

# Magnetic Properties of $\text{HCrO}_2$ and $\text{DCrO}_2$

R. G. MEISENHEIMER AND J. D. SWALEN  
*Shell Development Company, Emeryville, California*  
 (Received March 13, 1961)

Magnetic susceptibility measurements and electron paramagnetic resonance measurements have been made on powdered chromous acid ( $\text{HCrO}_2$ ) and deuterated chromous acid ( $\text{DCrO}_2$ ). The Curie constants, derived from the susceptibility results, are consistent with three unpaired electrons associated with each chromium ion. In addition, a large Curie-Weiss  $\theta$  temperature, indicating a strong exchange interaction, is necessary to account for the results. The most unusual feature of this particular exchange is that it is strongly influenced by deuteration.

The electron paramagnetic resonance spectra also show strongly exchange-narrowed lines with a variation between  $\text{HCrO}_2$  and  $\text{DCrO}_2$ . From a comparison between the calculated and observed linewidths and second moments, a value of the zero-field splitting is estimated.

Although no transition has been observed to an antiferromagnetic state, the Curie-Weiss  $\theta$  temperatures indicate that the ground state is undoubtedly antiferromagnetic for both  $\text{HCrO}_2$  and  $\text{DCrO}_2$ . Superexchange through the intervening proton or deuteron is probably the main source of any antiferromagnetic exchange coupling. Some of the various mechanisms proposed for superexchange are discussed in relation to chromous acid.

## INTRODUCTION

THE crystal structure of  $\text{HCrO}_2$  was determined by Douglass<sup>1</sup> with the exception of the hydrogen atom positions. Ibers *et al.*<sup>2</sup> recently made a thorough study of the nuclear magnetic resonance spectrum of  $\text{HCrO}_2$  in order to determine these hydrogen positions by the second moment of the proton resonance signal. The paramagnetic chromium atoms, however, produced a magnetic field at the proton positions and introduced a number of interactions. These indicated that chromous acid has a strong internal field. We have investigated the magnetic properties of  $\text{HCrO}_2$  and  $\text{DCrO}_2$  (85%  $\text{DCrO}_2$  and 15%  $\text{HCrO}_2$ ) by both static susceptibility measurements and electron paramagnetic resonance measurements. The strong exchange interaction has been observed and is discussed in relation to some of the current ideas on exchange and superexchange.

## EXPERIMENTAL

### Static Magnetic Susceptibility Method<sup>3</sup>

The static magnetic susceptibilities of the  $\text{HCrO}_2$  and  $\text{DCrO}_2$  samples were measured with a Gouy balance. The magnetic susceptibilities of two preparations of  $\text{HCrO}_2$  were measured. One sample was prepared by Adams<sup>2</sup> and the other by us, using the same method. Field-strength and temperature dependence data were obtained for these samples from  $H=0$  to  $H=9000$  gauss at temperatures from 66° to 530°K. There was no evidence of field-strength dependence. In Fig. 1 we have plotted  $\chi_M$  vs  $T$ ; in Fig. 2,  $1/\chi_M$  vs  $T$ . Figure 2 should give a straight line if the material obeys the Curie-Weiss law,  $\chi = C/(T-\theta)$ . It is clear from Fig. 2 that the data do fit the Curie-Weiss law very well.

<sup>1</sup> R. M. Douglass, *Acta Cryst.* **10**, 423 (1957).

<sup>2</sup> J. A. Ibers, C. H. Holm, and C. R. Adams, *Phys. Rev.* **121**, 1620 (1961).

<sup>3</sup> J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

A least-squares fit of the data of Fig. 2 gives  $C=1.9342$  and  $\theta=-275.6^\circ$ . The magnetic moment of  $\text{Cr}^{+3}$  is then obtained from Eq. (1) by assigning the Bohr magneton,  $\beta = eh/2mc$ , as the unit of magnetic moment.

$$\chi_M = \beta^2 \mu_B^2 N / 3kT, \quad (1)$$

therefore

$$\begin{aligned} \mu_B &= (3kT\chi_M/N\beta^2)^{1/2} \\ &= 2.827 (C_M)^{1/2} \\ &= 3.93 \text{ Bohr magnetons for } \text{HCrO}_2. \end{aligned} \quad (2)$$

This is quite good agreement with the value of 3.87 expected for a "spin-only" configuration of three unpaired electrons.

$$\mu^2 = g^2 S(S+1) \approx 4S(S+1). \quad (3)$$

The final expression for  $\text{HCrO}_2$  is then

$$\chi_M = 1.9342 / (T + 276).$$

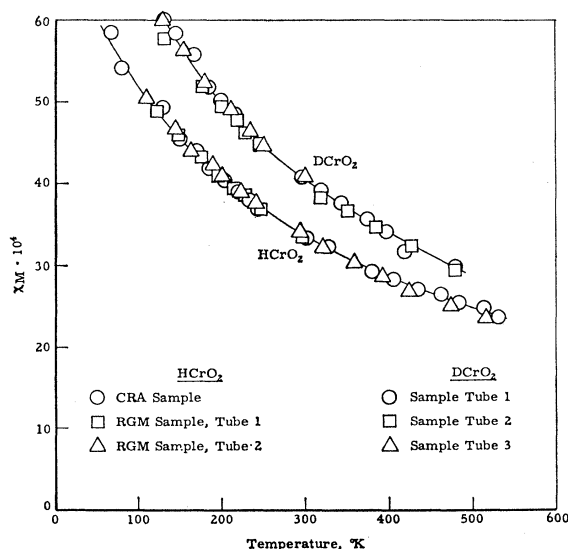


FIG. 1. Magnetic susceptibility of  $\text{HCrO}_2$  and  $\text{DCrO}_2$ .

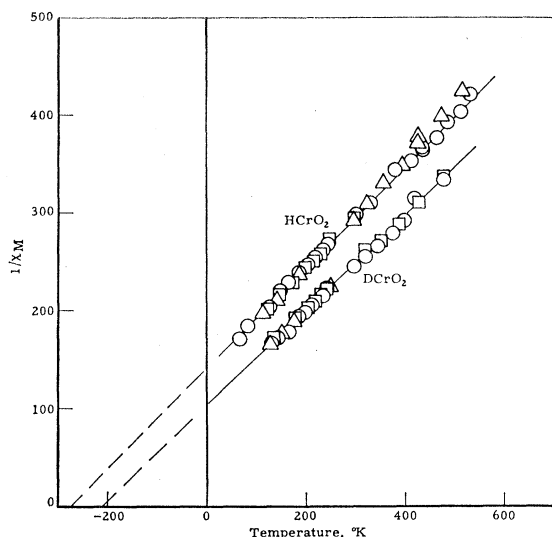


FIG. 2. Curie-Weiss plot for  $\text{HCrO}_2$  and  $\text{DCrO}_2$ .

Magnetic susceptibility measurements were made on a sample of 85%  $\text{DCrO}_2$ ·15%  $\text{HCrO}_2$ . This material was prepared in the same manner as the  $\text{HCrO}_2$  except that  $\text{D}_2\text{O}$  was used as a solvent in place of  $\text{H}_2\text{O}$ . (The hydrogen atoms present came from the water of hydration of the chromic nitrate.) No field-strength dependence was observed for this material. The  $\chi_M$  vs  $T$  data are plotted in Fig. 1 and  $1/\chi_M$  vs  $T$  in Fig. 2. A least-squares treatment of the data of Fig. 2 results in the expression for the Curie-Weiss law

$$\chi_M = 2.07/(T + 214).$$

The slope of this line corresponds to a magnetic moment of 4.07 Bohr magnetons from a use of the spin-only formula (3).

The significance of  $\theta$  lines in its relation to the Heisenberg exchange interaction,  $J_{jk}S_jS_k$ . Above the Curie temperature,  $T_c$ , the susceptibility follows the Curie-Weiss law, where  $\theta$  is related to the exchange integral  $J$  by the relation:

$$\theta = 2JzS(S+1)/3k. \quad (4)$$

Here,  $z$  is the number of nearest equidistant neighbors with which the atom has an exchange coupling. These are not necessarily the geometrically nearest neighbors. Below the Curie or transition temperature the material will become ferromagnetic or antiferromagnetic depending on the sign of the exchange interaction. The transition temperature, also called the Néel temperature, for antiferromagnetics is related to  $\theta$ , but not in a simple manner. The ratio  $\theta/T_c$  has been found in a number of antiferromagnetic materials to fall in the range of 1.5 to 5.<sup>4</sup> Since no transition is observed in either  $\text{HCrO}_2$  or  $\text{DCrO}_2$  down to 66°K, the ratio  $\theta/T_c$  must be greater than three.

<sup>4</sup> Charles Kittel, *Introduction to Solid-State Physics* (John Wiley & Sons, Inc., New York, 1953).

## Electron Paramagnetic Resonance

The electron paramagnetic resonance spectra of  $\text{HCrO}_2$  and of  $\text{DCrO}_2$  were recorded by a Varian 4500 spectrometer with a full field scan in order to sweep the magnetic field from 0 to ~6000 gauss. A small sample of Coppinger's radical was added to determine the free-electron spin position ( $g=2.003$ ). In addition a nuclear magnetic resonance probe was inserted in the magnetic field and the proton magnetic resonance was measured along the sweep to calibrate the field.

For both  $\text{HCrO}_2$  and  $\text{DCrO}_2$  a  $g$  value of 1.976 was obtained. This value is very close in value to the  $g$  values observed in many of the other chromium compounds studied by electron paramagnetic resonance<sup>5</sup> ( $g \sim 1.97-1.99$ ) and is a result of the large separation between the other crystalline field states. Even though  $\text{HCrO}_2$  and  $\text{DCrO}_2$  do not have cubic symmetry, the splittings of the excited states do not influence the  $g$  value appreciably.  $Dq$  is approximately 1700  $\text{cm}^{-1}$  and  $g = 2 - 8\lambda/10Dq$ , where  $\lambda$  is in the spin-orbit constant. For the free ion,  $\lambda$  is 91  $\text{cm}^{-1}$ . In  $\text{HCrO}_2$ ,  $\lambda$  is probably somewhat smaller in magnitude, about  $\frac{2}{3}\lambda$ , because of covalent bonding.<sup>6,7</sup>

According to the theory of Anderson and Weiss,<sup>8</sup> an exchange-narrowed line should be Lorentzian in the center and eventually become Gaussian in the tails. A Lorentzian line was fit to the center of the lines:

$$I = \frac{I_0}{\pi} \frac{\delta}{(\omega - \omega_0)^2 + \delta^2},$$

$$I' = \frac{I_0}{\pi} \frac{2(\omega - \omega_0)\delta}{[(\omega - \omega_0)^2 + \delta^2]^2}, \quad \delta = \omega_p^2/\omega_e. \quad (5)$$

Somewhere in the wings of the line, the observed line should deviate from the Lorentzian slope and become Gaussian:

$$I = \frac{I_0}{(2\pi)^{1/2}\omega_p} \exp[-(\omega - \omega_0)^2/2\omega_p^2]. \quad (6)$$

Within experimental error, the line shape for  $\text{HCrO}_2$  and  $\text{DCrO}_2$ , however, is completely Lorentzian. This result is consistent with the large  $\theta$  values and correspondingly large exchange interaction.

Ibers, Holm, and Adams<sup>2</sup> evaluated the dipolar contribution to the second moment,  $\langle \Delta\omega^2 \rangle$ , for the proton-proton interactions in  $\text{HCrO}_2$  according to the method of Van Vleck.<sup>9</sup> For a powder sample, the second moment resulting from the dipolar term is

$$\langle \Delta\omega^2 \rangle = (2/\hbar^2)S(S+1)\sum_k B_{jk}^2, \quad (7)$$

<sup>5</sup> K. D. Bowers and J. Owens, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 304.

<sup>6</sup> W. Low, *Paramagnetic Resonance in Solids* (Academic Press, Inc., New York, 1960).

<sup>7</sup> J. Owen, *Proc. Roy. Soc. (London)* **A227**, 183 (1955).

<sup>8</sup> P. W. Anderson and M. T. Weiss, *Revs. Modern Phys.* **25**, 269 (1953).

<sup>9</sup> J. H. Van Vleck, *Phys. Rev.* **74**, 1168 (1948).

where  $B_{jk} = g^2 \beta^2 / r_{jk}^3$ . Since the array of chromium atoms is the same as the protons, except for a translation, the proton second-moment sum can be used to calculate the chromium dipolar second moment according to Eq. (7) merely by correcting for the change in the  $g\beta$  from the nuclear case to the electron case, by correcting for the change in spin [ $I(\text{H}) = \frac{1}{2}$  and  $S(\text{Cr}^{+3}) = \frac{3}{2}$ ], and by adding the 10/3 factor for truncation.<sup>9</sup> The value thus calculated is

$$\langle \Delta\omega^2 \rangle / g^2 \beta^2 = 2.56 \times 10^7 \text{ gauss}^2.$$

Van Vleck<sup>9</sup> only considered the dipolar terms and the exchange terms, but for HCrO<sub>2</sub> the zero-field terms are also important. We evaluated the commutators and obtained a contribution of

$$(D^2/25\hbar^2)[4S(S+1)-3] \quad (8)$$

to the second moment. These two terms [Eqs. (7) and (8)] form the dominant contributions to the second moment, and together with the exchange term contribute to the fourth moment.

Anderson and Weiss<sup>8</sup> considered exchange as a random modulation of a Gaussian distribution of dipolar lines. By their analysis they arrived at the following relation between the second moment, the exchange frequency, and the half-width:

$$\langle \Delta\omega^2 \rangle = \omega_e \Delta\omega_{\frac{1}{2}}. \quad (9)$$

Combining these results, we obtain the following relation:

$$\langle \Delta\omega^2 \rangle_{\text{dipolar}} + \langle \Delta\omega^2 \rangle_{\text{zero field}} = \omega_e (\Delta\omega_{\frac{1}{2}})_{\text{obs}}. \quad (10)$$

Singer<sup>10</sup> has shown if  $D \gg \hbar\nu = g\beta H$ , then the powder spectrum of a Cr<sup>+3</sup> ion ( $S = \frac{3}{2}$ ) will be very asymmetric, with a maximum at a  $g$  of 4. Recently van Reijen and Swalen<sup>11</sup> have shown for the case  $D \ll \hbar\nu$  that the half-width is increased by  $D$ , but the line remains centered near  $g = 2$ . For the first case, the pattern is easily recognized and the analysis on the basis of Eq. (10) is not valid. For the second case, we are able to approximate our problem to arrive at an answer.  $\omega_e$  is related to  $J$  for a simple cubic lattice by the expression

$$\omega_e^2 = 8.48 (J^2/\hbar) [S(S+1)/3], \quad (11)$$

and since  $J$  and  $\theta$  are related by Eq. (4) an approximate calculation of  $D$  is then possible. (HCrO<sub>2</sub> and DCrO<sub>2</sub> deviate from a simple cubic, but this was not corrected for in our approximate calculations.) For HCrO<sub>2</sub> the measured linewidth was 352 gauss (half-width 176 gauss), and for DCrO<sub>2</sub> the measured linewidth was 429 gauss. The line was symmetric and, as mentioned before, the  $g$  value was close to 2. Therefore,  $D \ll \hbar\nu$  and Eq. (10) can be used. From the Curie-Weiss  $\theta$  values, Eq. (4) and Eq. (11), the exchange frequency can be calculated. Equations (8) and (10) were then used to estimate  $D$ .

<sup>10</sup> L. S. Singer, J. Chem. Phys. **23**, 379 (1955).

<sup>11</sup> L. L. van Reijen and J. D. Swalen (private communication).

TABLE I. Magnetic parameters for HCrO<sub>2</sub> and DCrO<sub>2</sub>.

Parameters	HCrO <sub>2</sub>	DCrO <sub>2</sub> (85% D)
$g$	1.976	1.976
$\mu_B$ (Bohr magnetons)	3.93	4.07
$\theta$ (°K)	276	214
$J$ ( $z=6$ )	18°K (13 cm <sup>-1</sup> )	14°K (10 cm <sup>-1</sup> )
$H_e(\theta)$	$4.16 \times 10^5$ gauss	$3.22 \times 10^5$ gauss
$\Delta H_{\frac{1}{2}}$	176 gauss	214 gauss
$D$	996 gauss (0.093 cm <sup>-1</sup> )	950 gauss (0.089 cm <sup>-1</sup> )

The results are given in Table I. The estimated  $D$  value is smaller than the value (0.192 cm<sup>-1</sup>) found for Cr<sup>+3</sup> in Al<sub>2</sub>O<sub>3</sub> doped with a small amount of Cr<sup>+3</sup>.<sup>5</sup>

## DISCUSSION

As shown by Douglass,<sup>1</sup> the environment of the chromium ions is distorted from cubic symmetry and the Cr-O-H-O-Cr system is not linear. The magnetic properties of HCrO<sub>2</sub> and DCrO<sub>2</sub> as determined in this investigation are consistent with a paramagnetic material which contains three unpaired electrons per chromium ion and a large exchange interaction between Cr<sup>+3</sup> ions along the 3 axis. The exchange in HCrO<sub>2</sub> is of the type called superexchange and takes place through two intervening oxygen ions and one proton or deuteron. The evidence pointing to this type of superexchange is the fact that the substitution of deuterium for hydrogen in the crystal results in a large change in the value of  $\theta$  in the Curie-Weiss law, and consequently in the value of the exchange integral Eq. (4).

The exchange postulated for this compound is unique in one respect; it occurs through *three* intervening ions. Exchange forces have been shown to operate over greater distances, but between two intervening atoms, e.g., in MnBr<sub>2</sub>.<sup>12</sup> The Mn-Mn nearest neighbor distance is 2.233 Å, while the superexchange occurs over 7.07 Å (4.787 Å in HCrO<sub>2</sub>) through two Br ions.

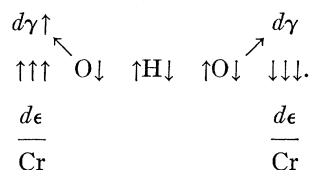
There are also cases where superexchange occurs through a nonlinear array of atoms. For example, Griffiths, Owen, Park and Partidge<sup>13</sup> work on K<sub>2</sub>IrCl<sub>6</sub>.

We visualize the superexchange process as follows: The chromium ions are surrounded by an octahedral arrangement of oxygen ions. The 3  $d\epsilon$  orbitals  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  are each singly occupied and constitute the  $A$  state. If we now use  $sp^3$  hybridized orbitals for the eight electrons in O<sup>=</sup>, we can construct the following model for HCrO<sub>2</sub>: The  $sp^3$  orbitals and the  $d\epsilon$  orbitals are orthogonal, and cannot take part in  $\sigma$ -bond formation. The  $sp^3$  and  $d\gamma$  orbitals are, on the other hand, not orthogonal and electron transfer can take place from the  $sp^3$  to the  $d\gamma$  orbital. We therefore envision the following process

<sup>12</sup> E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, Phys. Rev. **110**, 638 (1958).

<sup>13</sup> J. H. E. Griffiths, J. Owen, J. G. Park, and M. F. Partridge, Proc. Roy. Soc. (London) **A250**, 84 (1959).

of Anderson<sup>14</sup> as



An excited state exists where one electron is transferred from an oxygen ion to an unoccupied  $d\gamma$  orbital in the chromium ions. The lowest energy state occurs when this electron enters with a spin parallel to the three  $d\epsilon$  electrons, (Hund's rule) resulting in ferromagnetic coupling between Cr and O ions. This in turn results in the spin coupling as pictured above, leading to antiferromagnetically aligned Cr ions. There have been a number of other mechanisms proposed for superexchange. In general, they usually involve a transfer of more than one electron at a time. Kanamori<sup>15</sup> discusses these mechanisms most of which in the case of  $\text{Cr}^{+3}$  lead to antiferromagnetism. All of these mechanisms are really saying that the  $d\gamma$  wave function and the oxygen wave functions are mixed. Hund's rule leads to parallel spins between the  $d\gamma$  and  $d\epsilon$  wave functions. In order for bond pairs to occur in the chains, an antiferromagnetic coupling results. Recently Anderson<sup>16</sup> developed a crude method for estimating  $J$  and  $\theta$ . Using this method, we calculate a  $\theta$  value of 650°K. When empty  $d\gamma$  orbitals overlap this anion (the case in point here), Anderson points out that the antiferromagnetism should be weaker. These ideas are in crude agreement with  $\text{HCrO}_2$  and  $\text{DCrO}_2$ .

The change in the superexchange coupling in going from  $\text{HCrO}_2$  to  $\text{DCrO}_2$  could be caused by a number of effects. Two possible causes are the change in lattice spacing<sup>17</sup> and zero-point vibration effects. The chromium-chromium layer distance along the  $\bar{3}$  axis is increased by about 0.04 Å from  $\text{HCrO}_2$  to  $\text{DCrO}_2$ , and consequently the superexchange coupling decreases. In addition, the amplitude of the zero-point vibrations is decreased on deuteration. This means that the hydrogen wave function will be more diffuse than that of the deuterium. A larger overlap with the oxygen wave function and a larger exchange should then occur in the case of hydrogen. Probably the change in the lattice constants, however, causes the largest change in the  $\theta$  value. Disorder apparently does not contribute to the lowering of the  $\theta$  value in  $\text{DCrO}_2$  (85% D) since  $\text{DCrO}_2$  (100% D) gives a consistent value of  $\theta$ .

One final fact to consider is the Néel temperature. Recent neutron diffraction results<sup>17</sup> show that  $\text{HCrO}_2$  is not antiferromagnetic even at 4°K. This means  $\theta/T_n > 50$ —a very large value.

At present there is only a crude agreement between theory and experiment. Nevertheless, we have some idea about the relation between structure and magnetic properties for  $\text{HCrO}_2$  and  $\text{DCrO}_2$ .

*Note added in proof.* It has been noted that our Eq. (8), obtained by averaging over  $\theta$ , is related to an expression given without such averaging by U. Kh. Kopvillem, Soviet Physics—JETP **38**, 151 (1960) [translation **11**, 109 (1960)].

#### ACKNOWLEDGMENTS

The authors wish to thank Miss Edna F. Dean and W. E. Heller for discussions and assistance in this work.

<sup>14</sup> P. W. Anderson, Phys. Rev. **79**, 350 (1950).

<sup>15</sup> J. Kanamori, J. Chem. Phys. Solids **10**, 87 (1959).

<sup>16</sup> P. W. Anderson, Phys. Rev. **115**, 2 (1959).

<sup>17</sup> J. A. Ibers and W. C. Hamilton (private communication).