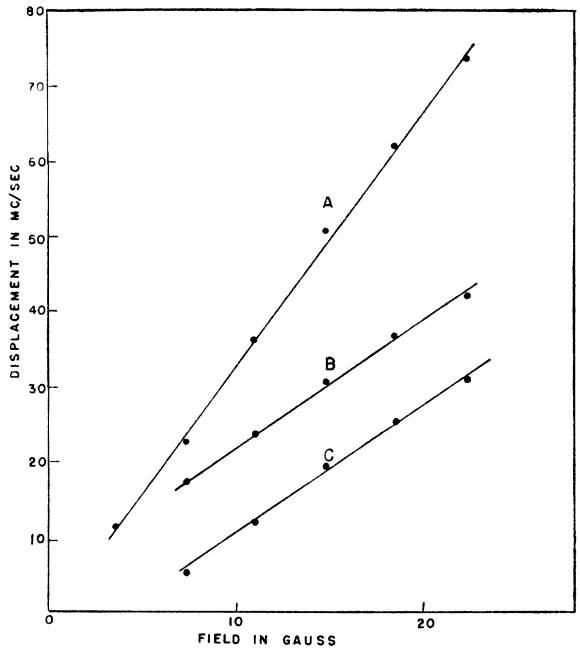

FIG. 3. Measured Zeeman displacements as a function of field strength for the $\Delta M=\pm 1$ components of the $J=0\rightarrow 1$, $K=1$ transition of O_2; (A) total separation of components, (B) displacement of high frequency components, (C) displacement of low frequency components.

unable to account for this discrepancy. Neglecting possible systematic errors of unknown origin, the disagreement lies well outside the estimated range of errors. It is surprising that the strong field magnetic resonance measurements of Beringer and Castle[6] and the strong field Zeeman measurements in the optical region by Schmid, Budó, and Zemplén[7] yield a g factor in agreement with the weak field case of the present measurement. Because of the apparent inconsistency further measurements of the weak field Zeeman effect are being made.

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Nuclear Relaxation in Gases by Surface Catalysis

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WHILE the interaction between the rotational motion and the nuclear moment provides, in the case of diatomic and polyatomic gases, an effective mechanism for the establishment of thermal equilibrium,[1] it is necessary for nuclear induction experiments with noble gases to provide a catalyst in order to obtain sufficiently short relaxation times. The admixture of oxygen was originally suggested for this purpose[2] and has since been successfully used[3] for He^3. However, the partial pressure of oxygen must be chosen here as high as 10 atmospheres to attain even a relaxation time $T_1\cong 1$ sec, and appreciably shorter relaxation times which are otherwise desirable would require excessive pressures. It seemed worth while, therefore, to consider another mechanism, which can lead to short relaxation times without an increase of pressure. Such a mechanism can be realized if the sample consists of a fine powder of a paramagnetic substance with the gas under investigation filling the space between the powder particles. Even with a densely packed powder, there will still be about half of the total volume available for the gas, so that under the same pressure the reduced amount of sample substance within the volume of the receiver coil does not cause serious reduction of the signal. Because of the molecular magnetic moments of the powder, there exist strong irregular magnetic fields within atomic distances from the surface of the powder particles. Consequently, the impact of a gas atom upon a surface causes a similar reorientation of the nuclear moment as is otherwise achieved in an impact with a molecule of admixed oxygen, and one can therefore expect that this mechanism can likewise contribute effectively towards establishment of thermal equilibrium.

To obtain a quantitative treatment of this surface catalysis, it is necessary to consider the self-diffusion of the gas in the space between the powder particles. It requires a slight generalization of the macroscopic differential equations which we gave earlier[4] with the difference that the components of the polarization vector $\mathbf{M}$ must be considered as functions not only of the time but also of the space coordinates. We shall assume that the mean change of the nuclear moment $\boldsymbol{\mu}$ by an impact on the surface is

$$\langle\delta\boldsymbol{\mu}\rangle_{Av}=-w(\langle\boldsymbol{\mu}\rangle_{Av}-\boldsymbol{\mu}_0), \tag{1}$$

where w measures the transition probability in an impact and $\boldsymbol{\mu}_0$ is the equilibrium value of $\langle\boldsymbol{\mu}\rangle_{Av}$. The rate of change of the total moment, contained in a gas volume V with the arbitrary boundary surface B can then be written in the form

$$\frac{d}{dt}\int_V \mathbf{M}d\tau=D\int_{B_1}\mathrm{grad}_\sigma\mathbf{M}d\sigma-\frac{w\bar{v}}{4}\int_{B_2}(\mathbf{M}-\mathbf{M}_0)d\sigma + \int_V\left[\gamma[\mathbf{M}\times\mathbf{H}]-\frac{\mathbf{M}_{tr}}{T_2'}\right]d\tau. \tag{2}$$

The first integral on the right side extends over the part B_1 of B which is situated within the gas and represents the contribution due to diffusion with the coefficient D. The second integral represents the effect of impacts, taking place over the part B_2 of B which is formed by the surface of powder particles; it follows from (1), since the mean number of impacts per unit area and unit time is given by $n\bar{v}/4$ (n=number of gas atoms per unit volume, $\bar{v}$=mean velocity) and since $n(\langle\boldsymbol{\mu}\rangle_{Av}-\boldsymbol{\mu}_0)=\mathbf{M}-\mathbf{M}_0$. The last integral represents the additional change of $\mathbf{M}$ within V due to the external field $\mathbf{H}$ and a possible field inhomogeneity ΔH, affecting the transverse part $\mathbf{M}_{tr}$ of $\mathbf{M}$ and measured by $1/T_2'=\gamma\Delta H$. An equivalent differential form of (2) is

$$\partial\mathbf{M}/\partial t=D\nabla^2\mathbf{M}+\gamma[\mathbf{M}\times\mathbf{H}]-\mathbf{M}_{tr}/T_2' \text{ within the gas,} \tag{3}$$

$$0=D\,\mathrm{grad}_\sigma\mathbf{M}+\tfrac{1}{4}w\bar{v}(\mathbf{M}-\mathbf{M}_0) \text{ on the surface.} \tag{3a}$$

In (2) and (3a) the subscript σ indicates the external normal component to the boundary B_1 and to the powder surface, respectively.

The variation of $\mathbf{M}$ in space can be neglected if the order of magnitude d of the distance between powder particles is sufficiently small. Extending V over the total volume of the gas, so that $B_2=S$ is the total surface of the powder particles, one obtains then from (2) the same differential equations for the time dependence of $\mathbf{M}$ as were obtained before (see reference 2) if

$$T_1=4V/w\bar{v}S \tag{4}$$

and

$$T_2=T_1T_2'/(T_1+T_2') \tag{4a}$$

are taken as longitudinal and transverse relaxation times, respectively. The necessary smallness of d implies merely that the time d^2/D, which is of the order of the time between impacts upon different particles, is small compared with either T_1 or T_2 and is well realized under normal conditions.

The effectiveness of this mechanism can be best estimated by comparing (4) with the value $(T_1)_{O_2}$ which one would obtain with a given partial pressure $(p)_{O_2}$ of admixed oxygen. Assuming the

magnetic moment per molecule and the distance of closest approach in an impact to be approximately the same for the powder and for oxygen the transition probability w will likewise be approximately the same in the two cases. One can then write

$$(T_1)_{O_2} \cong w\nu, \tag{5}$$

where ν is the number of collisions per unit time of a gas atom with an oxygen molecule. Expressing this number in terms of the gas kinetic cross section σ with oxygen, the pressure $(p)O_2$ and the mean velocity $\bar{v}$, which is likewise taken to be approximately the same in the two cases, one obtains from (4) and (5)

$$T_1 \cong (T_1)_{O_2}(4V\sigma A/SV_m)(p)_{O_2}, \tag{6}$$

where A is Avogadro's number, V_m the mole volume at one atmosphere, and where $(p)_{O_2}$ is measured in atmospheres.

A case to which (6) applies is a fine powder of Fe_2O_3, used here recently as a surface catalyst for xenon.[5] From an electron microscope picture V/S was estimated to be about 10^{-6} cm. With $\sigma \cong 10^{-15}$ cm^2, the "equivalent oxygen pressure" $(p)_{O_2}$ for which $(T_1)_{O_2} = T_1$ is here found from (6) to be about 10 atmospheres; this is in qualitative agreement with the observed equivalent pressure of approximately 30 atmospheres.

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On the Origin of Magnetism in Iron Sulfides with Various Sulfur Contents

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MAGNETIC,[1] electrical,[2] and thermal[3] behavior of a series of iron sulfides $FeS_x (1 \leq x < 2)$, together with their crystal structures,[4] have been studied by many investigators. It is especially noteworthy that the magnetic behavior is sensibly affected by the excess sulfur content in the substances.[1] A theoretical discussion of these magnetic characteristics is given below based on the following ideas: The formation of S- and γ-type superlattices of ions (explained later in this paper) is inferred from the nonmagnetic interactions between Fe^{++} (4 Bohr magnetons) and Fe^{+++} (5 Bohr magnetons) ions. Furthermore, assuming the exchange integral J between adjacent net planes perpendicular to the hexagonal axis to be negative, it may be shown that antiferro- or ferrimagnetism occurs for the superlattice type γ or S_x, respectively.

We shall consider at first the case $x = 1.12$, for which the value of spontaneous magnetization is largest. In this case the lattice on which Fe ions are situated can be divided into two simple hexagonal sublattices (1) and (2) whose lattice constants in the direction of the hexagonal axis are twice as large as that of the original one (see Fig. 1). By an appropriate choice of the above-mentioned interaction coefficients, it is shown that below a certain temperature T_s, which is somewhat higher than 325°C, there occurs an ordered arrangement (superlattice S) of Fe^{++} and Fe^{+++}, in which the sublattice (1) contains only Fe^{++}, while the sublattice (2) contains both Fe^{+++} and Fe^{++} [see Fig. 1(a)]. Since the exchange integral J between the sublattice (1) and (2) is negative, the directions of aligned spins on the two sublattices become antiparallel* with each other below 325°C ($= T_\beta$). So the total magnetic moment is given by the difference of the magnetic moments of two sublattices, and this magnetism, therefore, is a ferrimagnetism† introduced by Néel.[6] Using the approximational method of Bragg and Williams, the results obtained agreed satisfactorily with the observed values of the spontaneous magnetization as well as with its temperature dependence and with the anomalous specific heat.[3] When x became greater than 1.12, the phase of FeS_2 appeared[6] to mix with the former.

The range $1 \leq x \leq 1.04$ corresponds to the antiferromagnetic case. Using appropriate interaction coefficients, one can find the formation of another kind of superlattice γ which has a Curie point T_γ, ($T_s < T_\gamma$) and is more stable than the superlattice S. The coexistence of these two superlattices is also excluded. In the case of the superlattice γ, the lattice can be divided into new sublattices, in which the Fe ions are distributed in another kind of ordered configuration. For instance, three interpenetrating hexagonal sublattices are assumed, two of which (1′) contain Fe^{++} ions only, while the remaining one (2′) contains also Fe^{+++} ions. Or, assuming two monoclinic sublattices, the one (1″) contains Fe^{++} alone [see Fig. 1(b)]. Hence, in the new superlattice γ, Fe^{+++} ions are equally distributed among the former sublattices (1) and (2), so that in this case only antiferromagnetism, whose Curie point is T_β, can be observed. The occurrence of α "knick" in the curve of magnetic susceptibility χ *vs* temperature at about 135°C ($= T_\alpha$) may be understood by Haraldsen's idea or by the change of value of J due to the remarkable change of lattice constant near this temperature. This change may be caused by the order-disorder transformation of the vacant lattice points.

Next, in the range $1.05 \leq x \leq 1.09$, another peak γ was found in the curve of susceptibility *vs* temperature. For this range it is shown that such relations as $T_s < T_\gamma$ and $T_\alpha < T_\gamma$ were obtained by using the interaction parameters interpolated from those of the above two cases ($x = 1.12$ and $1 \leq x < 1.04$). Under such a condition the susceptibility χ at first increases with the fall of temperature according to the relation $\chi \sim (T - T_s)^{-1}$, but reaches a maximum value at T_γ. Since the formation of the superlattice γ counteracts the small unbalance of ionic arrangement between the sublattices (1) and (2) caused by the application of external magnetic field, χ decreases rapidly. The calculated behavior of χ agrees with that of the observed γ-anomaly.

The cause of A-type ferromagnetism found at $x = 1.10$ is now considered. For this case such a relation as $T_s \gtrapprox T_\gamma \gg T_\alpha$ is very probable. From this relation it follows that, as before, the spontaneous (ferri-) magnetization occurring at T_s may be completely destroyed at a temperature slightly lower than T_γ, because at this

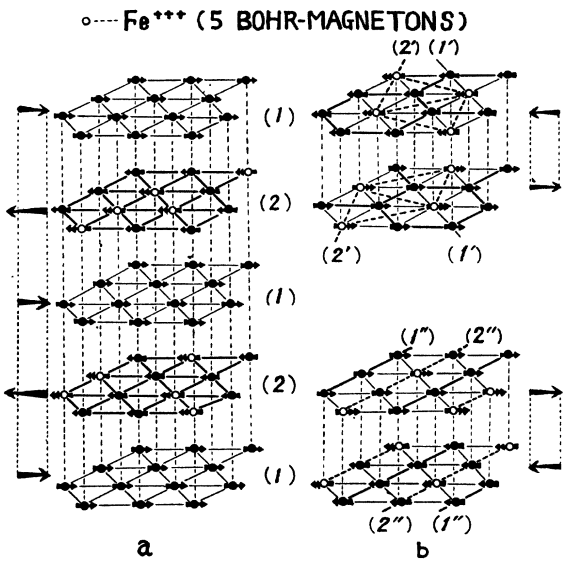

FIG. 1. The possible structures of two kinds of ionic superlattices S- and γ-type. The solid circles represent Fe^{++} ions and the open circles represent Fe^{+++} ions. Small arrows indicate the direction of the magnetic moment of each ion and large ones those of sublattices. (a): S-type ionic superlattice appearing when the substance is ferrimagnetic. (b): γ-type ionic superlattice appearing when the substance is antiferromagnetic.