Theoret. chim. Acta (Berl.) 9, 171—181 (1967)

Magnetic Properties of Transition Metal Ion Cubic $^5T_2$ Terms in Axial Ligand Fields

II. Average Magnetic Susceptibility

E. KÖNIG* and A. S. CHAKRAVARTY**

Mellon Institute, Pittsburgh, Pennsylvania 15213, USA

K. MADEJA

Institut für Anorganische Chemie, Universität Greifswald, Germany

Received August 28, 1967

Theoretical results for the average magnetic moment of cubic $^5T_2$ terms in axially distorted ligand fields are presented in numerical and in graphical form. The diagrams are plotted as function of kT/λ, δ/λ, and $\varkappa$, and are employed for direct comparison with experimental moment values.

Results of magnetic susceptibility measurements on high-spin [Fe phen$_2$ X_2] complexes, where phen = 1,10-phenanthroline, are reported and employed to demonstrate the application and the limits of the present theory. The moment values of compounds, where $X = Cl^-$, Br^-, N_3^-, OCN^-, and $HCOO^-$, are consistent with $\lambda = -80$ cm^{-1}, $\varkappa = 0.8$ and axially distorted ligand fields characterized by values of δ between +2000 and -1440 cm^{-1}.

Die Ergebnisse der Theorie für das mittlere magnetische Moment eines $^5T_2$ Grundterms in Ligandenfeldern axialsymmetrisch verzerrter Geometrie werden in numerischer sowie in graphischer Form angegeben. Die erhaltenen Diagramme stellen das Moment in Abhängigkeit von den Parametern kT/λ, δ/λ und $\varkappa$ dar und können unmittelbar mit experimentell bestimmten Momentwerten verglichen werden.

Messungen magnetischer Suszeptibilitäten an magnetisch normalen Komplexverbindungen [Fe phen$_2$ X_2] (phen = 1,10-Phenanthrolin) werden benutzt, um Anwendung und Grenzen der vorliegenden Theorie zu demonstrieren. Die Momentwerte von Verbindungen, bei denen $X = Cl^-$, Br^-, N_3^-, OCN^- und $HCOO^-$ ist, sind in Übereinstimmung mit $\lambda = -80$ cm^{-1}, $\varkappa = 0{,}8$ und mit axial verzerrten Ligandenfeldern, die durch Werte von δ zwischen +2000 und -1440 cm^{-1} gekennzeichnet werden können.

Les résultats théoriques pour le moment magnétique moyen des termes cubiques $^5T_2$ dans des champs des ligandes axialement distordus sont présentés numériquement et graphiquement. Les diagrammes sont présentés en fonction de kT/λ, δ/λ et $\varkappa$ pour permettre une comparaison directe avec les valeurs expérimentales du moment.

Les résultats de mesure de la susceptibilité magnétique des complexes spin-élevés [Fe phen$_2$ X_2] ou phen = 1,10 phénanthroline sont utilisés pour démontrer l'application et les limites de la théorie présentées ici. Les valeurs des moments des composés dans lesquelles $X = Cl^-$, Br^-, N^-, OCN_3^- et $HCOO^-$ correspondant à $\lambda = -80$ cm^{-1}, $\varkappa = 0{,}8$ et des champs des ligandes axialement distordus caractérisés par des valeurs δ entre +2000 et -1440 cm^{-1}.

---

[*] Visiting Fellow, Inorganic Chemistry, 1962—1965. Present adress: Institut für Physikalische Chemie, Universität Erlangen-Nürnberg, Germany.

[**] Postdoctoral Fellow, Theoretical Chemistry, 1963—1964. Present adress: Saha Institute of Nuclear Physics, Calcutta-9, India.

Introduction

In a ligand field of symmetry lower than cubic, the magnetic properties of an ion become anisotropic. However, axial fields influence also the average susceptibility and do frequently occur in many coordination compounds where single crystal studies are not feasible or extremely difficult.

Results of average susceptibility calculations including axial fields, which can readily be used for comparison with measured powder susceptibilities, are available for cubic A and E ground terms [1], and for cubic $^2T_2$ as well as $^3T_1$ terms lying lowest [2, 3]. For ions having cubic $^5T_2$ ground terms, a short note about calculations of this sort was published recently by Figgis et al. [4] and the results were employed to interpret powder susceptibility data of a few iron (II) compounds. However, the calculational results were neither presented in numerical nor in graphical form.

We concentrate therefore in part II of the present paper [5] on the susceptibility of powders and present average magnetic moments of cubic $^5T_2$ terms in axial ligand fields, computed as function of the parameters kT/λ, δ/λ, and $\varkappa$. The calculations were performed using theoretical expressions which were derived in part I. In addition, accurate susceptibility measurements were carried out on a series of high-spin iron(II)-bis(1,10-phenanthroline) complexes. The results are considered as suitable examples to demonstrate the validity and the limitations of the present theory. Comparison between both is used to deduce approximate values of the parameter δ characterizing the axial field.

Theoretical Results

In the first part of the present paper [5], it was shown that the cubic $^5T_2$ ground term of high-spin d^6 ions is split into nine levels by the influence of an axial ligand field component and of spin-orbit coupling. The remaining degeneracy of these levels is lifted by application of a magnetic field. Since it is the population of these levels that determines the magnetic susceptibility, expressions for $K_\parallel$ and $K_\perp$, the principal molecular susceptibilities in the directions parallel and perpendicular to the principal axis of symmetry, were set up employing the expression of Van Vleck [6]. The average magnetic moment $\bar{P}$ may be obtained from the principal moments $P_\parallel$ and $P_\perp$ according to

$$\bar{P} = \frac{1}{\sqrt{3}} [P_\parallel{}^2 + 2\, P_\perp{}^2]^{1/2}\,, \qquad (1)$$

where $P_\parallel$ and $P_\perp$ are determined by $K_\parallel$ and $K_\perp$ respectively according to Eq. (19) of part I.

We have calculated P as function of the parameters kT/λ, δ/λ, and $\varkappa$, where k is the Boltzmann constant, T the temperature (in °K), λ the spin-orbit coupling parameter*, δ the splitting due to the axial field**, and $\varkappa$ the orbital reduction factor [7]. The results are listed in numerical form in Tab. 1 for the following ranges of the parameters:

---

* The quantity λ will in general be different from the spin-orbit coupling constant of the free ion, λ^{free}, and is thus considered as an adjustable parameter.

** The term "axial field" includes both tetragonal and trigonal distortions of the basic octahedral geometry. The quantity δ is defined as the splitting of the $^5T_2$ state by the axial field in absence of spin-orbit coupling; δ is taken as positive, whenever the orbital doublet ^5E is lowest.

kT/λ: -0.1 to -5.0
δ/λ : 0 to -30.0, if $\delta > 0$
0 to $+30.0$, if $\delta < 0$
$\varkappa$: 1.0 to 0.5.

Table 1. *Average magnetic moments $\bar{P}$ (in Bohr magnetons) for a $^5T_2$ term under the combined action of an axial field and spin-orbit coupling as function of the parameters kT/λ, δ/λ, and $\varkappa$*

	kT/λ →	-.10	-.20	-.30	-.40	-.50	-.75	-1.00	-1.50	-2.00	-2.50	-3.00	-4.00	-5.00
κ = 1.0: Δ/λ ↓	30.0	4.97	5.00	5.01	5.01	5.01	5.02	5.02	5.03	5.03	5.04	5.05	5.06	5.07
	25.0	4.97	5.02	5.03	5.03	5.04	5.04	5.04	5.05	5.06	5.07	5.07	5.09	5.10
	20.0	4.97	5.05	5.06	5.07	5.07	5.07	5.08	5.09	5.10	5.11	5.12	5.13	5.15
	15.0	4.97	5.08	5.11	5.12	5.12	5.13	5.14	5.15	5.16	5.17	5.18	5.20	5.21
	10.0	4.95	5.14	5.19	5.21	5.22	5.23	5.24	5.26	5.27	5.28	5.29	5.30	5.29
	7.5	4.93	5.18	5.25	5.28	5.30	5.32	5.33	5.35	5.36	5.37	5.37	5.35	5.33
	5.0	4.89	5.21	5.32	5.37	5.40	5.44	5.47	5.49	5.48	5.47	5.45	5.40	5.36
	4.0	4.88	5.22	5.34	5.41	5.45	5.51	5.53	5.55	5.53	5.51	5.47	5.41	5.37
	3.0	4.90	5.22	5.35	5.44	5.49	5.57	5.60	5.61	5.58	5.54	5.50	5.43	5.37
	2.0	4.95	5.22	5.35	5.45	5.52	5.63	5.67	5.66	5.62	5.56	5.51	5.44	5.38
	1.0	5.04	5.22	5.34	5.45	5.54	5.66	5.71	5.69	5.64	5.58	5.52	5.44	5.38
	.0	5.08	5.22	5.34	5.45	5.54	5.67	5.72	5.70	5.64	5.58	5.53	5.44	5.38
	-1.0	5.05	5.22	5.35	5.45	5.54	5.66	5.71	5.70	5.64	5.58	5.52	5.44	5.38
	-2.0	5.02	5.23	5.36	5.46	5.54	5.65	5.69	5.68	5.62	5.57	5.52	5.44	5.38
	-3.0	5.02	5.25	5.37	5.47	5.54	5.63	5.66	5.65	5.60	5.55	5.50	5.43	5.38
	-4.0	5.04	5.26	5.39	5.47	5.53	5.62	5.64	5.62	5.58	5.53	5.49	5.42	5.37
	-5.0	5.06	5.27	5.40	5.48	5.53	5.60	5.62	5.60	5.56	5.52	5.48	5.41	5.36
	-7.5	5.10	5.29	5.41	5.48	5.53	5.58	5.58	5.55	5.51	5.47	5.44	5.39	5.35
	-10.0	5.12	5.30	5.42	5.48	5.53	5.57	5.56	5.52	5.47	5.44	5.41	5.36	5.33
	-15.0	5.14	5.31	5.42	5.48	5.52	5.55	5.53	5.48	5.43	5.39	5.36	5.32	5.29
	-20.0	5.15	5.31	5.42	5.48	5.51	5.54	5.52	5.46	5.40	5.36	5.33	5.29	5.27
	-25.0	5.16	5.31	5.41	5.48	5.51	5.53	5.51	5.45	5.39	5.35	5.31	5.27	5.25
	-30.0	5.16	5.31	5.41	5.47	5.51	5.52	5.50	5.44	5.38	5.33	5.30	5.26	5.23

	kT/λ →	-.10	-.20	-.30	-.40	-.50	-.75	-1.00	-1.50	-2.00	-2.50	-3.00	-4.00	-5.00
κ = 0.9: Δ/λ ↓	30.0	4.95	4.99	5.00	5.00	5.00	5.00	5.01	5.01	5.02	5.02	5.03	5.04	5.05
	25.0	4.96	5.01	5.02	5.02	5.02	5.02	5.03	5.03	5.04	5.05	5.05	5.06	5.08
	20.0	4.95	5.03	5.04	5.05	5.05	5.05	5.06	5.07	5.07	5.08	5.09	5.10	5.12
	15.0	4.94	5.06	5.08	5.09	5.10	5.10	5.11	5.12	5.13	5.14	5.15	5.16	5.17
	10.0	4.91	5.10	5.15	5.17	5.18	5.19	5.20	5.21	5.23	5.24	5.24	5.25	5.24
	7.5	4.88	5.12	5.20	5.23	5.25	5.27	5.28	5.30	5.31	5.31	5.31	5.29	5.27
	5.0	4.83	5.14	5.25	5.31	5.34	5.38	5.40	5.42	5.41	5.40	5.38	5.33	5.30
	4.0	4.82	5.14	5.26	5.33	5.37	5.43	5.46	5.47	5.46	5.43	5.40	5.35	5.31
	3.0	4.82	5.14	5.27	5.35	5.41	5.48	5.52	5.52	5.50	5.46	5.42	5.36	5.31
	2.0	4.87	5.14	5.26	5.36	5.43	5.53	5.57	5.57	5.53	5.48	5.44	5.37	5.32
	1.0	4.96	5.13	5.25	5.36	5.44	5.56	5.60	5.60	5.55	5.49	5.45	5.37	5.32
	.0	5.01	5.13	5.25	5.35	5.44	5.57	5.62	5.61	5.55	5.50	5.45	5.37	5.32
	-1.0	4.97	5.13	5.26	5.36	5.44	5.56	5.61	5.60	5.55	5.49	5.45	5.37	5.32
	-2.0	4.94	5.15	5.27	5.36	5.44	5.55	5.59	5.58	5.53	5.48	5.44	5.37	5.32
	-3.0	4.93	5.16	5.28	5.37	5.44	5.54	5.57	5.56	5.52	5.47	5.43	5.36	5.31
	-4.0	4.95	5.17	5.29	5.38	5.44	5.52	5.55	5.54	5.50	5.46	5.42	5.35	5.31
	-5.0	4.97	5.18	5.30	5.38	5.44	5.51	5.53	5.51	5.48	5.44	5.40	5.35	5.30
	-7.5	5.00	5.20	5.32	5.39	5.44	5.49	5.50	5.47	5.44	5.40	5.37	5.32	5.29
	-10.0	5.03	5.21	5.32	5.39	5.44	5.48	5.48	5.44	5.40	5.37	5.34	5.30	5.27
	-15.0	5.05	5.22	5.33	5.39	5.43	5.46	5.46	5.41	5.37	5.33	5.30	5.27	5.24
	-20.0	5.06	5.22	5.32	5.39	5.42	5.45	5.44	5.39	5.34	5.31	5.28	5.24	5.22
	-25.0	5.06	5.22	5.32	5.39	5.42	5.45	5.43	5.38	5.33	5.29	5.26	5.22	5.20
	-30.0	5.06	5.22	5.32	5.38	5.42	5.44	5.43	5.37	5.32	5.28	5.25	5.21	5.19

	kT/λ →	-.10	-.20	-.30	-.40	-.50	-.75	-1.00	-1.50	-2.00	-2.50	-3.00	-4.00	-5.00
κ = 0.8: Δ/λ ↓	30.0	4.94	4.98	4.98	4.99	4.99	4.99	4.99	5.00	5.00	5.01	5.01	5.02	5.03
	25.0	4.94	4.99	5.00	5.00	5.01	5.01	5.01	5.02	5.02	5.03	5.03	5.04	5.05
	20.0	4.93	5.01	5.02	5.03	5.03	5.03	5.04	5.04	5.05	5.06	5.06	5.07	5.08
	15.0	4.92	5.03	5.06	5.07	5.07	5.08	5.08	5.09	5.10	5.10	5.11	5.12	5.13
	10.0	4.87	5.06	5.11	5.13	5.14	5.15	5.16	5.17	5.18	5.19	5.20	5.20	5.19
	7.5	4.83	5.07	5.15	5.18	5.20	5.22	5.23	5.24	5.25	5.26	5.25	5.24	5.22
	5.0	4.77	5.07	5.18	5.24	5.27	5.31	5.33	5.35	5.34	5.33	5.31	5.27	5.24
	4.0	4.75	5.07	5.19	5.26	5.30	5.35	5.38	5.39	5.38	5.36	5.33	5.28	5.25
	3.0	4.75	5.06	5.19	5.27	5.32	5.40	5.43	5.44	5.42	5.38	5.35	5.29	5.25
	2.0	4.80	5.06	5.18	5.27	5.33	5.43	5.47	5.48	5.44	5.40	5.36	5.30	5.26
	1.0	4.88	5.05	5.17	5.26	5.34	5.46	5.50	5.50	5.46	5.41	5.37	5.30	5.26
	.0	4.93	5.05	5.16	5.26	5.34	5.47	5.51	5.51	5.47	5.42	5.37	5.31	5.26
	-1.0	4.90	5.05	5.17	5.26	5.34	5.46	5.51	5.50	5.46	5.41	5.37	5.30	5.26
	-2.0	4.86	5.06	5.18	5.27	5.34	5.45	5.49	5.49	5.45	5.40	5.36	5.30	5.26
	-3.0	4.85	5.07	5.19	5.28	5.35	5.44	5.47	5.47	5.43	5.39	5.36	5.30	5.25
	-4.0	4.86	5.08	5.20	5.29	5.35	5.43	5.46	5.45	5.42	5.38	5.35	5.29	5.25
	-5.0	4.88	5.09	5.21	5.29	5.35	5.42	5.44	5.43	5.40	5.37	5.33	5.28	5.24
	-7.5	4.91	5.11	5.23	5.30	5.35	5.40	5.42	5.39	5.36	5.33	5.31	5.26	5.23
	-10.0	4.93	5.12	5.23	5.30	5.35	5.39	5.40	5.37	5.34	5.31	5.28	5.24	5.22
	-15.0	4.95	5.12	5.23	5.30	5.34	5.38	5.38	5.34	5.30	5.27	5.25	5.21	5.19
	-20.0	4.96	5.12	5.23	5.30	5.34	5.37	5.37	5.32	5.28	5.25	5.23	5.19	5.17
	-25.0	4.96	5.12	5.23	5.30	5.33	5.37	5.36	5.31	5.27	5.24	5.21	5.18	5.16
	-30.0	4.96	5.12	5.23	5.29	5.33	5.36	5.35	5.31	5.26	5.23	5.20	5.17	5.14

Table 1 (Continued)

		kT/λ →	-.10	-.20	-.30	-.40	-.50	-.75	-1.00	-1.50	-2.00	-2.50	-3.00	-4.00	-5.00
$\kappa = 0.7$:	Δ/λ ↓	30.0	4.93	4.97	4.97	4.97	4.98	4.98	4.98	4.98	4.99	4.99	4.99	5.00	5.01
		25.0	4.92	4.98	4.99	4.99	4.99	4.99	5.00	5.00	5.00	5.01	5.01	5.02	5.03
		20.0	4.91	4.99	5.00	5.01	5.01	5.02	5.02	5.02	5.03	5.03	5.04	5.05	5.05
		15.0	4.89	5.00	5.03	5.04	5.05	5.05	5.05	5.06	5.07	5.07	5.08	5.09	5.09
		10.0	4.83	5.02	5.07	5.09	5.10	5.11	5.12	5.13	5.14	5.15	5.15	5.15	5.14
		7.5	4.78	5.02	5.10	5.13	5.15	5.17	5.18	5.19	5.20	5.20	5.20	5.18	5.16
		5.0	4.71	5.01	5.12	5.17	5.20	5.24	5.26	5.28	5.28	5.26	5.25	5.21	5.18
		4.0	4.68	5.00	5.11	5.18	5.22	5.27	5.30	5.32	5.31	5.29	5.27	5.22	5.19
		3.0	4.68	4.98	5.11	5.18	5.24	5.31	5.34	5.36	5.34	5.31	5.28	5.23	5.19
		2.0	4.72	4.97	5.09	5.18	5.24	5.34	5.38	5.39	5.36	5.32	5.29	5.24	5.20
		1.0	4.80	4.97	5.08	5.17	5.24	5.36	5.40	5.41	5.37	5.33	5.30	5.24	5.20
		.0	4.85	4.96	5.07	5.16	5.24	5.36	5.41	5.42	5.38	5.34	5.30	5.24	5.20
		-1.0	4.82	4.97	5.08	5.17	5.24	5.36	5.41	5.41	5.37	5.33	5.30	5.24	5.20
		-2.0	4.77	4.97	5.09	5.18	5.25	5.35	5.39	5.40	5.37	5.33	5.29	5.24	5.20
		-3.0	4.76	4.98	5.10	5.19	5.25	5.34	5.38	5.38	5.35	5.32	5.29	5.23	5.20
		-4.0	4.77	5.00	5.11	5.20	5.25	5.34	5.37	5.36	5.34	5.31	5.28	5.23	5.19
		-5.0	4.79	5.00	5.12	5.20	5.26	5.33	5.35	5.35	5.32	5.29	5.27	5.22	5.19
		-7.5	4.82	5.02	5.14	5.21	5.26	5.32	5.33	5.32	5.29	5.27	5.24	5.21	5.18
		-10.0	4.84	5.02	5.14	5.21	5.26	5.31	5.32	5.30	5.27	5.24	5.22	5.19	5.17
		-15.0	4.86	5.03	5.14	5.21	5.25	5.30	5.30	5.27	5.24	5.21	5.19	5.16	5.14
		-20.0	4.86	5.03	5.14	5.21	5.25	5.29	5.29	5.26	5.22	5.20	5.18	5.15	5.13
		-25.0	4.87	5.03	5.14	5.21	5.25	5.29	5.28	5.25	5.21	5.19	5.16	5.13	5.11
		-30.0	4.87	5.03	5.14	5.21	5.25	5.28	5.28	5.24	5.21	5.18	5.16	5.12	5.10

		kT/λ →	-.10	-.20	-.30	-.40	-.50	-.75	-1.00	-1.50	-2.00	-2.50	-3.00	-4.00	-5.00
$\kappa = 0.6$:	Δ/λ ↓	30.0	4.91	4.95	4.96	4.96	4.96	4.97	4.97	4.97	4.97	4.97	4.98	4.98	4.99
		25.0	4.91	4.96	4.97	4.97	4.98	4.98	4.98	4.98	4.99	4.99	4.99	5.00	5.00
		20.0	4.89	4.97	4.98	4.99	4.99	5.00	5.00	5.00	5.01	5.01	5.01	5.02	5.03
		15.0	4.86	4.98	5.01	5.02	5.02	5.03	5.03	5.03	5.04	5.04	5.05	5.05	5.06
		10.0	4.79	4.98	5.03	5.06	5.07	5.08	5.08	5.09	5.10	5.10	5.11	5.10	5.10
		7.5	4.73	4.97	5.05	5.08	5.10	5.12	5.13	5.14	5.15	5.15	5.15	5.13	5.12
		5.0	4.64	4.94	5.05	5.10	5.13	5.17	5.19	5.21	5.21	5.20	5.19	5.16	5.13
		4.0	4.61	4.92	5.04	5.10	5.15	5.20	5.22	5.24	5.24	5.22	5.20	5.17	5.14
		3.0	4.61	4.91	5.02	5.10	5.15	5.22	5.26	5.27	5.26	5.24	5.21	5.17	5.14
		2.0	4.65	4.89	5.00	5.09	5.15	5.24	5.29	5.30	5.28	5.25	5.22	5.18	5.14
		1.0	4.73	4.88	4.99	5.08	5.15	5.26	5.31	5.32	5.29	5.26	5.23	5.18	5.14
		.0	4.77	4.88	4.98	5.07	5.14	5.26	5.31	5.32	5.29	5.26	5.23	5.18	5.15
		-1.0	4.74	4.88	4.99	5.07	5.15	5.26	5.31	5.32	5.29	5.26	5.23	5.18	5.14
		-2.0	4.69	4.89	5.00	5.08	5.15	5.25	5.30	5.31	5.28	5.25	5.22	5.18	5.14
		-3.0	4.68	4.90	5.01	5.09	5.16	5.25	5.29	5.29	5.27	5.24	5.22	5.17	5.14
		-4.0	4.68	4.91	5.02	5.10	5.16	5.24	5.28	5.28	5.26	5.24	5.21	5.17	5.14
		-5.0	4.70	4.91	5.03	5.11	5.16	5.24	5.27	5.27	5.25	5.23	5.20	5.16	5.14
		-7.5	4.73	4.93	5.04	5.12	5.17	5.23	5.25	5.24	5.22	5.20	5.18	5.15	5.13
		-10.0	4.74	4.93	5.05	5.12	5.17	5.22	5.24	5.23	5.20	5.18	5.17	5.14	5.12
		-15.0	4.76	4.94	5.05	5.12	5.17	5.22	5.22	5.21	5.18	5.16	5.14	5.12	5.10
		-20.0	4.77	4.94	5.05	5.12	5.16	5.21	5.22	5.19	5.17	5.14	5.13	5.10	5.08
		-25.0	4.77	4.94	5.05	5.12	5.16	5.21	5.21	5.19	5.16	5.14	5.12	5.09	5.07
		-30.0	4.77	4.93	5.05	5.12	5.16	5.20	5.21	5.18	5.15	5.13	5.11	5.08	5.07

		kT/λ →	-.10	-.20	-.30	-.40	-.50	-.75	-1.00	-1.50	-2.00	-2.50	-3.00	-4.00	-5.00
$\kappa = 0.5$:	Δ/λ ↓	30.0	4.90	4.94	4.95	4.95	4.95	4.95	4.95	4.96	4.96	4.96	4.96	4.96	4.97
		25.0	4.89	4.94	4.96	4.96	4.96	4.96	4.96	4.97	4.97	4.97	4.97	4.98	4.98
		20.0	4.87	4.95	4.97	4.97	4.97	4.98	4.98	4.98	4.98	4.99	4.99	5.00	5.00
		15.0	4.83	4.95	4.98	4.99	5.00	5.00	5.00	5.01	5.01	5.01	5.02	5.02	5.02
		10.0	4.75	4.94	5.00	5.02	5.03	5.04	5.04	5.05	5.06	5.06	5.06	5.06	5.06
		7.5	4.68	4.92	5.00	5.03	5.05	5.07	5.08	5.09	5.10	5.10	5.10	5.08	5.07
		5.0	4.58	4.88	4.98	5.04	5.07	5.11	5.13	5.14	5.15	5.14	5.13	5.10	5.08
		4.0	4.54	4.85	4.97	5.03	5.07	5.12	5.15	5.17	5.17	5.15	5.14	5.11	5.09
		3.0	4.53	4.83	4.94	5.02	5.07	5.14	5.17	5.19	5.19	5.17	5.15	5.12	5.09
		2.0	4.57	4.81	4.92	5.00	5.06	5.15	5.19	5.21	5.20	5.18	5.16	5.12	5.09
		1.0	4.65	4.80	4.90	4.98	5.05	5.16	5.21	5.23	5.21	5.18	5.16	5.12	5.09
		.0	4.70	4.80	4.89	4.98	5.05	5.16	5.21	5.23	5.21	5.19	5.16	5.12	5.09
		-1.0	4.66	4.80	4.90	4.98	5.05	5.16	5.21	5.23	5.21	5.18	5.16	5.12	5.09
		-2.0	4.61	4.80	4.91	4.99	5.06	5.16	5.20	5.22	5.20	5.18	5.16	5.12	5.09
		-3.0	4.59	4.81	4.92	5.00	5.06	5.15	5.19	5.21	5.20	5.17	5.15	5.12	5.09
		-4.0	4.60	4.82	4.93	5.01	5.07	5.15	5.19	5.20	5.19	5.17	5.15	5.11	5.09
		-5.0	4.61	4.82	4.94	5.02	5.07	5.15	5.18	5.19	5.18	5.16	5.14	5.11	5.09
		-7.5	4.63	4.83	4.95	5.03	5.08	5.15	5.17	5.17	5.16	5.14	5.13	5.10	5.08
		-10.0	4.65	4.84	4.96	5.03	5.08	5.14	5.16	5.16	5.14	5.13	5.11	5.09	5.07
		-15.0	4.66	4.84	4.96	5.03	5.08	5.14	5.15	5.14	5.12	5.11	5.09	5.07	5.06
		-20.0	4.67	4.84	4.96	5.03	5.08	5.13	5.14	5.13	5.11	5.09	5.08	5.06	5.05
		-25.0	4.67	4.84	4.96	5.03	5.08	5.13	5.14	5.13	5.11	5.09	5.07	5.05	5.04
		-30.0	4.68	4.84	4.96	5.03	5.08	5.13	5.14	5.12	5.10	5.08	5.07	5.05	5.03

Since we are dealing with a d^6 configuration, λ is always taken as negative. The results for $\varkappa = 1.0$, 0.8, and 0.6 are illustrated in Fig. 1, 2, and 3, respectively. Calculations were carried out also for values of $\varkappa$ and δ/λ intermediate between those listed. It was shown that these results may be obtained with sufficient accuracy by interpolating between the values of Table 1.

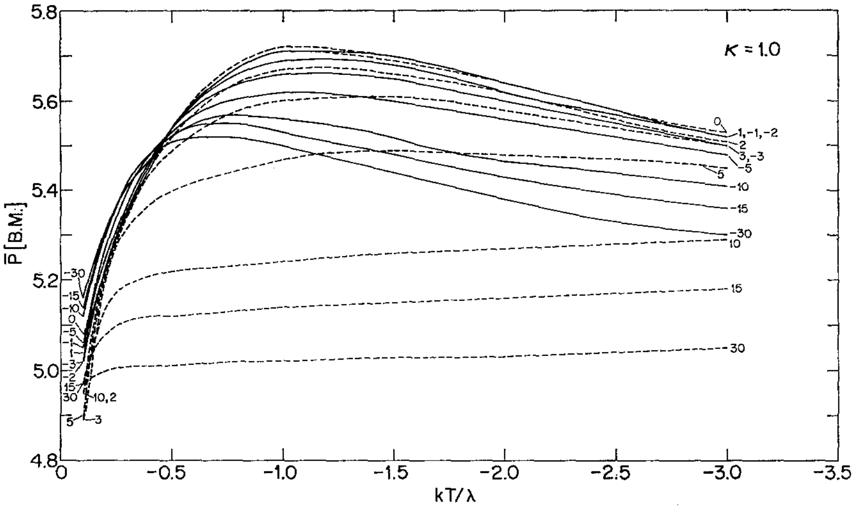

Fig. 1. Average magnetic moment $\bar{P}$ (in B.M.) for a ${}^5T_2$ term under the combined action of an axial ligand field and spin-orbit coupling. Values of the parameter δ/λ are indicated at the end of each curve. Full curves for $\delta > 0$, broken curves for $\delta < 0$. $\varkappa = 1.0$

The results show that axial distortions of the ligand field have a significant influence on the magnetic moment only if $\delta > \lambda$. Considering negative values of δ (δ/λ positive), the variability of the moment with temperature is the smaller, the larger the distortion of the field. In the case of positive δ (δ/λ negative), the temperature dependence of the moment is much more pronounced and is increasing with increasing values of δ. As for the principal moments [5], $\bar{P}$ approaches the spin-only value of 4.90 B.M. with decreasing values of the parameter $\varkappa$.

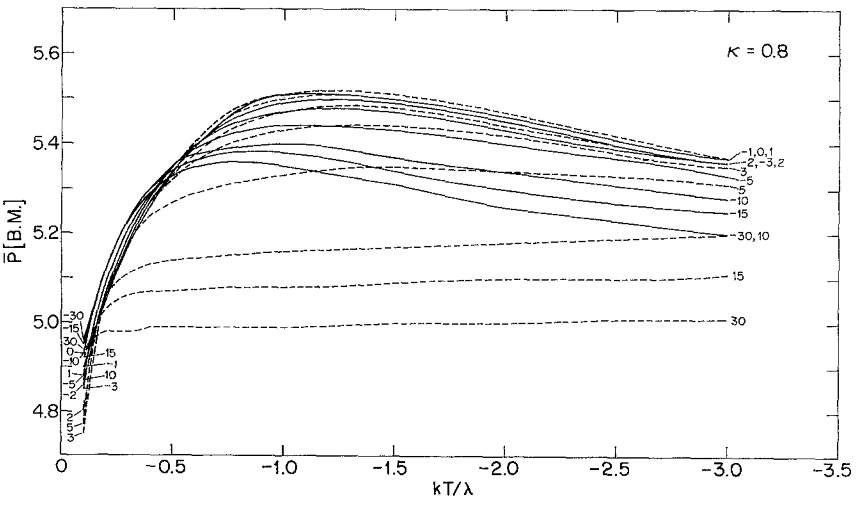

Fig. 2. Average magnetic moment $\bar{P}$ (in B.M.) as in Fig. 1. $\varkappa = 0.8$

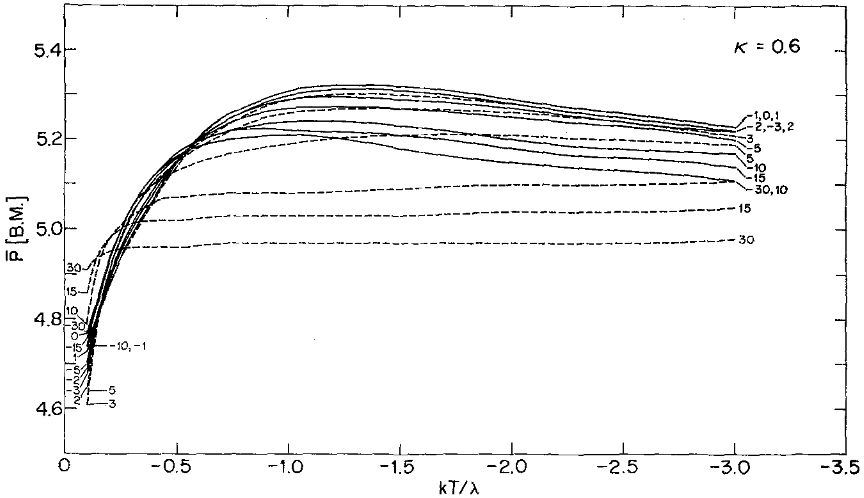

Fig. 3. Average magnetic moment $\bar{P}$ (in B.M.) as in Fig. 1. $\varkappa = 0.6$

Experimental

The preparation of iron(II)-bis(1,10-phenanthroline) complexes [Fe phen$_2X_2$], where $X = \mathrm{Cl}^-$, Br^-, N_3^-, OCN^-, and HCOO^- has been described elsewhere [8, 9]. The composition and purity of the compounds was checked by chemical analyses [9] and by measurements of the infrared vibrational spectra [10] as well as the visible and ultraviolet electronic spectra [8]. The preparation, storage and all measurements were performed under high purity dry nitrogen to prevent oxidation and/or decomposition by moisture.

Magnetic susceptibilities of polycrystalline samples were measured repeatedly by the Faraday method to avoid errors due to packing of the material. The vacuum microbalance used records weight changes of 1 μg. The small sample (10—30 mg) is contained in a quartz bucket suspended from one pan of the balance by means of a quartz fiber. The bucket is adjusted into the region of maximum field strength within the gap of a Varian 4-in. electromagnet equipped with Henry type pole pieces [11]. The bucket is enclosed by a cryostat of a similar design as that employed by Soling]12[. Temperature control is achieved by regulation of the heater input voltage by means of an automatic motor driven variac in conjunction with a Leeds and Northrup series 60 control unit whose sensing element is a copper-constantan thermocouple mounted directly below the bottom of the sample container.

The results of our susceptibility determinations, which are the average of five independent measurements, are compiled in Table 2. The ultimate accuracy is believed to be ±1% or better in gram susceptibility. All measurements were made at three different field strengths and no field dependence of the magnetic susceptibility was observed. The measured molar susceptibility values were corrected for diamagnetism using the following corrections: Fe^{2+}, -13; phen, -128; Cl^-, -26; Br^-, -36; N_3^-, -17; OCN^-, -21; HCOO^-, -17 in units of 10^{-6} c.g.s/mole. The effective magnetic moment μ_{eff} was obtained from the relation $\mu_{\mathrm{eff}} = 2.84 \sqrt{\chi'_m \cdot T}$, χ'_m being the fully corrected molar susceptibility and T the temperature

Table 2. *Magnetic data for high-spin* [Fe phen$_2$ X_2] *compounds* [*each set of three numbers gives* T (°K), χ_m (10^{-6} emu/mole), *and* μ_{eff} (B.M.)]

[Fe phen$_2$ Cl$_2$]			
439.9, 7335, 5.21;	419.7, 7699, 5.21;	399.8, 7945, 5.16;	379.9, 8377, 5.16;
359.7, 8854, 5.16;	349.8, 9120, 5.16;	340.1, 9411, 5.17;	330.3, 9729, 5.17;
320.2, 10051, 5.18;	310.1, 10342, 5.16;	299.9, 10714, 5.17;	292.9, 11032, 5.18;
279.6, 11357, 5.13;	269.9, 11782, 5.13;	260.1, 12239, 5.13;	249.5, 12759, 5.13;
239.9, 13291, 5.13;	229.8, 13905, 5.14;	220.2, 14544, 5.14;	209.6, 15016, 5.09;
200.2, 15739, 5.09;	190.5, 16552, 5.09;	180.3, 17470, 5.09;	170.3, 18170, 5.04;
160.0, 19206, 5.02;	149.8, 20432, 5.01;	140.2, 21821, 5.00;	130.2, 23356, 4.99;
119.4, 25488, 4.99;	108.2, 28315, 5.00;	98.1, 31343, 5.01;	87.8, 35102, 5.01;
77.1, 40696, 5.05			
[Fe phen$_2$ Br$_2$]			
439.9, 7409, 5.24;	419.8, 7796, 5.25;	399.9, 8244, 5.26;	380.1, 8704, 5.27;
360.0, 9247, 5.28;	349.9, 9338, 5.23;	340.3, 9619, 5.23;	330.4, 9937, 5.23;
319.6, 10270, 5.23;	309.8, 10564, 5.22;	293.3, 11287, 5.24;	279.9, 11687, 5.21;
269.8, 12106, 5.20;	259.5, 12606, 5.21;	250.2, 13033, 5.19;	239.6, 13627, 5.20;
230.1, 14240, 5.20;	219.7, 14931, 5.20;	210.2, 15619, 5.20;	200.2, 16372, 5.20;
190.4, 17258, 5.20;	181.0, 17942, 5.17;	170.6, 18979, 5.16;	160.2, 19785, 5.10;
149.2, 21088, 5.08;	140.7, 22467, 5.09;	130.0, 24241, 5.08;	119.1, 26506, 5.08;
109.9, 28556, 5.06;	99.7, 31595, 5.07;	91.8, 34581, 5.09;	77.4, 41719, 5.12
[Fe phen$_2$ (OCN)$_2$]			
439.8, 6999, 5.09;	419.7, 7350, 5.09;	399.9, 7738, 5.10;	379.4, 8040, 5.06;
360.7, 8451, 5.05;	349.3, 8735, 5.05;	339.5, 9023, 5.06;	329.9, 9299, 5.06;
319.8, 9630, 5.06;	309.4, 9927, 5.05;	293.6, 10548, 5.07;	279.7, 11091, 5.07;
269.9, 11480, 5.07;	260.0, 11841, 5.05;	249.7, 12343, 5.05;	239.7, 12916, 5.06;
229.7, 13469, 5.05;	219.9, 14107, 5.06;	210.0, 14784, 5.06;	200.7, 15516, 5.06;
190.5, 16280, 5.05;	179.2, 16758, 4.97;	169.7, 17698, 4.96;	160.0, 18740, 4.96;
150.0, 20054, 4.96;	140.7, 21443, 4.97;	131.1, 23127, 4.98;	121.5, 25086, 4.99;
110.8, 26881, 4.93;	99.9, 30051, 4.95;	90.7, 33393, 4.97;	77.4, 40343, 5.04
[Fe phen$_2$ (HCOO)$_2$]			
439.9, 7311, 5.20;	419.7, 7622, 5.18;	399.8, 8070, 5.20;	379.8, 8522, 5.20;
359.7, 9029, 5.20;	349.8, 9324, 5.21;	340.0, 9772, 5.26;	330.2, 10116, 5.27;
320.2, 10428, 5.26;	310.1, 10814, 5.27;	293.3, 11431, 5.27;	279.8, 11755, 5.22;
269.8, 12253, 5.23;	259.7, 12729, 5.22;	250.1, 13345, 5.25;	239.9, 14040, 5.27;
230.2, 14305, 5.21;	219.6, 15340, 5.26;	209.5, 16120, 5.27;	200.0, 16972, 5.28;
190.0, 17849, 5.27;	179.8, 18842, 5.27;	170.3, 20247, 5.31;	160.4, 21388, 5.30;
149.8, 22939, 5.30;	140.2, 24399, 5.29;	129.8, 26376, 5.29;	119.7, 28667, 5.29;
110.4, 31428, 5.32;	101.0, 34664, 5.34;	91.0, 38864, 5.36;	77.3, 47186, 5.44
[Fe phen$_2$ (N$_3$)$_2$]			
439.7, 7106, 5.13;	419.9, 7470, 5.13;	399.5, 7851, 5.13;	379.8, 8306, 5.14;
359.9, 8911, 5.17;	340.1, 9474, 5.18;	320.0, 10097, 5.18;	303.0, 10716, 5.19;
293.1, 11143, 5.20;	282.8, 11305, 5.15;	268.2, 11964, 5.15;	256.5, 12555, 5.16;
246.9, 13026, 5.15;	236.6, 13756, 5.18;	226.9, 14370, 5.18;	216.9, 15113, 5.19;
207.1, 15801, 5.19;	196.9, 16412, 5.15;	187.0, 17329, 5.16;	177.0, 18258, 5.15;
166.8, 19132, 5.11;	158.1, 20435, 5.14;	146.8, 21647, 5.10;	136.9, 23235, 5.10;
127.2, 25022, 5.10;	117.7, 26958, 5.09;	107.9, 29624, 5.10;	97.6, 32949, 5.12;
87.6, 37102, 5.14;	77.4, 42832, 5.19		

Table 3. *Room temperature moments and Weiss constants*

Compound	μ_{eff}, B.M.	Θ, °K
[Fe $phen_2$ Cl_2]	5.18	−10
[Fe $phen_2$ Br_2]	5.24	− 8
[Fe $phen_2$ $(N_3)_2$]	5.20	0
[Fe $phen_2$ $(OCN)_2$]	5.07	− 9
[Fe $phen_2$ $(HCOO)_2$]	5.27	+ 9

in °K. Also, the reciprocals of the corrected molar susceptibility χ'_m were plotted against temperature and found to be straight lines with minor deviations from linearity below 180 °K. The over-all temperature dependence of χ'_m in the range between 77 and 450 °K for all the compounds studied may thus be reasonably well reproduced by the Curie-Weiss law, $\chi'_m = C_m/(T - \Theta)$. The room temperature moments μ_{eff} and the Weiss constants Θ are listed in Table 3.

Comparison between Experimental Results and Theory

The results of magnetic measurements on iron(II)-bis(1,10-phenanthroline) complexes are compared in Fig. 4 in terms of the magnetic moment μ_{eff} with plots of $\bar{P}$ obtained on the basis of the theory outlined above. It may be visualized easily from Fig. 1 to 3 that a completely independent fit of all the parameters involved, i.e. λ, δ, and $\varkappa$, is generally not feasible from powder data within the electronic configuration d^6. Thus a treatment of the experimental data analogous to that in part I of this paper should be employed. However, due to the problems discussed below, this approach is not an advantage in the present case. Therefore, a direct fitting of the calculated curves to the experimental data is used, as originally suggested by Figgis [2]. Taking into account that four of the six coordinating

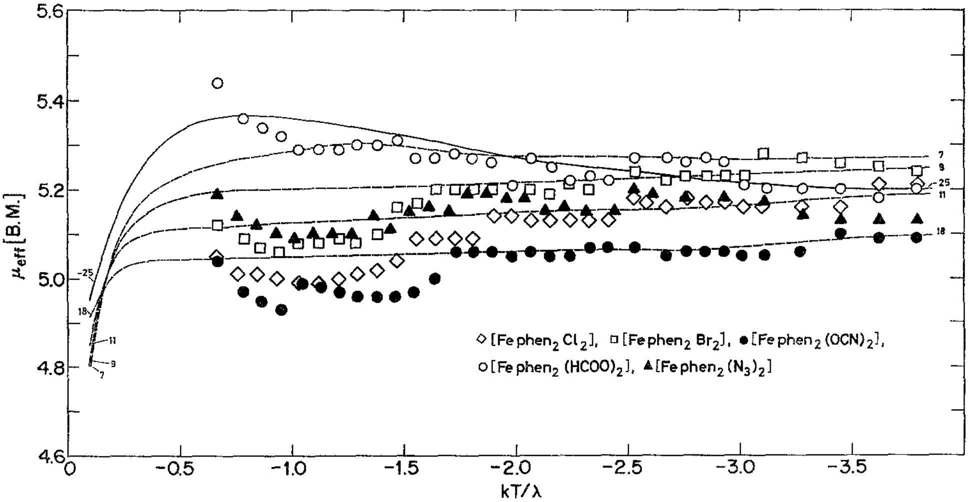

Fig. 4. Comparison of $\bar{P}$ (in B.M., assuming $\lambda = -80$ cm^{-1}, $\varkappa = 0.8$) with measured effective magnetic moments μ_{eff}. ◇ [Fe $phen_2$ Cl_2], □ [Fe $phen_2$ Br_2], ● [Fe $phen_2$ $(OCN)_2$], ○ [Fe $phen_2$ $(HCOO)_2$], and ▲ [Fe $phen_2$ $(N_3)_2$]

positions are occupied by two phenanthroline ligands, we have fixed $\lambda = -80\ \text{cm}^{-1}$. This corresponds to an approximately 20% reduction in the free ion value of λ ($\lambda^{\text{free}} = -103\ \text{cm}^{-1}$). Comparison with theoretical curves shows that the magnitude of the experimental moments determines $\varkappa > 0.7$. Thus we have chosen $\varkappa = 0.8$ for all the compounds studied, which value commonly is found in many complex compounds. The scatter of experimental values, which amounts to about ±0.05 B.M. or ~1%, still adds considerable inaccuracy to the curve fitting procedure. It should be observed, therefore, that the values of the parameter δ may be in error by up to ±25%.

Disregarding at first the peculiar behavior of μ_{eff} at lower temperatures, one finds that the magnetic moments of the compounds [Fe phen$_2$ X_2], where $X =$ Cl$^-$, Br$^-$, and OCN$^-$, require an axial distortion having $\delta < 0$ and thus an orbital singlet ground state. The distortion may be well described by the values of $\delta = -880\ \text{cm}^{-1}$ for [Fe phen$_2$ Cl$_2$], $\delta = -720\ \text{cm}^{-1}$ for [Fe phen$_2$ Br$_2$], and $\delta = -1440\ \text{cm}^{-1}$ for [Fe phen$_2$(OCN)$_2$]. On the other hand, the slope of experimental μ_{eff} vs. T curves for [Fe phen$_2$ X_2] compounds, where $X =$ HCOO$^-$ and N$_3^-$, renders a decision between $\delta > 0$ and $\delta < 0$ difficult. If $\delta > 0$ and thus a ^5E ground term is assumed, the distortion has to be characterized by $\delta \sim +2000\ \text{cm}^{-1}$ for [Fe phen$_2$ (HCOO)$_2$] and $\delta > +4000\ \text{cm}^{-1}$ for [Fe phen$_2$ (N$_3$)$_2$]. The first value is close to and the second beyond the limit of applicability of the present theory ($\delta/\lambda \sim -30$). Although the value of δ obtained for [Fe phen$_2$ (HCOO)$_2$] may apply, the computed results for [Fe phen$_2$ (N$_3$)$_2$] are either not adequate or the suggestion of $\delta > 0$ is not correct. On the other hand, if one takes $\delta < 0$, one arrives at the estimate of $\delta = -560\ \text{cm}^{-1}$ for [Fe phen$_2$ (HCOO)$_2$] and $\delta = -880\ \text{cm}^{-1}$ for [Fe phen$_2$ (N$_3$)$_2$]. At present, a choice between the two δ values for [Fe phen$_2$ (HCOO)$_2$] is not possible.

Discussion

The present investigation was undertaken principally with the aim of obtaining some information about stereochemistry and bonding in the iron(II)-bis(1,10-phenanthroline) complexes [Fe phen$_2$ X_2]. Within these compounds, the study of magnetic properties is of particular interest, since, in the electronic spectra, the ligand field bands are obscured for the most part by high intensity charge-transfer bands [8]. In addition, paramagnetic resonance provides far less complete information in high-spin d^6 systems than in most of the other transition group ions [13, 14].

The compounds [Fe phen$_2$ X_2], where $X =$ CN$^-$, CNO$^-$, and NO$_2^-$ as well as the [Fe phen$_3$]$^{2+}$ ion, are practically diamagnetic [8, 15, 16] and belong thus to the low-spin type with a singlet ground state. Compounds having $X =$ NCS$^-$ and NCSe$^-$ exhibit a complicated temperature dependence of the magnetic moment. Mössbauer effect studies and spectroscopic investigations have shown that these compounds undergo a transition between $^5T_2$ and $^1A_1$ ground states at temperatures $T_c = 174$ and 232 °K, respectively [17]. The compounds [Fe phen$_2$ ox] ·5H$_2$O and [Fe phen$_2$ mal] ·7 H$_2$O, where ox = oxalate, mal = malonate, show magnetic moments of 3.98 and 3.80 B.M. respectively, very slightly dependent on temperature, indicating a triplet ground state with an orbital contribution of ~1.0 B.M. [18]. Finally, for the compounds having $X =$ Cl$^-$, Br$^-$, N$_3^-$, OCN$^-$, HCOO$^-$, which are studied in this paper, a quintet ground state is indicated by the moment values of 5.07 to 5.27 B.M. at 298 °K and by the applicability of the Curie-Weiss law in the temperature range between 77 and 450 °K. These compounds are thus of the high-spin type. Since the molecular symmetry is certainly lower than cubic, the threefold orbital degeneracy of the cubic $^5T_2$ ground term will be partially lifted. It is assumed that a pseudo-axial field is sufficient to account for the resulting splitting of the $^5T_2$ term. With this assumption, splittings characterized by δ values of magnitude between $+2000$ and -1440 cm^{-1} have been deduced above by comparison with theory.

An independent check on the approximate magnitude of the axial-field splitting parameter δ is provided by Mössbauer spectroscopy. From the temperature dependence of the quadrupole splitting ΔE_Q, we have estimated [19] $\delta = -720$cm^{-1} for [Fe phen$_2$ Cl$_2$] and $\delta = -640$ cm^{-1} for [Fe phen$_2$ Br$_2$] in good agreement with the present values. The axial field splittings of the remaining [Fe phen$_2$ X_2] compounds are somewhat lower than those obtained from magnetic susceptibility data.

Golding, Mok, and Duncan [20] recently reported correlations between values of the quadrupole splitting ΔE_Q and the magnetic moment μ_{eff} in high-spin iron(II) compounds. In an application to [Fe phen$_2$ Cl$_2$], based on their Mössbauer effect studies and published susceptibility data, they claim that the pseudo-axial ligand field splitting should be characterized by values of δ between -1900 and -2400 cm^{-1}. Although this result is certainly influenced by the fact that bonding effects were completely neglected (our μ_{eff} data of [Fe phen$_2$ Cl$_2$] yield $\delta = -1280$ cm^{-1} if $\varkappa = 1.0$ is assumed), the larger part of the discrepancy between our estimate of δ and that of Golding et al. [20] is probably due to differences in both ΔE_Q and μ_{eff}. In this respect, we refer to [8, 19] and the experimental part of this paper. Golding et al. suggest that band splittings observed by us [8] in the electronic spectra of high-spin [Fe phen$_2$ X_2] compounds support their ground state splittings of 2000 cm^{-1}. We *disagree*. It is the electronic transition $^5T_2 \rightarrow {}^5E$ (in the notation of O_h symmetry) which shows two distinct maxima at 8470 and 10510 cm^{-1} for [Fe phen$_2$ Cl$_2$] e.g., and which thus reflects a splitting of the electronic excited and not the ground state.

The splitting of the excited ^5E state thus indicates a lower than octahedral symmetry in the studied [Fe phen$_2$ X_2] compounds [8]. If a *trans* arrangement of the ligands X is assumed, the two component bands would correspond to transitions to the ^5A_g and $^5B_{1g}$ states in D_{2h} symmetry. On the other hand, if the ligands X are arranged in *cis* position, transitions to the ^5A and ^5B states in C_2 symmetry would be expected. In both cases, the ^5E level originating from the $^5T_2$ ground term should be split slightly. As shown above, no indication of such splitting is observed in the magnetic behavior at temperatures above ~180 °K. However, there is a peculiar temperature dependence of μ_{eff} between 77 and ~180 °K (*cf.* Fig. 4). The deviation from the $\bar{P}$ vs. T curves, which are calculated on the assumption of an axially distorted $^5T_2$ ground state, consists of a slight minimum at about 130 to 160 °K and μ_{eff} rising to higher values than predicted at 77 °K. This inequality occurs in all the high-spin [Fe phen$_2$ X_2] complexes studied and was verified by repeated measurements on different samples of the same compounds. Since Baker and Bobonich [21] reported a similar observation, although in a more limited range of temperature, we are inclined to believe that the deviations are real. No quantitative explanation of the effect can be offered at present.

Table 4. *Comparison of room temperature moments (in B.M.) obtained by different authors*

Author Method	K. MADEJA and E. KÖNIG [8] Foex-Forrer	K. MADEJA [15] Gouy	W. A. BAKER and H. M. BOBONICH [21] Gouy	Present Investigation Faraday
[Fe phen$_2$ Cl$_2$]	5.12	5.26	5.26	5.18
[Fe phen$_2$ Br$_2$]	5.10	5.34	5.16	5.24
[Fe phen$_2$ (N$_3$)$_2$]	5.28	5.16	5.14	5.20

However, it is suggested that rhombic field splittings of *d* electron levels may account for the observed magnetic behavior.

A word of caution should be added concerning the absolute magnitude of room temperature moments. In Table 4 are listed moment values as reported by different authors and obtained by different methods. Since the variation in μ_{eff} is in the same order of magnitude (i.e. up to $\sim$5%) as the variation of the moments for different high-spin compounds in the series [Fe phen$_2$ X_2], it is likely that conclusions drawn from the comparison of absolute moment values at one temperature [21] might be seriously in error.

Acknowledgements. The authors appreciate the stimulating discussions with Dr. L. VASKA and the assistance of Mr. R. E. RHODES in the earlier phases of the experimental part of this work.

References

1. FIGGIS, B. N.: Trans. Faraday Soc. **56**, 1553 (1960).
2. — Trans. Faraday Soc. **57**, 198 (1961).
3. —, and J. LEWIS: Progr. Inorg. Chem. **6**, 37 (1964).
4. — —, F. MABBS, and G. A. WEBB: Nature **203**, 1138 (1964).
5. KÖNIG, E., u. A. S. CHAKRAVARTY: Theoret. chim. Acta **9**, 151, (1967).
6. VAN VLECK, J. H.: The theory of electric and magnetic susceptibilities. Oxford: University Press 1932.
7. STEVENS, K. W. H.: Proc. Roy. Soc. (London) **A 219**, 542 (1953).
8. MADEJA, K., and E. KÖNIG: J. Inorg. Nucl. Chem. **25**, 377 (1963).
9. —, W. WILKE, u. S. SCHMIDT: Z. Anorg. Allgem. Chem. **346**, 306 (1966).
10. KÖNIG, E.: Unpublished results.
11. HEYDING, R. D., J. P. TAYLOR, and M. L. HAIR: Rev. Sci. Instr. **32**, 161 (1961).
12. SOLING, H.: Acta chem. Scand. **12**, 1005 (1958).
13. LOW, W.: Paramagnetic resonance in solids. Solid State Physics Suppl. **2**, New York 1960.
14. MCGARVEY, B. R.: Transition metal chemistry **3**, p. 90. Ed. CARLIN, R. L. New York: M. Dekker 1966.
15. MADEJA, K.: Chem. Zvesti **19**, 186 (1965).
16. BECK, W., u. E. SCHUIERER: Chem. Ber. **95**, 3048 (1962).
17. KÖNIG, E., and K. MADEJA: Inorg. Chem. **6**, 48 (1967).
18. — — J. Am. chem. Soc. 88, 4528 (1966).
19. —, S. HÜFNER, E. STEICHELE, und K. MADEJA: Z. Naturforsch. **22a**, 1543 (1967).
20. GOLDING, R. M., K. F. MOK, and J. F. DUNCAN: Inorg. Chem. **5**, 774 (1966).
21. BAKER, W. A., and H. M. BOBONICH: Inorg. Chem. **3**, 1184 (1964).

Note added in proof: Very recently, FIGGIS *et al.* published results of calculations on the average magnetic susceptibility of $^5T_{2g}$ terms in lower symmetry which were obtained in an analogous approach (cf. FIGGIS, B. N., J. LEWIS, F. E. MABBS, and G. A. WEBB: J. Chem. Soc. **1967**, 442). The computational results of FIGGIS *et al.* are in complete agreement with the results presented here.

Dr. E. KÖNIG
Institut für physikalische Chemie II
der Universität Erlangen-Nürnberg
8520 Erlangen, Fahrstraße 17