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# Isotope Effect on the Néel Temperature of $CoCl_2 \cdot 6H_2O$†

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Using the nuclear-magnetic-resonance technique, it has been discovered that an increase of approximately 6% in the Néel temperature $T_N$ of $CoCl_2 \cdot 6H_2O$ is obtained when 92% of the protons are replaced by deuterons. The anisotropy of $T_N$ decreases from 0.08°K for 0% deuteration to slightly less than 0.05°K for 92% deuteration. Following a conjecture by Haseda, a semiempirical attempt is made to establish a connection among $T_N$, the exchange energy, and the potential energy of a proton in a hydrogen bond. The picture presented is that $T_N$ rises on deuteration because of a change in the average of the exchange energy over the vibrational state of the hydrogen atom.

## I. EXPERIMENT

THE effect of replacing the protons in $CoCl_2 \cdot 6H_2O$ by deuterons on the Néel temperature $T_N$ at which the crystal goes from the paramagnetic to the antiferromagnetic phase has already been reported.[1] It was found that $T_N$ increased by about 6% when 92% of the protons were replaced by deuterons. In the present paper we give a discussion of the results and their interpretation in view of a possible connection between the observed change in $T_N$ on deuteration, the superexchange-interaction energy, and the potential of a proton in a hydrogen bond. The picture presented is that $T_N$ increases because of a change in the average of the superexchange energy over the ground vibrational state of the hydrogen atom.

After the above observation was made, it was discovered that Haseda[2] had already suggested that $T_N$ might change appreciably in $CoCl_2 \cdot 6H_2O$ when protons are replaced by deuterons. In fact, Haseda tried unsuccessfully to observe this effect from the difference in the magnetic susceptibility $\chi$-versus-temperature curves of $CoCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6D_2O$. According to the molecular-field theory,[3] the slope of the $\chi$-versus-$T$ curve does have a discontinuity at $T_N$. However, because of the short-range magnetic order existing in real systems, the curve has a rounded maximum[4] at a temperature above $T_N$ which makes it difficult to determine $T_N$ accurately from a $\chi$-versus-$T$ curve. For this reason, Haseda was unable to detect the effect discussed here.

In studying the phase transition, we employed the much more sensitive technique of nuclear magnetic resonance (NMR). The use of the NMR technique to monitor the transition between the paramagnetic and antiferromagnetic phases of a substance was first developed by Poulis and Hardeman.[5] By monitoring the proton resonance as a function of temperature, $T_N$ can be accurately measured since (1) the number of proton resonance lines doubles as the temperature is lowered below $T_N$; (2) whereas the spectrum reproduces itself when the external field $\mathbf{H}_0$ is reversed in the paramagnetic phase, this is not so in the antiferromagnetic phase; (3) individual proton resonance lines broaden anomalously and vanish as $T_N$ is approached from the high- and low-temperature side.

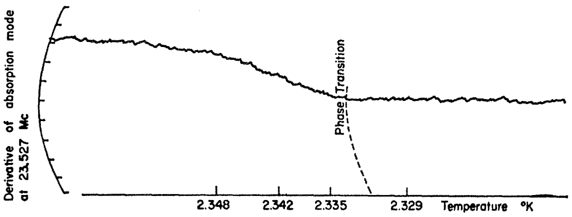

FIG. 1. Recording of the derivative of the NMR absorption signal of the protons in $CoCl_2 \cdot 6H_2O$ as a function of temperature. The frequency and external field are kept constant in this experiment.

The method of Poulis and Hardeman was applied to $CoCl_2 \cdot 6H_2O$ by Sawatzky and Bloom.[6] They have given the dependence of the proton resonance frequencies and intensities in $CoCl_2 \cdot 6H_2O$ on temperature and on the magnitude and orientation of $\mathbf{H}_0$. In the measurements discussed here, which were made using the same methods as Sawatzky and Bloom, the changes in $T_N$ produced by deuteration of $CoCl_2 \cdot 6H_2O$ could be measured to within $6 \times 10^{-3}$ °K. A typical measurement of $T_N$ is shown in Fig. 1. This measurement was made at a fixed $\mathbf{H}_0$ and with the frequency of the NMR spectrometer fixed as well. The signal plotted in Fig. 1 as a function of temperature is the derivative of the NMR signal. The frequency of the spectrometer was first adjusted to maximize the signal at a temperature more than $20 \times 10^{-3}$ °K above $T_N$. Then, the temperature of the helium bath was varied slowly and uniformly at a rate of about $2 \times 10^{-3}$ °K per min by varying the pressure of the helium vapor in equilibrium with the bath. As the temperature was lowered, the signal gradually disappeared. The temperature at which the signal disappeared into noise was identified with $T_N$.

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[2] T. Haseda, J. Phys. Soc. Japan **15**, 483 (1960).

[3] T. Nagamiya, K. Yoshida, and R. Kubo, Advan. Phys. **4**, 1 (1955).

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[5] N. J. Poulis and G. E. G. Hardeman, Physica **18**, 201 (1952).

[6] E. Sawatzky and M. Bloom, Can. J. Phys. **42**, 657 (1964).

All the temperature measurements were made by monitoring the vapor pressure of the helium bath.

In these measurements, the vanishing of the NMR signals has to be interpreted rather carefully. We have to be sure that the signal disappears because of broadening and not due to shifts in the position of the lines in the frequency spectrum. In the results reported here, the lines did not shift by more than a tenth of their linewidth during a temperature sweep of 20 mdeg above the Néel temperature.

The coexistence of two phases over a region of 6 mdeg around $T_N$ poses another problem.[6] For some proton lines, as the temperature is being varied, an antiferromagnetic line appears before the disappearance of a paramagnetic line. The frequencies of these antiferromagnetic lines, which have been studied in detail by Sawatzky and Bloom,[6] are very sensitive to temperature. These lines usually disappear about 20 mdeg below $T_N$ because of the shift in their frequencies with temperature and cannot be relied upon for the measurement of Néel temperature. However, on closer examination it is found that the recorder trace shows a slight turn at the temperature at which the antiferromagnetic line tunes in. Such traces usually give a false Néel temperature and should be rejected. One can then resort to other available paramagnetic lines for the detection of the phase change. Different proton lines were used as indicators of the phase transition for each orientation of the external magnetic field with respect to the crystal axes. These lines disappear at different points of the coexistence region. The 6-mdeg scatter in the measured values of $T_N$ for a fixed orientation is thus merely a measure of the width of the coexistence region. This was confirmed by studying the full proton spectrum as a function of temperature in the vicinity of $T_N$ for one fixed orientation. The uncertainty of 6 mdeg caused by the coexistence of two phases is much bigger than the errors caused by the background noise in the NMR spectra and serves as an upper limit on the errors in these measurements of $T_N$. For strict comparison $T_N$ was measured in $CoCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6D_2O$ at the same magnetic field. Also, for each percentage of deuteration, the measurements were made on two crystals grown from different solutions. The measurements were made in samples containing 0, (30±2), and (92±5)% deuterium for different orientations of $\mathbf{H}_0$ with respect to the crystal axes. In the case of 30% deuterated crystals, the relative concentration of deuterium was estimated from the relative proportion of $H_2O$ and $D_2O$ in the parent solutions. For the 92% deuterated samples, the value of relative concentration obtained by this method was against that obtained from the relative strength of deuteron and proton signals.

Figure 2 shows that the Néel temperature varies with a period of 180° as $\mathbf{H}_0$ is rotated about the *b* axis perpendicular to the *a-c* plane. The crystal alignment was known to an accuracy of 5°. On deuteration, the Néel temperature rises for all orientations; the more deuterium that is introduced, the higher the transition point. The maximum increase of approximately 6% in the Néel temperature is obtained for a 92% concentration of deuterium. In addition, the anisotropy in $T_N$ decreases from approximately 0.08°K for 0% deuteration to slightly less than 0.05°K for 92% deuteration. The orientation-averaged Néel temperature seems to vary linearly with the cube root of the relative concentration of deuterium.[7] An x-ray[7] analysis of the powder samples of $CoCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6D_2O$ was carried out to investigate the possibility of change in $T_N$ caused by a likely variation of cell dimensions on deuteration. The analysis shows that both the deuterated and nondeuterated samples have the same symmetry and their cell dimensions do not differ by more than 0.2% at room temperature. The infrared spectra of $CoCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6D_2O$ were also measured. They will be referred to later in order to provide some justification for an assumption made in the "explanation" of the effect.

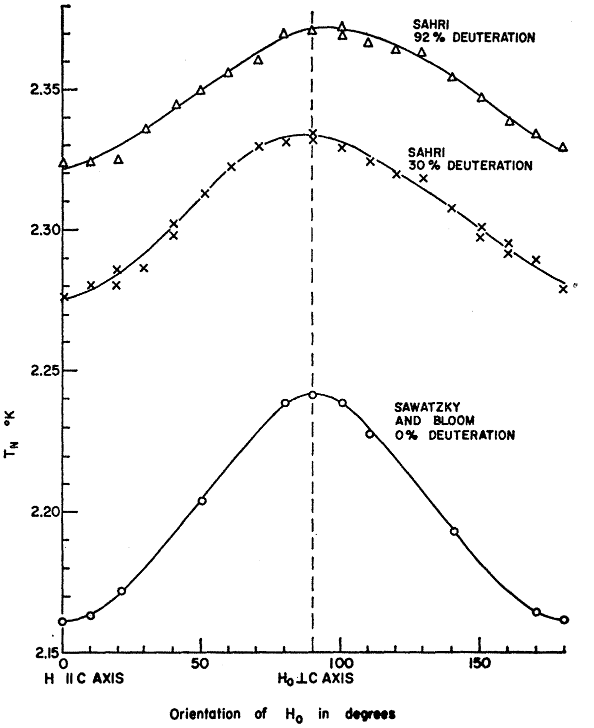

FIG. 2. Plot of the Néel temperature as a function of orientation of the external field for single crystals of cobaltous chloride containing 0, 30, and 92% deuterium, respectively. The external field was 5000 G.

## II. A SEMIEMPIRICAL MODEL

The antiferromagnetic alignment arises from the Heisenberg-Dirac Hamiltonian for the exchange inter-

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[7] D. S. Sahri, Ph.D. thesis, University of British Columbia, 1966 (unpublished).

action between pairs of spins, which is of the form

$$\mathcal{H}_{\mathrm{ex}}=-\sum_{i,j} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j, \qquad (1)$$

where $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spin operators associated with magnetic atoms $M_i$ and $M_j$, respectively, and $J_{ij}$ is the exchange energy[8] associated with $M_i$ and $M_j$. As originally suggested by Kramers[9] and later developed by Anderson and others,[10] the presence of nonmagnetic $X$ atoms between magnetic atoms $M_i$ and $M_j$ gives rise to a so-called superexchange contribution to $J_{ij}$. Pink[11] has suggested that the effect of variation of the isotopic mass of the $X$ atoms on $T_N$ can be understood in terms of the change in the vibration amplitude of the $X$ atoms as the latter are replaced by their isotopes. In order to make some quantitative predictions we make the following simplifying assumptions.

*Assumption* 1. $J_{ij}=0$, except for nearest neighbors, for which $J_{ij}=J=-|J|$. For this model, we can write

$$T_N=C|J|, \qquad (2)$$

where the constant of proportionality $C$, which depends on the crystal structure, shall not be of interest to us in the following discussion.

*Assumption* 2. The exchange interaction is assumed to be due solely to superexchange[11] which arises from a second lattice of nonmagnetic atoms $X$, superimposed on the lattice of magnetic atoms $M$. The lattice structure is taken to be so simple that, corresponding to any nearest-neighbor pair of magnetic atoms $M_1$ and $M_2$, there is one and only one $X$ atom $X_{12}$ which plays the role of the intervening atom in the superexchange interaction between $M_1$ and $M_2$. Then the exchange integral $J_{12}$ between $M_1$ and $M_2$ is a function of the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ joining $M_1$ and $M_2$, respectively, to $X_{12}$ and we write

$$J_{12}=J_{12}(\mathbf{r}_1,\mathbf{r}_2). \qquad (3)$$

*Assumption* 3. We assume that the $M$ atoms are much heavier than the $X$ atoms so that the former are practically stationary as compared with the latter. Then the exchange integral $J_{12}$ is a function of $\mathbf{a}_1+\mathbf{q}$ and $\mathbf{a}_2+\mathbf{q}$, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are the vectors joining the equilibrium positions of $M_1$ and $M_2$, respectively, to the equilibrium position of $X_{12}$, and $\mathbf{q}$ is the displacement of $X_{12}$ from equilibrium. Expanding $J_{12}(\mathbf{r}_1,\mathbf{r}_2)$ in a Taylor series in $\mathbf{q}$, we have

$$\begin{aligned}J_{12}(\mathbf{r}_1,\mathbf{r}_2)&=J_{12}(\mathbf{a}_1+\mathbf{q},\mathbf{a}_2+\mathbf{q})\\&=J_{12}(\mathbf{a}_1,\mathbf{a}_2)+\sum_{\alpha=1}^{3} q_\alpha J_{12}{}^{\alpha}(\mathbf{a}_1,\mathbf{a}_2)\\&\quad+\tfrac{1}{2}\sum_{\alpha,\beta=1}^{3} q_\alpha q_\beta J_{12}{}^{\alpha,\beta}(\mathbf{a}_1,\mathbf{a}_2)+\cdots,\end{aligned} \qquad (4)$$

where $q_\alpha$, $q_\beta$ take on values $q_1$, $q_2$, $q_3$ which are the three components of $\mathbf{q}$, and

$$\begin{aligned}J_{12}{}^{\alpha}(\mathbf{a}_1,\mathbf{a}_2)&=[(\partial/\partial q_\alpha)J_{12}(\mathbf{a}_1+\mathbf{q},\mathbf{a}_2+\mathbf{q})]_{\mathbf{q}=0},\\J_{12}{}^{\alpha,\beta}(\mathbf{a}_1,\mathbf{a}_2)&=[(\partial^2/\partial q_\alpha\partial q_\beta)J_{12}(\mathbf{a}_1+\mathbf{q},\mathbf{a}_2+\mathbf{q})]_{\mathbf{q}=0}.\end{aligned} \qquad (5)$$

The quantity $J$ in Eq. (2) is then obtained by averaging $J_{12}(\mathbf{r}_1,\mathbf{r}_2)$ over the vibrations of the $X$ atoms at the temperature of the solid. By definition, $\langle q_\alpha\rangle=0$, so that we obtain

$$J=\langle J_{12}\rangle=J_{12}(\mathbf{a}_1,\mathbf{a}_2)[1+\eta(T,m)+\cdots], \qquad (6)$$

where

$$\eta(T,m)=\frac{\sum_{\alpha,\beta}\langle q_\alpha q_\beta\rangle J_{12}{}^{\alpha,\beta}(\mathbf{a}_1,\mathbf{a}_2)}{2J_{12}(\mathbf{a}_1,\mathbf{a}_2)}. \qquad (7)$$

The average $\langle q_\alpha q_\beta\rangle$ is a function of the temperature $T$ of the solid and of the isotopic mass $m$ of the $X$ atoms. It is supposed that $\eta(T,m)\ll 1$ and that higher-order terms in the Taylor expansion of $J_{12}$ may be neglected. Then, if the $X$ atoms can have two isotopes $X_1$ and $X_2$ of masses $m_1$ and $m_2$, respectively, the change in the Néel temperature $\Delta T_N$ when atoms $X_1$ are replaced by atoms $X_2$ is found using Eqs. (2) and (6) to be

$$\Delta T_N/T_N\simeq\eta(T_N,m_2)-\eta(T_N,m_1). \qquad (8)$$

*Assumption* 4. We assume that all the interatomic interactions are harmonic and that the interaction potentials are independent of the isotopic mass of the $X$ atoms.

Since the $X$ atoms have been assumed to be much lighter than the $M$ atoms, we may discuss the high- and low-temperature limiting cases in terms of $kT_N\gg\hbar\omega_{\mathrm{opt}}$ and $kT_N\ll\hbar\omega_{\mathrm{opt}}$, respectively, where $\hbar\omega_{\mathrm{opt}}$ is a typical energy associated with the optical phonon branch.

*High-temperature limit*: From the equipartition theorem $\langle q_\alpha q_\beta\rangle$ is independent of $m$ for this case and

$$\Delta T_N/T_N=0.$$

*Low-temperature limit*: For this case

$$\langle q_\alpha q_\beta\rangle\propto m^{-1/2}, \qquad (9)$$

and Eqs. (7) and (8) give the result

$$\Delta T_N/T_N\approx\eta(0,m_1)[(m_1/m_2)^{1/2}-1]. \qquad (10)$$

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[8] The exchange interaction in $CoCl_2\cdot 6H_2O$ is known to be very anisotropic so that Eq. (1) does not hold for this substance. In any detailed theory of the isotope effect on $T_N$ in $CoCl_2\cdot 6H_2O$, the anisotropic nature of the exchange interaction would have to be taken into account.

[9] H. A. Kramers, Physica **1**, 182 (1934).

[10] P. W. Anderson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. 1, p. 52.

[11] D. Pink (private communication).

Equation (10) gives the maximum possible isotope effect on $T_N$. In order to apply this result to a discussion of some physical systems, however, it is necessary to make further assumptions about the form of $J_{12}(\mathbf{r}_1, \mathbf{r}_2)$.

## III. HASEDA'S CONJECTURE AND THE CASE OF $CoCl_2 \cdot 6H_2O$

We shall apply the results of Sec. II to the measurements of the isotope shift of $T_N$ in $CoCl_2 \cdot 6H_2O$. This procedure is of questionable validity for several reasons: (a) The exchange interaction between neighboring $Co^{++}$ ions in this solid is very anisotropic,[12] so that Eq. (1) does not hold. (b) There are several possible superexchange paths for the exchange interaction[2] and there is no available theory to indicate the dependence of the superexchange parameters on the positions of the intervening atoms. Therefore, we shall have to make some further drastic simplifications in order to use the model. In order to obtain a quantitative comparison between theory and experiment, we shall make use of a conjecture by Haseda[2] that there is a relationship between the effect of deuteration on hydrogen bonding in $CoCl_2 \cdot 6H_2O$ and its effect on the superexchange parameter. The quantitative statement of Haseda's conjecture which we shall make has no theoretical justification at this time. The fact that it leads to correct sign and order of magnitude of $\Delta T_N/T_N$ suggests that it may be worthwhile investigating theoretically the proposed linear relationship between the dependence of the superexchange parameter on the position of the hydrogen atom and the potential energy of the hydrogen atom.

One of the superexchange paths in $CoCl_2 \cdot 6H_2O$ proposed by Haseda[2] is the following:

$$\text{Co}—\text{Cl}—\text{H}----\text{O}—\text{Co}.$$

In order to use the model developed in Sec. II we identify the hydrogen with the $X$ atom of the model and the Co-Cl and O-Co pairs with $M_1$ and $M_2$, respectively. Since $T_N$ is only of the order of 2°K, we use the expression for $\Delta T_N/T_N$ given by Eq. (10), which is appropriate to the low-temperature limit. In this expression $m_1$ and $m_2$ are the proton and deuteron masses, respectively, so that $m_1/m_2=0.5$.

The infrared spectrum of $CoCl_2 \cdot 6H_2O$ and a partially deuterated modification have been measured at room temperature.[7] Absorption peaks in $CoCl_2 \cdot 6H_2O$ have been observed at 3450 $\text{cm}^{-1}$ due to stretching of the O–H bond and at 1605 $\text{cm}^{-1}$ due to bending of the $H_2O$ molecule. These frequencies are quite close to those for water in the liquid state. For the partially deuterated salt there is observed, in addition to these lines, a stretching mode for the O–D bond at 2530 $\text{cm}^{-1}$ and bending modes for HDO and $D_2O$ at 1425 and 1190 $\text{cm}^{-1}$, respectively.

We assume that the superexchange parameter varies much more for stretching motions of the hydrogen atom than for the bending motions, so that

$$J_{12}^{\alpha,\beta}(\mathbf{a}_1, \mathbf{a}_2) = J_{12}^{1,1}(\mathbf{a}_1, \mathbf{a}_2)\,\delta_{\alpha 1}\delta_{1\beta}. \tag{11}$$

From the infrared results, we conclude that the hydrogen atoms vibrate independently of each other so that at low temperatures the mean-square amplitude of oscillation for the proton is

$$\langle q_1^2 \rangle = (\hbar^2/m_1\xi)^{1/2}, \tag{12}$$

where $\xi = m\omega^2$ is the force constant associated with the potential well for the hydrogen atom near its equilibrium position. For the proton, the infrared measurements give $\omega = 6.4\times 10^{14}$ $\text{sec}^{-1}$, which gives the result $\xi = 6.84\times 10^5$ g $\text{sec}^{-2}$.

Using Eqs. (7), (10), (11), and (12), and $m_2=2m_1$, we have

$$\frac{\Delta T_N}{T_N} = -\frac{0.293 J_{12}^{1,1}(\mathbf{a}_1, \mathbf{a}_2)}{2 J_{12}(\mathbf{a}_1, \mathbf{a}_2)} \frac{\hbar}{(m_1\xi)^{1/2}}. \tag{13}$$

*Haseda's conjecture*: Haseda[2] has suggested that when the superexchange path includes a hydrogen bond, there exists a relationship between the hydrogen bonding and the superexchange. A possible quantitative relationship is the following:

$$J_{12}(\mathbf{a}_1+\mathbf{q}, \mathbf{a}_2+\mathbf{q})/V(\mathbf{q}) = \text{const}, \tag{14}$$

where $V(\mathbf{q})$ is the potential energy of the proton when it is displaced from its equilibrium position by an amount $\mathbf{q}$. Substituting Eq. (14) into Eq. (13), we have

$$\frac{\Delta T_N}{T_N} = -\frac{0.293}{2} \frac{V^{1,1}(0)}{V(0)} \frac{\hbar}{(m_1\xi)^{1/2}}, \tag{15}$$

where $V^{1,1}(0)$ is the second derivative of $V(\mathbf{q})$ with respect to displacements along the O–H bond, evaluated at $\mathbf{q}=0$. Since, $V^{1,1}(0)=\xi$, we may write Eq. (15) in the form

$$\Delta T_N/T_N = -0.293[\tfrac{1}{2}\hbar\omega/V(0)]. \tag{16}$$

The quantity in square brackets in Eq. (16) is the ratio of the zero-point energy of a hydrogen atom to its potential energy at the equilibrium position. A typical value of the depth of the potential well of the hydrogen band according to Reid[13] is $-1.6\times 10^{-12}$ erg. Using the value of $\omega = 6.4\times 10^{14}$ $\text{sec}^{-1}$ obtained from the infrared measurement, we obtain

$$\Delta T_N/T_N \approx +0.06. \tag{17}$$

This result is in agreement with the measured isotope shift in deuterated $CoCl_2 \cdot 6H_2O$. This agreement seems fortuitous in view of the crudeness of the model used. However, the fact that the correct sign of $\Delta T_N$ has been obtained is significant as is the fact that the model does

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[12] M. Date, J. Phys. Soc. Japan **16**, 1337 (1961).

[13] C. Reid, J. Chem. Phys. **30**, 182 (1958).

give order-of-magnitude agreement with experiment. A theoretical problem suggested by this agreement is to justify the use of Eq. (14), at least for small $\mathbf{q}$, and to investigate whether the neglect of the bending modes of the $H_2O$ molecule is justified.

## IV. APPLICATION TO OTHER SUBSTANCES

The model developed in Sec. II can also be applied to solids like CoO and MnO, in which $O^{16}$ atoms are replaced by $O^{17}$ atoms. In order to make a crude estimate of the isotopic shift of $T_N$ in such substances, we make a further *ad hoc* approximation, which exploits the fact that the oxygen atoms are located half-way between their neighboring magnetic ions, i.e.,

$$J_{12}(\mathbf{r}_1, \mathbf{r}_2) = K(\mathbf{r}_1)K(\mathbf{r}_2). \qquad (18)$$

Following the same procedure as before,

$$\frac{\Delta T_N}{T_N}\approx\left[\frac{K^{1,1}(a)}{K(a)}-\left(\frac{K^1(a)}{K(a)}\right)^2\right]\langle q_1^2\rangle_{m_1}\left[\left(\frac{m_1}{m_2}\right)^{1/2}-1\right]. \qquad (19)$$

As recently reported by Bloch,[14] there is experimental evidence that $J_{12}\propto a^{-10}$, $(2a)^3$ being the volume of the cubic unit cell. Then $K(a)\propto a^{-5}$ and replacing $O^{16}$ by $O^{17}$ will give $m_1/m_2=16/17$. The fractional change in $T_N$ would, in this case, be

$$\Delta T_N/T_N = -0.15\langle q_1^2\rangle_{16}/a^2. \qquad (20)$$

It is anticipated that $\langle q_1^2\rangle/a^2\approx 10^{-2}$, giving $\Delta T_N/T_N\approx -10^{-3}$. Since typical values of $T_N$ for transition element oxides are of the order of 200°K, this would predict a *downward* shift in $T_N$ of approximately 0.2°K, which could be easily detected by specific-heat measurements.

To obtain a better estimate of $\Delta T_N$, it is necessary to make a more realistic estimate of $J_{12}(\mathbf{r}_1, \mathbf{r}_2)$ than is given by Eq. (18) and to estimate $\langle q_\alpha^2\rangle$ theoretically. Since the values of $T_N$ in these oxides are not much smaller than the Debye temperatures, the temperature dependence of $\langle q_\alpha^2\rangle$ becomes important and $\langle q_\alpha^2\rangle$ has to be evaluated at $T_N$. Also, the $M$ atoms have masses comparable to the $X$ atoms; therefore the former cannot be considered as stationary as compared to the latter.

## ACKNOWLEDGMENTS

Our thanks are due to Dr. K. Gray and Dr. N. K. Jha for assistance in the experimental work. We also thank Dr. D. Pink for a private communication.

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[14] D. Bloch, J. Phys. Chem. Solids **27**, 881 (1966).

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# Erratum

**Nuclear-Magnetic-Resonance Study of Self-Diffusion in a Bounded Medium,** R. C. WAYNE AND R. M. COTTS [Phys. Rev. **151,** 264 (1966)]. An error in calibration of the magnetic-field gradient coils used in this experiment has been detected. All observed values of the diffusion coefficients $D'$ and $D$ reported should be increased by a factor of 1.30. The experiment is mainly concerned with relative changes in $D'$ expressed as the ratio $(D'/D)$; thus the main conclusions are not changed, since all values of the ratio $(D'/D)$ remain unchanged. The value of $D$ for methane gas at a temperature of 17°C and pressure of 1,000 psi is then measured to be $D=2.20\pm 0.2\times 10^{-3}$ cm$^2$/sec. The values of $t'=tD/a^2$ are also changed by the same factor, and the corrected graph of $(D'/D)$ versus $t'$ in Fig. 4 is shown.

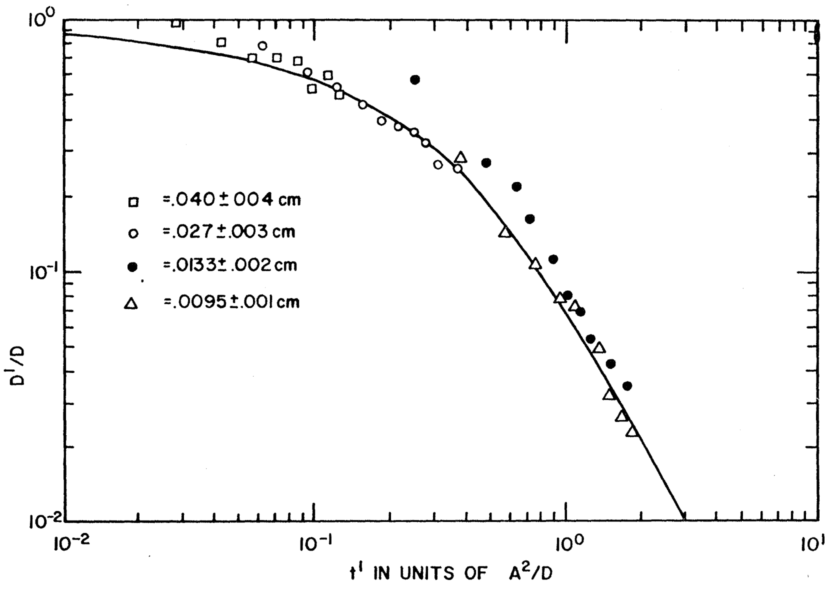

FIG. 4. The smooth curve represents the theoretical value of $(D'/D)$ versus $t'$, where $t'=tD/a^2$. Data for all values of $a$ are shown.