

Van Vleck
lecturing
in Sterling Hall



Attendees at the Sixth Solvay Conference, 1930. Van Vleck is in the back row, third from the right, standing next to Enrico Fermi. Albert Einstein is seated in the front row, fifth from the right.

**J. H. Van Vleck and Magnetism at the
University of Wisconsin: 1928 -1934**

Susceptibilities

Local Fields

Van Vleck Susceptibility Papers: 1928-1929

1) On Dielectric Constants and Magnetic Susceptibilities in the New Quantum Mechanics, Part III, Phys. Rev. **31**, 587 (1928). (Minnesota)

2) The Effect of Second Order Zeeman Terms on Magnetic Susceptibilities in the Rare Earth and Iron Groups, Phys. Rev. **34**, 1494 (1929) (with Amelia Frank).

Paramagnetic Susceptibilities

$$M = \chi H \quad \chi > 0$$

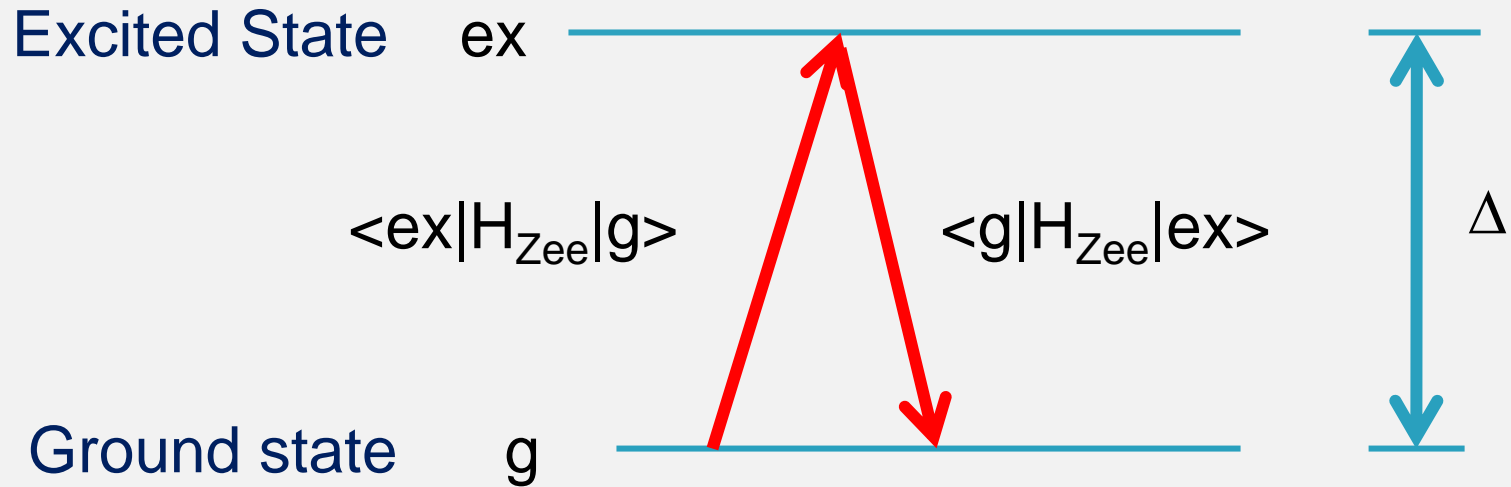
Free ion, LS coupling

Zeeman interaction: $g_J \mu_B J_z H$

$$\chi = (1/3) g_J^2 \mu_B^2 J(J+1) / kT$$

Temperature-dependent!

Van Vleck Temperature-Independent Paramagnetism



Zeeman interaction: $H_{Zee} = \mu_B H(L_z + 2S_z)$

Van Vleck Paramagnetism (con't)

Magnetic field admixes excited state wave function into ground state and ground state into excited state:

$$\psi_g' = \psi_g - (\langle ex | H_{Zee} | g \rangle / \Delta) \psi_{ex}$$

$$\psi_{ex}' = \psi_{ex} + (\langle g | H_{Zee} | ex \rangle / \Delta) \psi_g$$

Usual case: $kT \ll \Delta$. Only ground state occupied.

Temperature-independent contribution to susceptibility:

$$\delta\chi = 2N\mu_B^2 |\langle ex | (L_z + 2S_z) | g \rangle|^2 / \Delta$$

Ion	La+++	Ce+++	Pr+++	Nd+++	Pm+++	Sm+++	Eu+++	Gd+++
$(2S+1)L_J$	$1S_0$	$2F_{5/2}$	$3H_4$	$4I_{9/2}$	$5I_4$	$6H_{5/2}$	$7F_0$	$8S_{7/2}$
Old	0	2.54	3.58	3.62	2.68	0.84	0	7.9
V V-Frank	0	2.56	3.62	3.69	2.87	1.83	3.56	7.9
Expt. Cabrera	0	2.39	3.60	3.62	_____	1.54	3.61	8.2
Expt. Meyer	0	_____	3.47	3.51	_____	1.32	3.12	8.1

Apparent Bohr magneton numbers for first half of rare earth group

$$\text{Apparent magneton number} = [3kT\chi_{\text{exp}}(T)/N\mu_B^2]^{1/2}$$

Table from Van Vleck and Frank, 1929

Crystal Field Effects (Crystalline Stark Effect)

Van Vleck-Frank paper dealt with free ions.

Effects of interactions between magnetic ion and neighboring non-magnetic ions?

H. Bethe, Ann. d. Physik **3**, 133 (1929)

Susceptibility Papers: 1932

- 1) The Influence of Crystalline Fields on the Susceptibilities of Salts of Paramagnetic Ions. I. The Rare Earths, Especially Pr, and Nd, W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932). (Van Vleck post-docs!)
- 2) Theory of the Variations in Paramagnetic Anisotropy Among Different Salts of the Iron Group, J. H. Van Vleck, Phys. Rev. **41**, 208 (1932). (follows Penney-Schlapp paper)
- 3) The Influence of Crystalline Fields on the Susceptibilities of Salts of Paramagnetic ions. II. The Iron Group, Especially Ni, Cr, and Co, R. Schlapp and W. G. Penney, Phys. Rev. **42**, 666 (1932). (companion to Van Vleck paper)

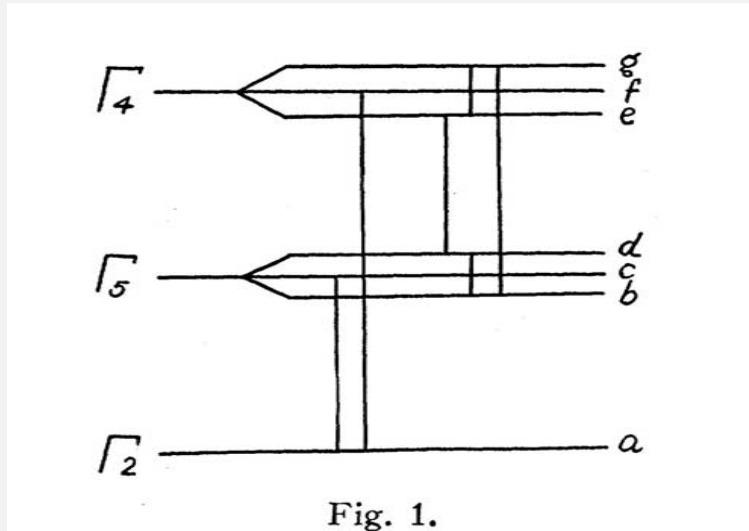
Paramagnetic Anisotropy in Iron

Group Salts: Ni⁺⁺ vs Co⁺⁺

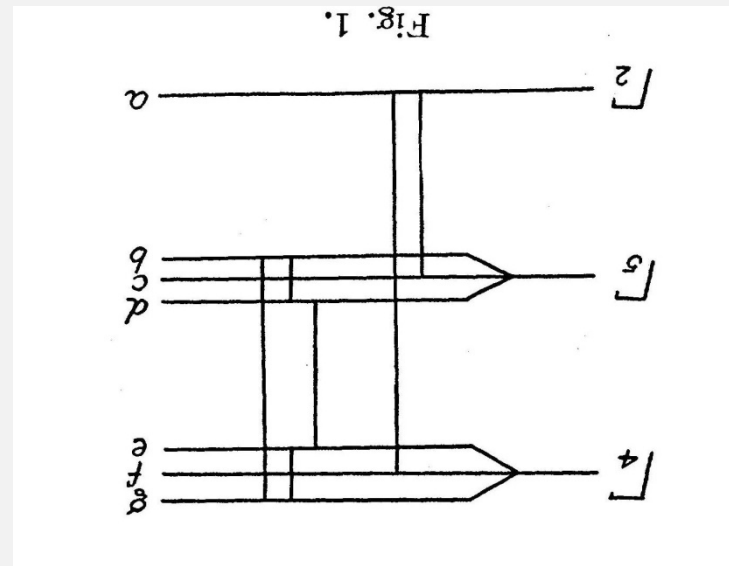
- 1) Ni⁺⁺ has nearly isotropic susceptibility with a 'spin only' Curie constant
- 2) Co⁺⁺ has significant anisotropy in susceptibility
- 3) Ni⁺⁺ and Co⁺⁺ are adjacent in periodic table and in orbital F states

Van Vleck Explanation: Crystal Field Effects

1) Reversal of crystal field levels $d^8 \ ^3F$ (Ni^{++}) \rightarrow $d^7 \ ^4F$ (Co^{++})



Ni^{++}



Co^{++}

2) Quenching of ground state orbital magnetic moment (Ni^{++})

The Theory of Electric and Magnetic Susceptibilities

J. H. Van Vleck

Professor of Theoretical Physics in
The University of Wisconsin

Oxford University Press

1932

(manuscript completed in 1931)

Notes for a Second Edition

(given to Chun Lin by Abigail Van Vleck after John's death)

- I. Classical Foundations (minor changes)
- II. Classical Theory of the Langevin-Debye Formula (minor changes)
- III. Dielectric Constants, Refraction, and the Measurement ... (minor changes)
- IV. The Local Field and Dielectric Constants of Condensed Media (new chapter)**
- V. The Classical theory of Magnetic Susceptibilities (minor changes)
- ~~V. Susceptibilities in the Old Quantum Theory Contrasted with the New~~
- VI. Quantum-Mechanical Foundations (changes)

Sections of the Local Field Chapter

25. Depolarizing (or Demagnetizing) Corrections

26. The Lorentz Field and its $4\pi/3$ Catastrophe

27. The Onsager Local Field

28. Dipole Interaction Treated by Statistical Mechanics

29. Short Range Order – Kirkwood's Formula

30. Limits of Validity of the Clausius-Mossotti Formula – The Translational Fluctuation Effect

31. Inadequacy of the Local Field Concept

32. Incipient Saturation Effects

Local Field

“The effective average field to which a molecule is subjected when a macroscopic field \mathbf{E} is applied”

J. H. Van Vleck (from *The Theory of Electric and Magnetic Susceptibilities*)

Phenomenological Electrostatic Theories for the Local Field

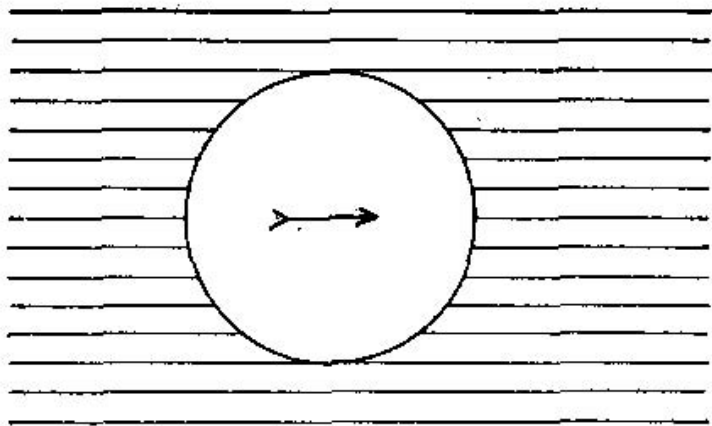
Lorentz (1878)

$$\mathbf{e}_{\text{Loc}} = \mathbf{E} + (4\pi/3)\mathbf{P} = [(2 + \varepsilon)/3]\mathbf{E}$$

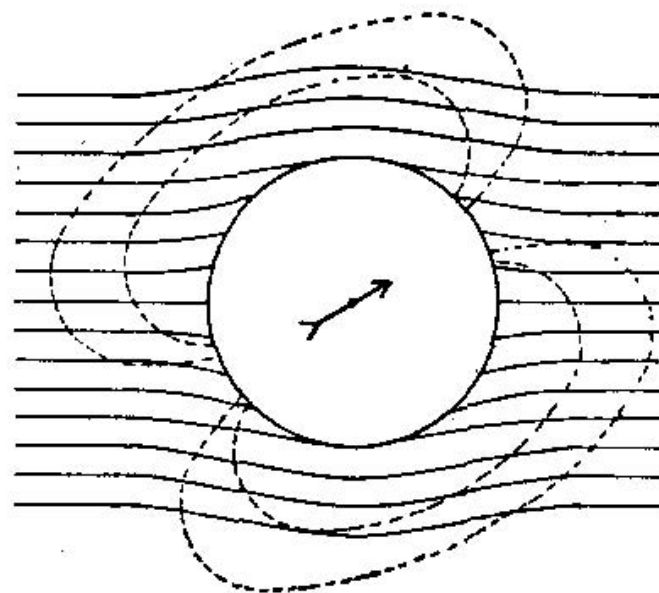
Onsager (1936)

$$\mathbf{e}_{\text{Loc}} = [3\varepsilon/(2\varepsilon + 1)]\mathbf{E} \quad (\text{polar molecules})$$

$$\mathbf{e}_{\text{Loc}} = [(2 + \varepsilon)/3]\mathbf{E} \quad (\text{polarizable molecules})$$



Lorentz



Onsager (polar)

J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937)

Which is the better approximation?

Van Vleck's Footnote

“Apparently the first attempt to treat dipolar coupling in dielectrics by means of statistical mechanics, using this interaction in the partition function instead of employing electromagnetic theory, was made by the writer (J. Chem. Phys. **5**, 320, and especially, 556 (1937)). The analysis in the present section follows to a considerable extent that in this earlier work but is presented in improved and somewhat more condensed form.”

Van Vleck's Analysis

Microscopic calculation of the dielectric constant for a liquid with molecules that are both polar and polarizable ($\alpha \neq 0$). (1) Expand the partition function to second order in the dipolar interaction. (2) Calculate the dielectric constant. (3) Use the Clausius-Mossotti (C-M) equation as the basis for comparison with Lorentz-Debye and Onsager theories.

$$\text{C-M Eq. } (\epsilon - 1)/(\epsilon + 2) = (4\pi N/3V)[\alpha + ?]$$

Conclusion

According to Van Vleck, “the results of [this] calculation are thus about half way between those of the Onsager and [Lorentz-]Debye models.”

Edited Chapter IV is available as a pdf from the UW-Physics web site

<http://www.physics.wisc.edu/vanvleck/>

Van Vleck Biographical Memoirs

P. W. Anderson, National Academy of Sciences,
1987

B. Bleaney, Fellows of the Royal Society, 1982

Van Vleck's Local Field Analysis (con't)

Lorentz-Debye:

$$(\epsilon - 1)/(\epsilon + 2) = (4\pi N/3V)(\alpha + \mu^2/3kT)$$

Onsager:

$$(\epsilon - 1)/(\epsilon + 2) = (4\pi N/3V)(\alpha + 3\epsilon\gamma(\mu^2/kT)/[(\epsilon+2)(2\epsilon+1)])$$

α = polarizability, μ = dipole moment, $\gamma = f(\alpha, \epsilon)$