit coupling $\zeta_0=+104\ \mathrm{cm}^{-1}$ (cf. ref. 3 and 10). The experimental values of effective mean square moment agree much better with our theory than Siegert's[14)] (Fig. 2). In the liquid air range the behaviours of NH_4 and Tl alums are appreciably different from those of Rb and Cs alums, which themselves behave alike[11)]. This is due to differences of the crystal field in the salts. Moreover, there are small systematic deviations of the experimental values from the theory which must be interpreted as due to thermal expansion of the lattice.

(*b*) *Ti^{3+} alum*[15)]. Since the electrostatic field model fails to explain the behaviours of Ti^{3+} caesium alum at very low temperatures, we have started with the more general molecular orbital method[7) 8) 12)] and on the assumption of an anisotropic admixture of the $3d$-orbits of Ti^{3+} and p-orbits of the ligand oxygens, so that both the spin-orbit coupling coefficient ζ_i and the effective orbital splitting factor k_i are rendered anisotropic along and perpendicular to the trigonal symmetry axis of the ligand cluster, have derived the susceptibility tensor K_i, as a rather complicated function of the anisotropic orbital triplet separation Δ and of $k_\parallel$, $k_\perp$ and $\zeta_\parallel$, $\zeta_\perp$.

Values of $g_\parallel=1.25$ and $g_\perp=1.14$ at helium temperature[16)] may be fitted exactly with any value of Δ between 30 to $200\ \mathrm{cm}^{-1}$, with value of ζ_i suitably reduced and reasonable values of the overlap integral. For example, we get $\Delta=170\ \mathrm{cm}^{-1}$, $\zeta_\parallel=142.6\ \mathrm{cm}^{-1}$, $\zeta_\perp=157.4\ \mathrm{cm}^{-1}$, $k_\parallel=0.800$, $k_\perp=0.580$; whereas, Bleaney gets $\Delta=50\ \mathrm{cm}^{-1}$, $k=0.7$. In the absence of reliable susceptibility measurements in helium range uniqueness in the values of the parameters could not be achieved. Now the accurate susceptibility values[11)] between 100° and 300 °K can be reasonably fitted with the theory only if we take $\Delta=800\ \mathrm{cm}^{-1}$ and the other parameters practically the same as before, so that $g_\parallel=1.919$, $g_\perp=1.775$, $(3k/N\beta^2)K_c=1526\times10^{-6}$ (Table II). Thus, it appears that the magnetic behaviours of Ti^{3+} alum are very different in liquid air and liquid helium ranges, the trigonal field separation changing from $800\ \mathrm{cm}^{-1}$ to about $100\ \mathrm{cm}^{-1}$, obviously due to

Table II. The theoretical and experimental effective Bohr magnetons of $TiCs(SO_4)_2\cdot12H_2O$.

T°K	p_f^2 (Theo.)	p_f^2 (Expl.)
300	2.849	2.875
240	2.793	2.807
200	2.763	2.755
140	2.724	2.680
100	2.693	2.625

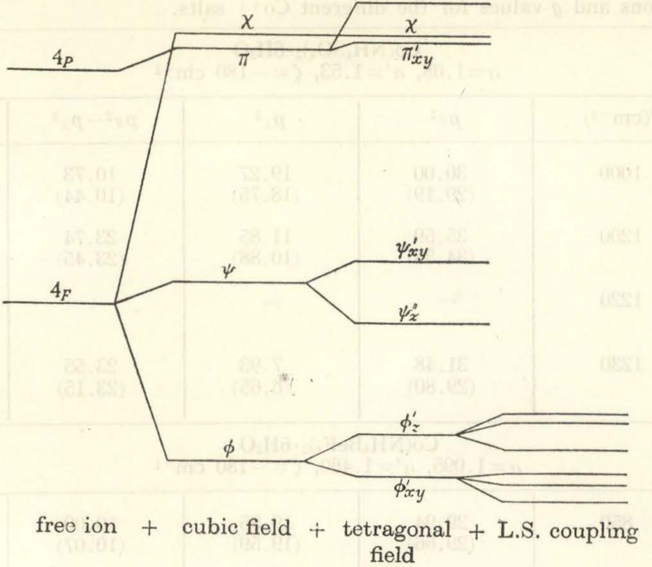

Fig. 3. Energy levels for Co^{2+} in a field of tetragonal symmetry. (From Abragam and Pryce.)

thermal expansion of the lattice and possibly some kind of phase transition. The decrease in spin-lattice relaxation from 10^{-7}sec[17] at liquid air range to 10^{-3} sec[18] at helium range also supports this finding[19]. In the liquid air range the second and fourth order anisotropic field parameters are found to be 3192 cm^{-1} and 3400 cm^{-1} similar to V^{3+}.

(*c*) *Co^{2+} Tutton salts*[20]. Considering the $Co^{2+}\cdot 6H_2O$ cluster in these salts to have an approximate tetragonal symmetry and the tetragonal axis elongated[21] and using Pryce's perturbation method the fine structure for the Co^{2+} ion including the ^4P term, in the crystal has been derived (Fig. 3). The expressions for the g_i values and the principal susceptibilities are very complicated functions of Δ, α, α' and ζ. It is important to note that unless the anisotropic field parameter Δ is varied to some extent, the agreement with g values[21] [25] and with both the absolute susceptibility and the anisotropies[22] at all temperatures was found to be impossible. The values of α and α' are found to be appreciably constant with temperature but vary somewhat from salt to salt particularly with changing alkali cation. Similar change of Δ is found to occur from salt to salt, specially with changing alkali cation. The values of $\zeta=-180$ cm^{-1} is the same as free ion in all cases. (For example, in $Co(NH_4SO_4)_2 6H_2O$, $\alpha=1.08$, $\alpha'=1.53$ but $\Delta=1000$ cm^{-1} at 290°K and 1230 cm^{-1} at 14.5°K. In $Co(NH_4BeF_4)_2 6H_2O$, $\alpha=1.095$, $\alpha'=1.460$ and $\Delta=850$ cm^{-1} at 297°K and 680 cm^{-1} at 87°K. In $Co(KSO_4)_2 6H_2O$, $\alpha=1.245$, $\alpha'=1.280$ while $\Delta=250$ cm^{-1} at 300°K and 740 cm^{-1} at 20°K) (Table III). The cubic and tetragonal field parameters and term separation in Co^{2+} salts are found to be $G=23100$ cm^{-1}, $H=3935$ cm^{-1}, $I=3780$ cm^{-1} and $E_p=11500$ cm^{-1} in reasonable agreement with the experimental results. These are different from V^{3+} and Ti^{3+} as is to expected.

(*d*) *Fe^{2+} Tutton salts*[23]. Following the same lines of calculation as above and with the assumption of approximate tetragonal symmetry the energy states for the Fe^{2+} ion has been found out (Fig. 4) and the expression for susceptibility and g values derived as a complicated function of Δ and ζ, α being$=\alpha'\approx 1$ for D-state. Laborious calculation shows that with the assumption of $K_\parallel > K_\perp$ we could obtain good agreement of the experimental susceptibility and anisotropy data for $Fe(NH_4SO_4)_2 6H_2O$[22] [24] with the theory. (Hence the ambiguity as to the sign of Δ in the absence of structural data is removed). Here again as in Ti^{3+} and Co^{2+} we find that unless Δ is made to vary from 650 cm^{-1} to 400 cm^{-1} between 300°K and 90°K, no fit with experimental results can be obtained[22] (Table IV). Such changes in Δ is also suggested by the large increase of relaxation time at helium temperatures. The value of ζ has also to be

Table III. The theoretical as well as the experimental values (in parentheses) of the effective Bohr magnetons and g-values for the different Co^{++} salts.

T°K	Δ(cm^{-1})	$p_{\parallel}^2$	$p_{\perp}^2$	$p_{\parallel}^2-p_{\perp}^2$	$g_{\parallel}$	$g_{\perp}$
$Co(NH_4SO_4)_2\cdot 6H_2O$ $\alpha=1.08$, $\alpha'=1.53$, $\zeta=-180$ cm^{-1}						
290	1000	30.00 (29.19)	19.27 (18.75)	10.73 (10.44)	—	—
77.2	1200	35.59 (34.33)	11.85 (10.88)	23.74 (23.45)	—	—
20	1220	—	—	—	6.33 (6.45)	3.12 (3.06)
14.5	1230	31.48 (29.80)	7.93 (6.65)	23.55 (23.15)	—	—
$Co(NH_4BeF_4)_2\cdot 6H_2O$ $\alpha=1.095$, $\alpha'=1.460$, $\zeta=-180$ cm^{-1}						
296.7	850	29.94 (29.66)	19.85 (19.59)	10.09 (10.07)	—	—
185.8	700	31.46 (29.58)	19.28 (17.56)	12.18 (12.02)		
86.8	680	29.49 (28.09)	15.30 (13.65)	14.19 (14.44)		
$Co(KSO_4)_2\cdot 6H_2O$ $\alpha=1.245$, $\alpha'=1.280$, $\zeta=-180$ cm^{-1}						
300	250	29.77 (29.49)	22.33 (23.08)	7.44 (7.41)	—	—
200	270	31.42 (30.14)	20.72 (19.42)	10.70 (10.72)	—	—
100	300	30.19 (29.23)	16.34 (15.19)	13.85 (14.04)	—	—
20	740	—	—	—	6.80 (6.60)	3.01 (2.71)

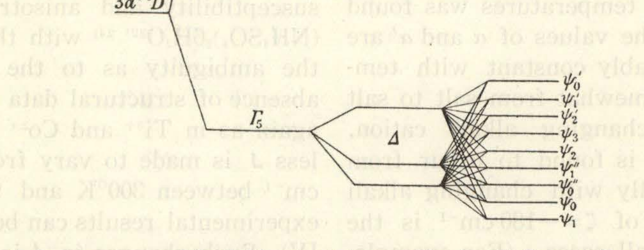

Fig. 4. Energy level diagram (not to scale) of Fe^{++} in a field of tetragonal symmetry and L-S coupling.

taken as 23% lower than the free ion value indicating covalency overlap of charge clouds. The experimental g values are not available for the Tutton salt but the calculated value in liquid hydrogen range is of the same order as that for FeF_2 in ZnF_2[25].

Table IV. The effective Bohr magnetons for $Fe(NH_4SO_4)_2 \cdot 6H_2O$ ($\zeta = -180$ cm^{-1}).

T°K	Δ(cm^{-1})	$p_{/\!/}^2$	$p_{\perp}^2$	$p_{/\!/}^2 - p_{\perp}^2$
300	650	36.26 (36.25)	26.31 (26.22)	9.95 (10.03)
160	500	44.12 (44.01)	24.72 (24.56)	19.40 (19.45)
90	400	51.80 (51.77)	21.28 (21.23)	30.52 (30.54)

The values in the parentheses are from Bose's data.

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For a complete list of references, 9) 11), 15), 20) and 23) should be consulted.

DISCUSSION

W. MARSHALL: It seems difficult to accept the rapid temperature variation of Δ in Ti^{3+} alum.

A. BOSE: The methods of calculation are standard ones and at high temperatures (liquid air range) the value of $\Delta = 800$ cm^{-1} can be fairly uniquely decided from susceptibility measurements. At low temperatures (helium range) resonance values of $g_{\perp}$ and $g_{\parallel}$ give $\Delta = 30$ to 200 cm^{-1} in reasonable fit with spectroscopic parameters. The change may be due to lattice expansion or due to a phase change. The finding agrees with deductions from paramagnetic relaxation measurements.

S. MAEKAWA: It is known that alums have temperature sensitive properties at low temperatures. For instance in the case of NH_4-Fe alum diluted with NH_4-Al alum we have recently observed by measurements of electron spin resonance a new type of transition different from the usual phase transition or lattice constant variation in the range between room temperature and liquid air temperature.

The measurements suggest that configurations of H_2O molecules around the Fe^{3+} ion change at these temperatures (about 230°K, 150°K) to produce different values of the crystalline field parameters. Is there a possibility of the occurence of this kind of change in the crystalline electric fields for your V^{3+}. and Ti^{3+} alums? This effect as well as the phase transition and lattice constant variation must be considered when treating the crystalline field in these temperature ranges.

A. BOSE: A phase change can occur in our case but as yet we have no direct evidence for such changes. The changes in most cases appear to be perfectly reversible, and hence may be only a lattice expansion effect or may be the effect you mention.

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The Energy Band Structure of Body Centred Iron

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The density of states curve of iron has been calculated using the Slater-Koster interpolation scheme and data due to J. H. Wood. The relevance of the results in the theory of ferromagnetism is discussed.

Wood[1)] obtained a density of states, $N(E)$, curve for iron directly from energy levels at 55 non-equivalent points of the Brillouin zone, calculated by the augmented plane wave method. As this number of points is insufficient for an accurate calculation of $N(E)$, levels at altogether 396 evenly spaced non-equivalent points were obtained from Wood's data, using the Slater-Koster interpolation scheme[2)]. Here 9 Bloch sums

$$\psi_{nk}(\boldsymbol{r})=C\sum_{l}\exp(i\boldsymbol{k}\cdot\boldsymbol{R}_l)\phi_n(\boldsymbol{r}-\boldsymbol{R}_l)\,,$$

based on atomic s, p and d functions ϕ_n, were used; values of 30 energy integrals were obtained which reproduced nearly all Wood's energy levels very well.

Fig. 1 shows $N(E)$ for the lowest 6 bands; this agrees well with a more accurate calculation[3)] of $N(E)$ where the critical points, which give rise to discontinuities of $N'(E)$, are taken into account. The figure shows a peak at -0.01 Ry., agreeing well with that obtained by Wood at -0.03 Ry.; elsewhere, however, the figure differs markedly from Wood's. For 'non-ferromagnetic' iron the Fermi energy is here -0.01 Ry. where $N(E)=36.9$ Ry.$^{-1}$, corresponding to an electronic heat coefficient $\gamma=15.3\times10^{-4}$ cal mol^{-1} deg^{-2}. If the exchange forces are assumed to shift completely the sub-bands containing electrons with opposite spin so as to give an unbalance of 2.2 electrons per atom, the two corresponding energies lie at -0.13 and 0.07 Ry., as shown in Fig. 1. The calculated value of γ is then 6.3×10^{-4} cal mol^{-1} deg^{-2}, compared with the experimental value 12.0×10^{-4}. Both these energies for ferromagnetic iron correspond to relatively high values of $N(E)$, agreeing with a suggested interpretation[4)] of the magnetic properties of iron alloys.

The one-electron wave functions are given by

$$\psi_k(\boldsymbol{r})=\sum_n a_n(\boldsymbol{k})\psi_{nk}(\boldsymbol{r})\,,$$

$$\sum_n |a_n(\boldsymbol{k})|^2=1\,,$$

and selected values of $A_d=\sum|a_n(\boldsymbol{k})|^2$, corresponding to the 5 atomic d functions only, are shown as functions of $E(\boldsymbol{k})$ in Fig. 2. It appears that A_d is large only in the range $-0.4<E<0.3$ Ry. approximately, over most of which range $N(E)$ is also high. Between -0.7 and -0.4 Ry., only A_s is large and both A_s and A_p are appreciable above about 0.3 Ry. Hence the original basis of the collective electron treatment of ferromagnetism[4)] of overlapping d and $s-p$ bands is not unreasonable.