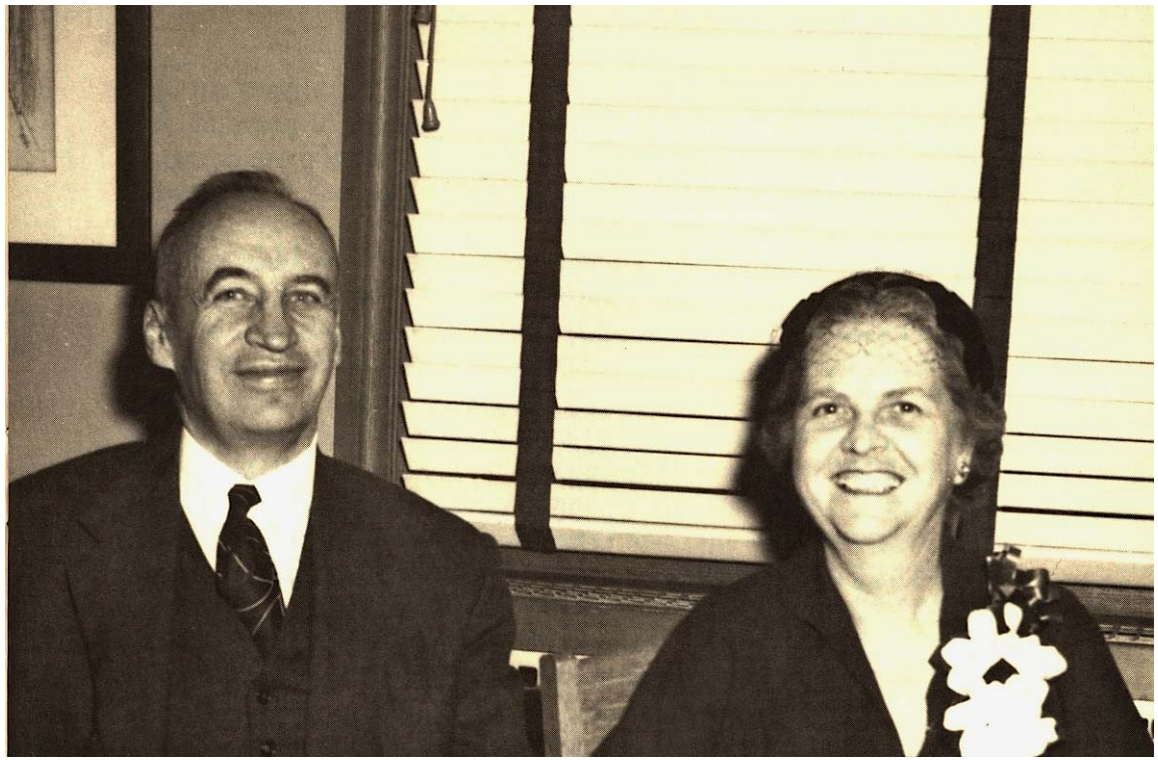
John Hasbrouk Van Vleck

Magnetic Gases and Garnets



John H. and Abigail Van Vleck ~ 1954

ON DIELECTRIC CONSTANTS AND MAGNETIC SUSCEPTIBILITIES IN THE NEW QUANTUM MECHANICS

PART III- APPLICATION TO DIA- AND PARAMAGNETISM

BY J.H. VAN VLECK

PHYSICAL REVIEW VOL.31, p.587, APRIL 1928

THE THEORY OF ELECTRIC AND MAGNETIC SUSCEPTIBILITIES

BY J.H.VAN VLECK

PROFESSOR OF THEORETICAL PHYSICS IN THE UNIVERSITY OF WISCONSIN

OXFORD UNIVERSITY PRESS, 1932

Chapter X #66. The Oxygen Molecule

#67. The Nitric Oxide Molecule

Oxygen O_2: "The only known paramagnetic molecule with an even number of electrons, whereas paramagnetism is the usual rule for molecules with an odd number of electrons"

Assumptions: Lowest energy states are 3 closely spaced ^3S levels.
Structure splitting << k_BT

Curie's law for S = 1 :

$$\chi = N\beta^2 4S(S+1)/3k_BT$$

Prediction confirmed by experiments down to 136 K (Boiling point : 90 K)

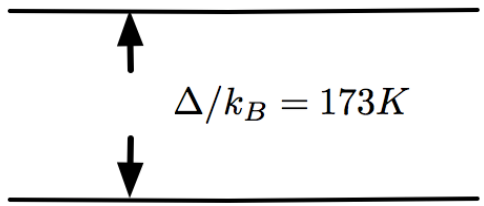
In liquid and solid state, $\chi(O_2$ diluted in $N_2)$ obeys Curie's law
(Perrier & Kamerlingh Onnes)

But what happens below 60 K when $k_BT \sim {}^3S$ structure splitting ??

Prediction for free $O^{16}O^{16}$ gas : $\chi \rightarrow$ Const. , as $T \rightarrow 0$
(A.H. Cooke and W.P. Wolf , Proc. Roy. Soc.**225A**,112,[1954])

Nitric Oxide NO : $^2\Pi$ doublet

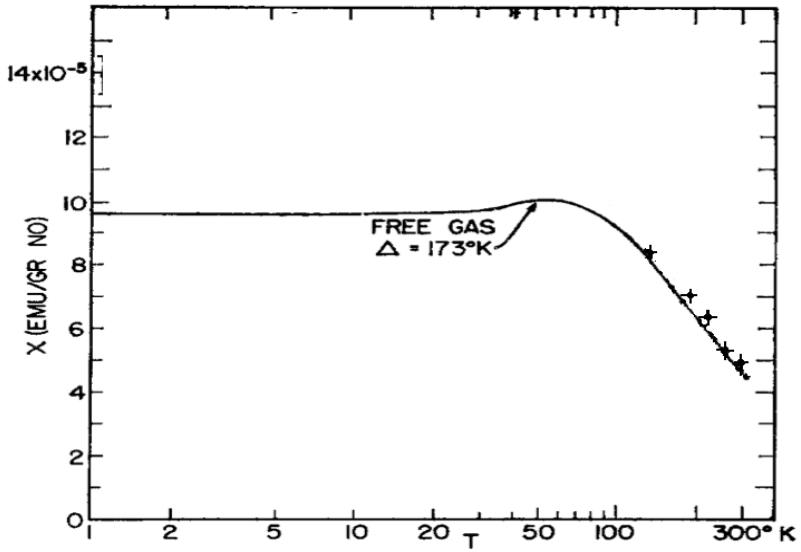
$\Sigma = ½$



$\Sigma = -½$

$\Lambda = 1$ orbital angular momentum

$\chi = (N\beta^2/3k_BT) \times \Phi(173/T)$ Free gas



Experimental results from several labs above 120 K

Molecules trapped in β-quinol clathrates

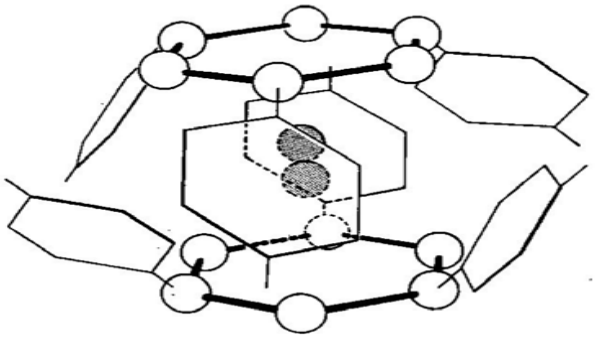
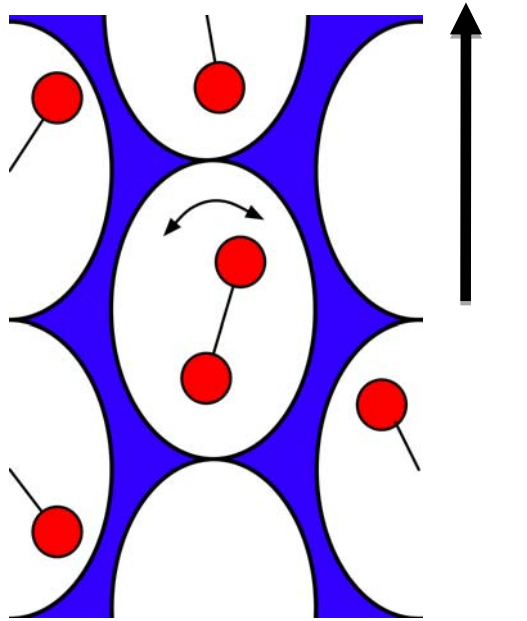
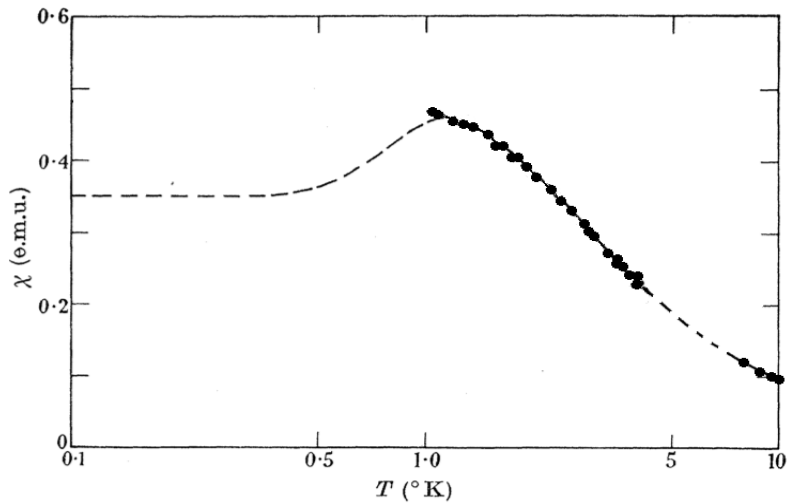


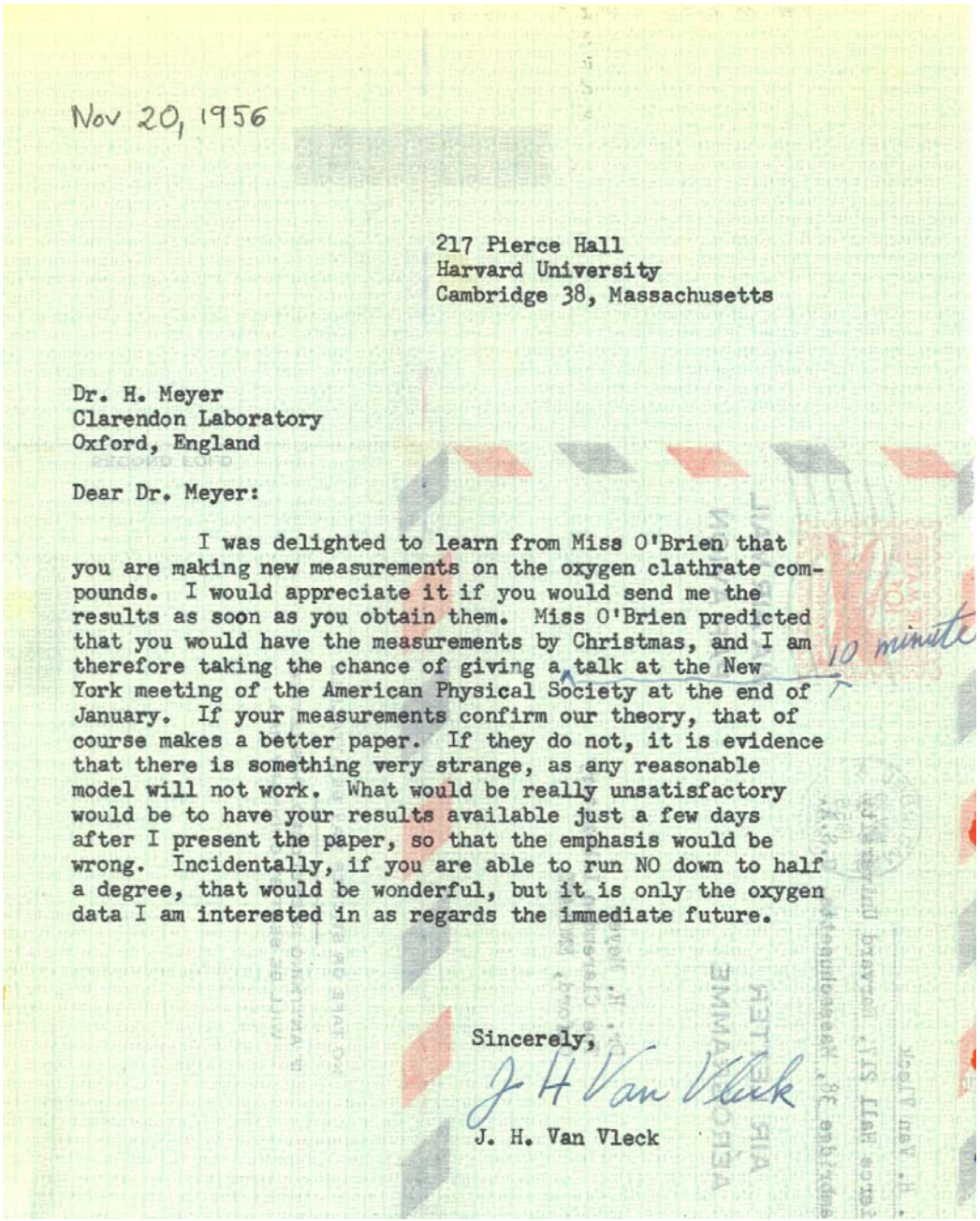
FIG. 1. Structure of a β-quinol clathrate cage containing a trapped diatomic molecule (shaded). The heavy black lines represent indirect bonds formed by hydrogen atoms between neighboring oxygens (unshaded spheres), not direct bonds. The hexagons represent benzene rings.



Experiments on susceptibility of O_2 (A.H. Cooke et al. Proc. Roy. Soc.**225A**,112,[1954])

Symbols : Data . **Dashed line** : Predictions for the free O_2 gas





Nov 20, 1956

217 Pierce Hall
Harvard University
Cambridge 38, Massachusetts

Dr. H. Meyer
Clarendon Laboratory
Oxford, England

Dear Dr. Meyer:

I was delighted to learn from Miss O'Brien that you are making new measurements on the oxygen clathrate compounds. I would appreciate it if you would send me the results as soon as you obtain them. Miss O'Brien predicted that you would have the measurements by Christmas, and I am therefore taking the chance of giving a talk at the New York meeting of the American Physical Society at the end of January. If your measurements confirm our theory, that of course makes a better paper. If they do not, it is evidence that there is something very strange, as any reasonable model will not work. What would be really unsatisfactory would be to have your results available just a few days after I present the paper, so that the emphasis would be wrong. Incidentally, if you are able to run NO down to half a degree, that would be wonderful, but it is only the oxygen data I am interested in as regards the immediate future.

10 minute

Sincerely,

J H Van Vleck

J. H. Van Vleck

Nov. 20, 1956

I was delighted to learn from Miss O'Brien that you are making measurements on the oxygen clathrate compounds. I would appreciate it if you would send me the results as soon as you obtain them…… I am therefore taking the chance of giving a 10 minute talk at the N.Y. meeting of the APS at the end of January. If your measurements confirm our theory, that of course makes a better paper…….
Incidentally if you are able to run NO down to half a degree, that would be wonderful, but it is the oxygen data I am interested in as regards the immediate future.

Sincerely

J.H. Van Vleck

O'Brien and Van Vleck theory :
O_2 molecules are not free to rotate, but are subject to a hindering potential V_o/k_B = 32K, as derived from the Oxford 1954 χ experiments.

H.Meyer, M. O'Brien and J.H. Van Vleck (Proc Roy Soc. 24**3A**, 414 (1957)

Solid curve: *Theory with hindered rotation (O'Brien, Van Vleck)*
Dashed curve : *Theory for free gas $^{16}O^{16}O$* ***Symbols*** *(Open circles): New data*

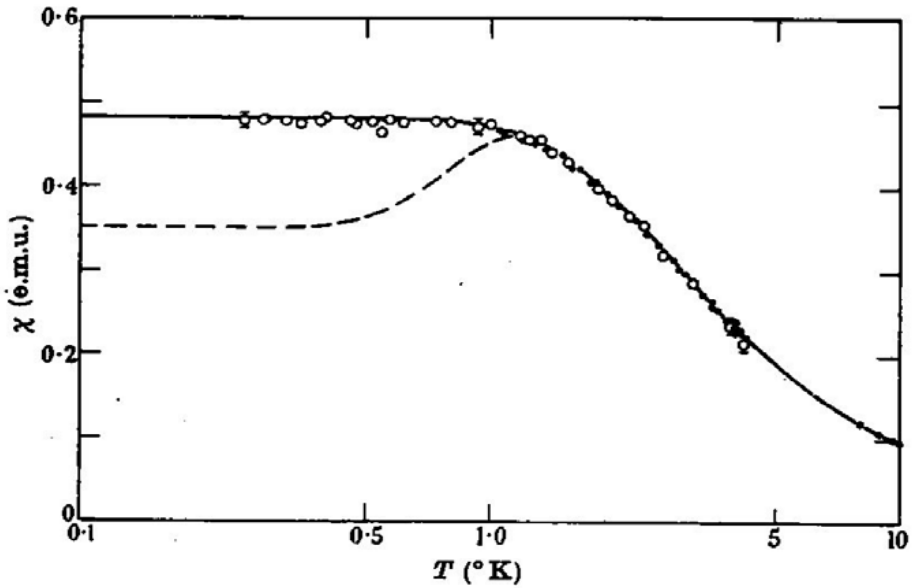
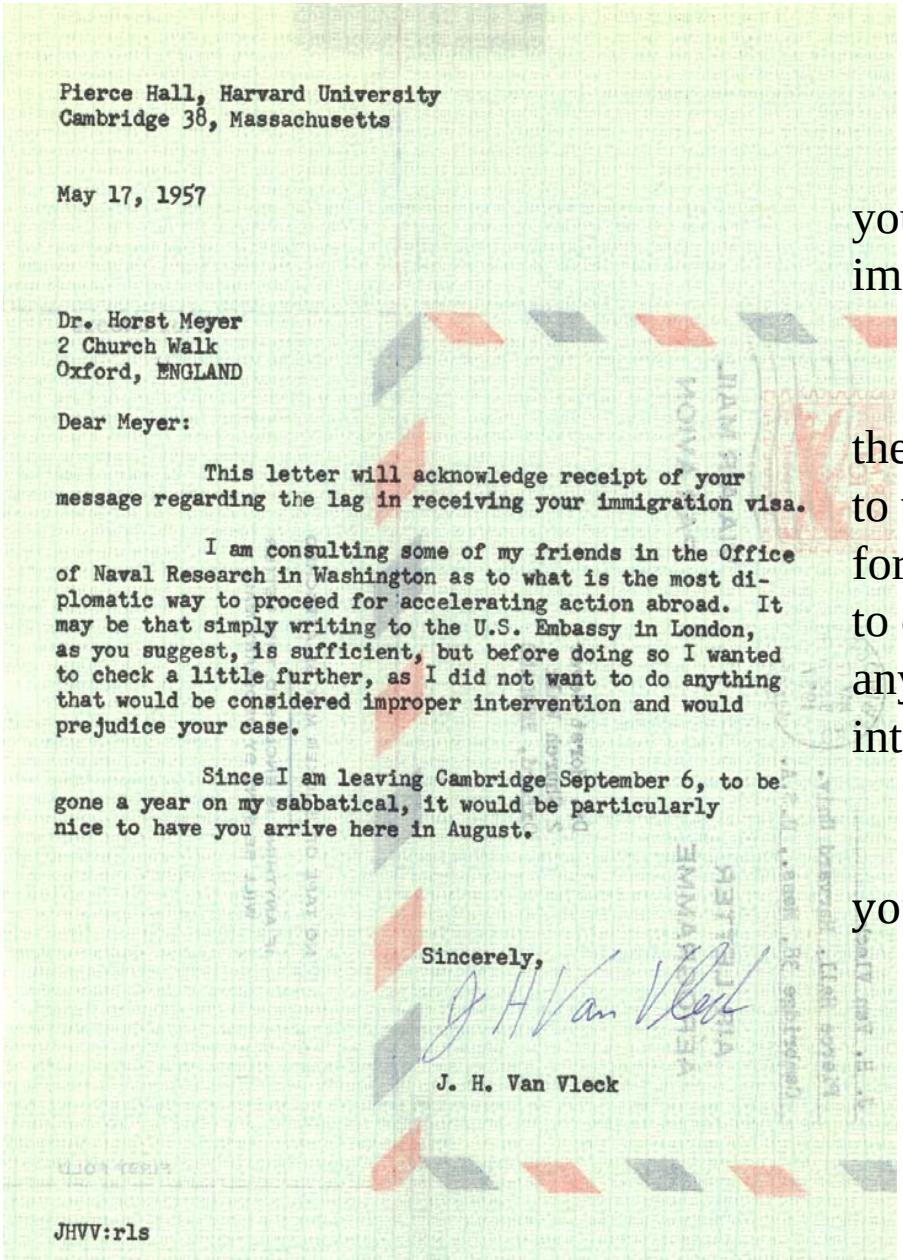


FIGURE 4. Comparison of the present theory with the experimental values of the susceptibility (in e.m.u./mole) down to 0·25° K. •, Cooke *et al.* (1954); O, new results. Full line, calculated with $D/k = 4{\cdot}15°$ K; broken line, calculated susceptibility of free $^{16}O^{16}O$.

V_o/k_B = 32 K ----→ hindered rotation frequency $\nu = 0.49 \times 10^{12}$ sec^{-1}



Pierce Hall, Harvard University
Cambridge 38, Massachusetts

May 17, 1957

Dr. Horst Meyer
2 Church Walk
Oxford, ENGLAND

Dear Meyer:

This letter will acknowledge receipt of your message regarding the lag in receiving your immigration visa.

I am consulting some of my friends in the Office of Naval Research in Washington as to what is the most diplomatic way to proceed for accelerating action abroad. It may be that simply writing to the U.S. Embassy in London, as you suggest, is sufficient, but before doing so I wanted to check a little further, as I did not want to do anything that would be considered improper intervention and would prejudice your case.

Since I am leaving Cambridge September 6, to be gone a year on my sabbatical, it would be particularly nice to have you arrive here in August.

Sincerely,

J. H. Van Vleck

JHVV:rls

May 17, 1957

This letter will acknowledge receipt of your message regarding the lag in receiving the immigration visa.

I am consulting some of my friends at the Office of Naval Research in Washington as to what is the most diplomatic way to proceed for accelerating action abroad…….I wanted to check a little further, as I did not want to do anything that would be considered improper intervention and would prejudice your case

…..it would be particularly nice to have you arrive here in August

J. Phys. Chem. Solids Pergamon Press 1961. Vol. 20, Nos. 3/4, pp. 241–254. Printed in Great Britain.

THEORY OF THE MAGNETIC SUSCEPTIBILITY OF THE NITRIC OXIDE CLATHRATE

J. H. VAN VLECK
Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts
(*Received* 20 *March* 1961)

a) Crystalline Potential of trigonal symmetry
– corresponding to that of the clathrate

b) Estimated hindering potential $V/k_B = 45$ K ,
in-between that of N_2 (75 K) and O_2 (33 K)

Success in fitting the experimental data with this potential,
However: the predicted 1/T term, which should be 6% of
main term at 1 K, was not observed.

Search for ESR resonance measurements on single NO clathrate crystals to detect the weak paramagnetic term, predicted by Van Vleck, unsuccessful in detecting a signal over estimated range.(E.R.Hunt and H. Meyer, 1964)

J. Phys. Chem. Solids Pergamon Press 1961. Vol. 20, Nos. 3/4, pp. 238–240. Printed in Great Britain.

THE SUSCEPTIBILITY OF NO IN β-QUINOL CLATHRATES

H. MEYER*
The Clarendon Laboratory, Oxford University
(*Received* 20 *March* 1961)

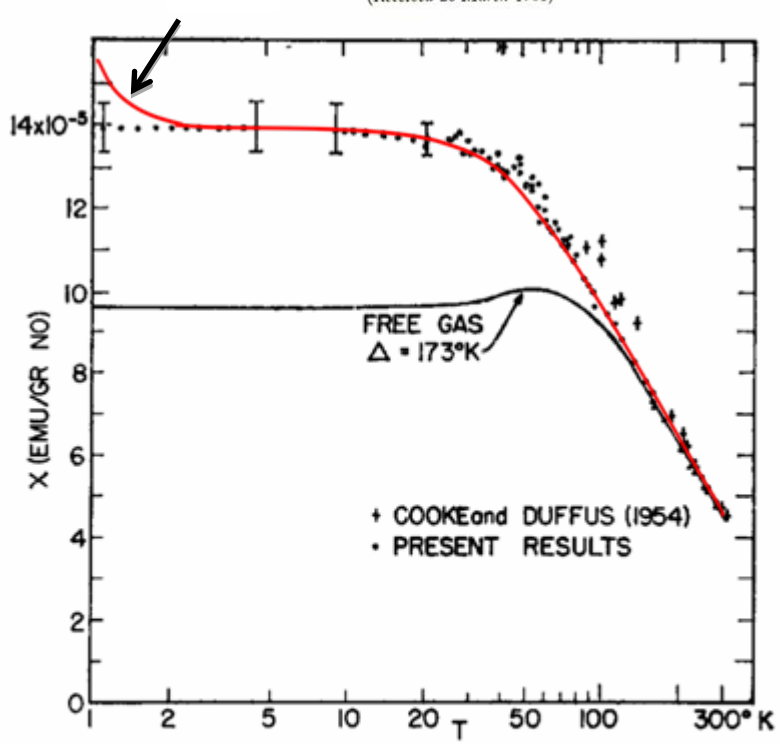


FIG. 1. The paramagnetic susceptibility of NO in randomly oriented clathrate crystals ● present results; + results by COOKE and DUFFUS. The susceptibility measured by these authors at 10°K is 23×10^{-5} e.m.u./g NO.

O_2

Confirmation of the O'Brien and Van Vleck theory by paramagnetic resonance experiments of O_2 in clathrates :
(S. Foner, H.Meyer and W.H. Kleiner , J. Phys. Chem. Solids, **18**, 273, [1961])

Hindered potential → V_o/k_B = 34 K. (O'B,VV : V_o/k_B = 32 K)

Fine structure of resonance observed: Interaction with molecules in neighboring cages

NO

Infrared spectra measurements
(J.C.Burgiel, H.Meyer and P.L. Richards, J. Chem. Phys.43, 4291 [1965])

→ Hindering potential energy V/k_B =47 K . Van Vleck's estimate : V/k_B= 45 K

Rare- Earth Iron Garnets

$2Fe_2O_3.\ 3Fe_2O_3.\ 3M_2O_3$ where M is trivalent Y^{3+} or a Rare Earth

a **d** **c** interpenetrating sublattices

Trivalent Fe^{3+} has spin S = 5/2 . The **a** and **d** sublattices have antiparallel spin alignment → Ferrimagnet .

RE spins (on **c** sublattice) interact mostly with the **d** sublattice and align antiparallel.

Van Vleck was principally interested in Europium Iron Garnet.
The reason for this:
Ground State J = 0, First excited state of the J=1 triplet : E/k_B = 458 K
Second-order Zeeman effect important because of the proximity of triplet state.
Hence Eu^{+3} has a magnetic moment and a sublattice magnetization.

JOURNAL OF APPLIED PHYSICS VOLUME 39, NUMBER 2 1 FEBRUARY 1968

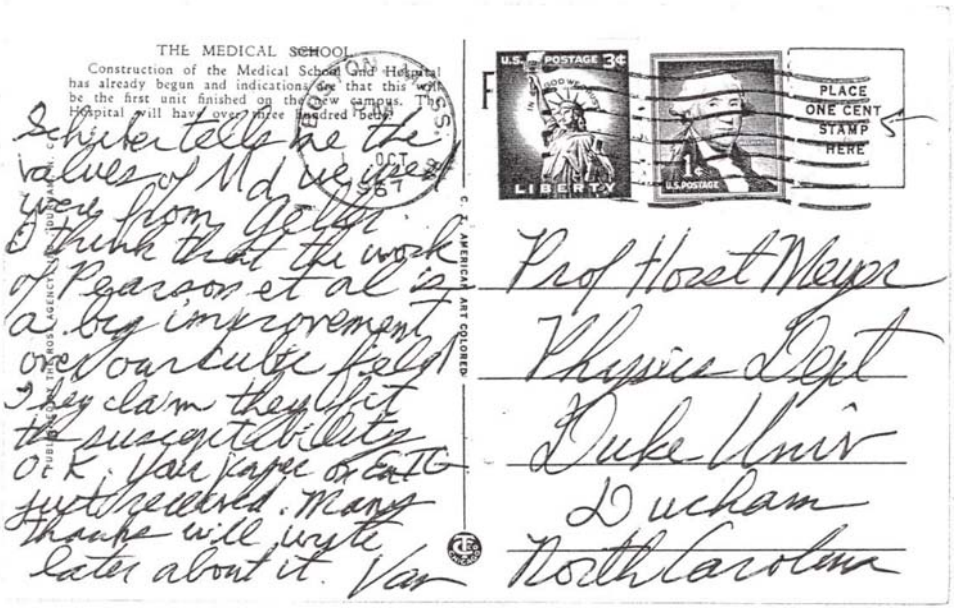
Opening Session

I. S. JACOBS, *Chairman*

Magnetic Case History of the Eu^{3+} Ion

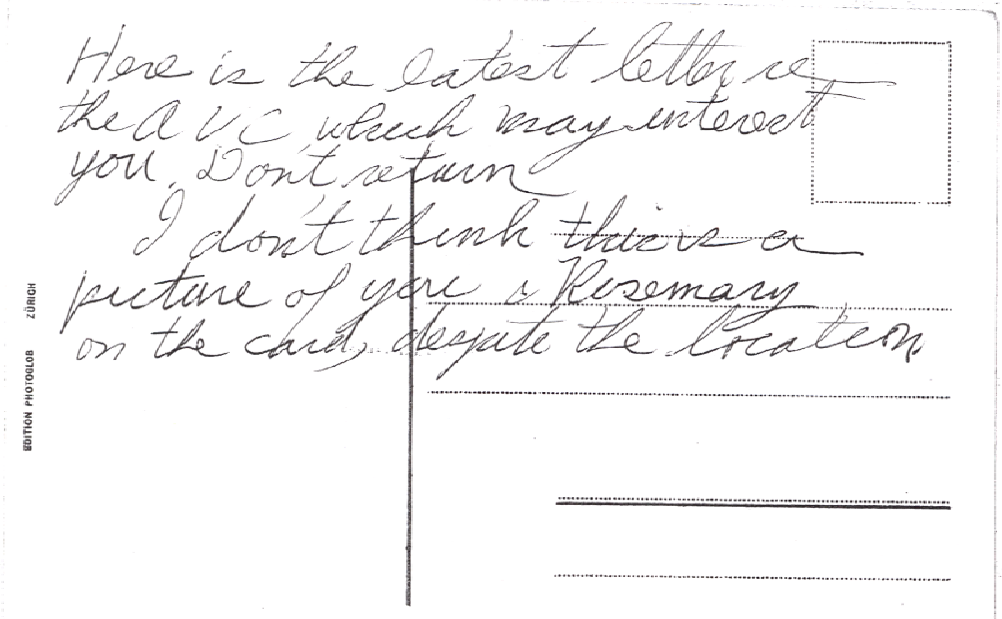
J. H. VAN VLECK

Harvard University, Cambridge, Massachusetts



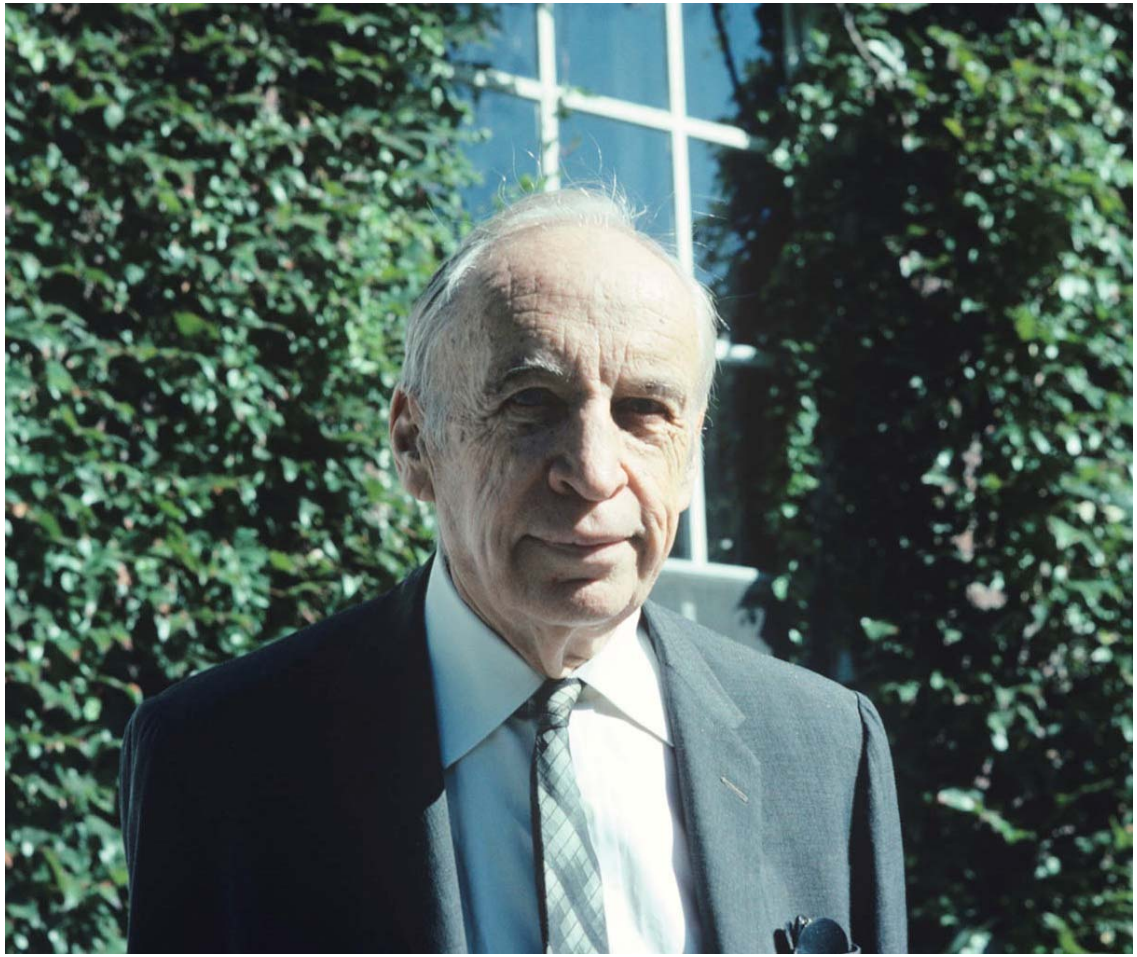
Schieber tells me the values of M_d we used were from Geller. I think that the work of Pearson et al. is a big improvement over our cubic field. They claim they fit the susceptibility O.K. Your paper on EulG just received. Many thanks. Will write about it later.

Van



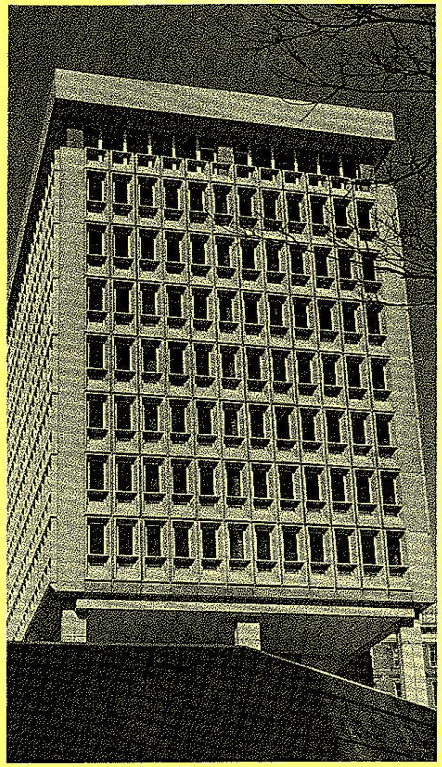
Here is the latest letter re the AVC which may interest you. Don't return.

I do not think this is a picture of you and Rosemary on the card, despite the location



John H. Van Vleck, at Harvard, 1975

FINE STRUCTURE OF MOLECULAR SPECTRA IN MADISON AND INTERSTELLAR SPACE



VanVLECK HALL

BY

J. H. VanVLECK

JULIAN E. MACK LECTURE

DEPARTMENT OF PHYSICS

UNIVERSITY OF WISCONSIN–MADISON

MAY 1, 1979

Van Vleck's last lecture at the University of Wisconsin, (May 1st, 1979)

Graves of Abigail and John H. Van Vleck, Madison, Wisconsin (Photo credit: C.C. Lin)

Vive la Suisse !

Van

Separatum
HELVETICA PHYSICA ACTA
Vol. 41, Fasc. 6/7, p. 1234–1235 (1968)

My Swiss Visits of 1906, 1926, and 1930

by

J. H. Van Vleck

Vive **V**an **V**leck !!