[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Susceptibilities of Cr_2O_3–Al_2O_3 and of Fe_2O_3–Al_2O_3 Solid Solutions

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Magnetic susceptibility measurements from 90 to 300°K. have been made for the solid solutions Cr_2O_3–Al_2O_3 and Fe_2O_3–Al_2O_3. At infinite magnetic dilution the Cr^{+3} ion has a magnetic moment of 3.8 Bohr magnetons. The Weiss constant is zero. The Fe^{+3} ion under similar conditions has a moment of 5.9 and a Weiss constant of zero. The moment of the Fe^{+3} ions decreases rapidly with increasing magnetic concentration. These results tend to favor conclusions previously reached concerning the structure of supported iron sesquioxide on high area alumina, and the structure of hydrous iron sesquioxide and of transition group oxide supported catalysts and gels in general.[1]

Previous papers from this Laboratory have shown that the iron in supported iron sesquioxide has a magnetic moment of 4.0 to 4.4 Bohr magnetons, instead of the expected 5.9 magnetons predicted by the spin-only formula for the five unpaired electrons supposed to exist in the Fe^{+3} ion.[2] The subnormal moment also occurs in hydrous, or gel-like, iron sesquioxide.[3] This effect has been considered[4] to be due to some degree of wave function overlapping between adjacent iron ions in accordance with the suggestion of Haraldsen and Klemm[5] of covalent bonds between adjacent positive paramagnetic ions. Some significance has been attached to this in the interpretation given previously for the magnetic properties of disperse transition group oxides in relation to the paramagnetic neighborhood. The reasoning involved will be reviewed briefly.

In terms of exchange interaction the Weiss constant is $\Delta = 2JzS(S + 1)/3k$ where J is the exchange integral, z the number of nearest paramagnetic neighbors possessed by each paramagnetic ion, S the spin quantum number and k the Boltzmann constant. For oxides in the supported or gel-like forms such as chromia supported on alumina, or as chromia gel, the only structural difference between these disperse states and the massive (crystalline) state must reside in J or in z, or in both.

The problem of whether the structural difference between disperse and massive states resides in J or in z has not been resolved, but the low moment found for iron in the disperse forms of iron sesquioxide has been taken as evidence that J is not appreciably different in the crystalline pure sesquioxide and in the gel. It is known that J is dependent on the third power of the distance between adjacent iron ions. It was felt that if the minimum distance between adjacent iron ions is greater in the disperse state than in the massive state, then the exchange integral and hence both the Weiss constant *and* the magnetic moment would be very sensitive to this increase. Failure to find an increase of moment with increasing dispersion in dilute supported iron sesquioxide on alumina was, therefore, regarded as evidence that z was the only quantity appreciably different in the two cases.

It is well known that magnetically dilute substances containing ionically bound (+3) iron show a normal, spin-only, moment of 5.9 to 6.0 magnetons. There is, nevertheless, the possibility that some kind of covalent bond may exist between iron and oxygen, leading to a subnormal moment in the several disperse forms of iron sesquioxide. A method for examination of this idea is to study the susceptibility of Fe^{+3} ions at effectively infinite magnetic dilution but with the iron–oxygen relation virtually unchanged. This may be done by preparing solid solutions of iron sesquioxide in alumina. The susceptibilities are then measured at several temperatures over a range of concentration sufficient to permit extrapolation to infinite magnetic dilution. The magnetic moment may thus be calculated for conditions where no exchange effects occur.

Experimental Part

Preparation of Cr_2O_3–Al_2O_3 Solid Solutions.—Measured quantities of chromic nitrate and of aluminum nitrate analyzed stock solution were mixed and poured into excess dilute ammonium hydroxide solution. The coprecipitated mixture was diluted, filtered, dried at 110°, and calcined in hydrogen at 1100° for 3–5 hours. The products ranged from ruby-pink at the low chromia end to green at the high chromia end. Homogeneity was established by X-ray studies on all samples. No further change of X-ray pattern occurred on longer calcination. The oxides formed were, of course, those corresponding to alpha alumina. Two or three samples gave evidence of slight ferromagnetism. These were discarded.

Preparation of Fe_2O_3–Al_2O_3 Solid Solutions.—The method used for these solutions was parallel to that described for chromia–alumina. Several of the samples became ferromagnetic as revealed by a slight field strength dependence of susceptibility. These were discarded.

Experimental Methods.—All X-ray and some magnetic measurements were made as described in earlier papers from this Laboratory. Most of the magnetic measurements were made on a Faraday balance to be described later.

Results

Results on the Cr_2O_3–Al_2O_3 series are given in Table I. The quantity χ is the magnetic susceptibility per gram of sample, χ_{Cr} is the susceptibility per gram of chromium after corrections have been made for the diamagnetism of the oxide, aluminum and chromic ions.

Table II shows similar results on the Fe_2O_3–Al_2O_3 series.

Discussion of Results

It will be noted that the susceptibilities of both chromium and of iron ions increase greatly with increasing dilution. This effect is so great that, for instance, the susceptibility per gram of sample

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[1] This is the ninth paper on the susceptibility isotherm from this Laboratory. The eighth, by Selwood and Lyon, appeared in Discussions of the Faraday Society "Heterogeneous Catalysis." No. 8, 1950, p. 222.

[2] P. W. Selwood, M. Ellis and K. Wethington, THIS JOURNAL, **71**, 2181 (1949).

[3] P. W. Selwood, M. Ellis and C. F. Davis, Jr., *ibid.*, **72**, 3549 (1950).

[4] F. N. Hill and P. W. Selwood, *ibid.*, **71**, 2522 (1949).

[5] H. Haraldsen and W. Klemm, *Z. anorg. allgem. Chem.*, **220**, 183 (1934).

TABLE I

MAGNETIC DATA ON CHROMIA–ALUMINA SOLID SOLUTIONS

Cr_2O_3, %	Temp., °K.	$\chi \times 10^6$	$\chi_{Cr} \times 10^6$
2.6	300	1.7	113
	230	2.3	153
	215	2.5	165
	200	2.6	174
	184	3.1	189
	148	4.0	248
	128	4.2	259
	84	6.8	405
5.3	300	3.0	92
	230	4.4	131
	184	5.5	161
	128	7.9	228
	82	12.3	318
8.2	300	6.1	112
	230	6.9	129
	215	7.6	141
	200	8.0	148
	184	8.6	159
	128	12.1	222
	83	17.5	317
17.6	300	10.9	94
	230	13.4	114
	215	14.5	123
	200	15.2	129
	184	16.1	137
	167	17.3	147
	128	22.0	186
	84	27.9	235
25.0	300	12.7	74
	230	15.9	94
	215	17.2	102
	200	17.8	105
	184	18.5	109
	128	23.6	140
	83	33.8	198
33.0	300	15.0	67
	230	18.4	82
	215	19.3	87
	200	20.1	89
	184	21.5	96
	167	23.0	102
	128	30.0	133
43.0	300	16.8	58
	230	20.4	70
	215	20.4	70
	200	21.8	75
	184	22.8	79
	167	24.3	84
	128	34.2	117
	83	52.0	179
54.0	300	19.1	53
	230	22.7	62
	215	23.5	56
	200	24.2	66
	184	26.5	73
	128	36.6	100
	83	47.0	129
74.6	300	22.6	44
	230	25.7	51
	215	26.2	52
	200	26.3	52
	184	26.8	53
	167	27.2	54
	90	32.0	63
81.6	300	23.6	43
	230	26.3	48
	215	27.0	49
	200	27.2	49
	184	27.6	50
	90	29.5	53

TABLE II

MAGNETIC DATA ON FERRIC OXIDE–ALUMINA SOLID SOLUTIONS

Fe_2O_3, %	Temp., °K.	$\chi \times 10^6$	$\chi_{Fe} \times 10^6$
2.0	300	3.3	236
	230	4.4	336
	184	5.2	393
	138	6.8	507
	128	7.5	560
	86	9.5	700
5.0	300	6.1	183
	230	7.8	232
	215	8.2	243
	200	9.1	268
	184	9.9	291
	167	11.0	323
	148	12.7	371
	128	14.6	426
	86	19.7	571
10.5	300	11.8	166
	230	15.1	211
	215	15.8	221
	200	16.7	235
	184	18.7	260
	167	19.7	274
	148	21.1	293
	128	25.0	340
	86	32.5	450
20.0	300	15.8	114
	230	20.5	148
	215	21.8	157
	200	22.3	161
	184	22.9	165
	167	25.1	181
	148	27.3	197
	128	31.0	223
	86	38.9	279
40.0	300	17.7	64.0
	230	20.0	72.1
	215	20.8	75.0
	200	21.5	77.5
	184	22.4	80.8
	167	22.9	82.5
	148	25.6	92.2
	128	27.5	99.0
	86	34.2	123
80	300	37.1	66.2
	86	44.2	79.0

for the sample containing 43.0% chromia is actually twice as large, at liquid air temperature, as is the susceptibility of pure crystalline chromia at the same temperature. It will be noted also that the Curie–Weiss law describes the behavior of both Cr_2O_3–Al_2O_3 and Fe_2O_3–Al_2O_3 systems at moderate and low concentrations of the paramagnetic ions. For the lowest chromia concentration studied, 2.6% the Weiss constant is +4°, which is scarcely distinguishable from zero. The moment is 3.7, in good agreement with the spin-only value of 3.8. Extrapolation of the susceptibilities to infinite magnetic dilution yields a Weiss constant of zero and a moment of 3.8 magnetons. It should be mentioned that the low temperature susceptibility of chromia is quite sensitive to the presence of alumina in little more than trace amounts. This is probably a consequence of the ability of a diamagnetic ion present in effect as a lattice defect to unlock the antiparallel spins of all paramagnetic ions in its vicinity.

The extrapolated susceptibilities for the Fe^{+3} ion at infinite dilution give a Weiss constant of zero and a moment of 5.9 magnetons. It is interesting to note the tenacity with which one iron ion seems attracted to another. Below 5% iron the Weiss constant is effectively zero, but the moment is changing rapidly with concentration. Thus at 1.4% iron the moment is 5.9; at 3.5% iron it is 5.0; while at 14% iron the moment is 4.3, with a Weiss constant in the last case of 52°.

The moment of the iron ions at infinite dilution supports the view previously expressed, namely, that the subnormal moment observed in the disperse systems containing iron sesquioxide is due to a species of covalent bond between adjacent iron ions. This in turn supports the view that the susceptibility isotherms shown by almost all transition group oxides owe their shape more to the quantity z, that is, the number of paramagnetic neighbors, and less to possible changes in the minimum iron–iron distance in the transition from crystalline massive oxide to amorphous gel-like oxide.

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