Thus, there seems to be two energy ranges which cause softening of the surface layer of germanium crystals: one in the infrared with an energy range of 0.3–0.4 ev and another in the ultraviolet with energy higher than 3.0 ev.

The study of p-type germanium crystals was much less extensive. Two of these, containing 10^{14} and 10^{15} cm^{-3} concentration of ionized impurities, were tested. Their behavior was similar to that of n-type germanium crystals of the same purity. However, one p-type silicon crystal (purity unknown) exhibited much larger light softening (70%) than either n or p-type germanium [Fig. 1 (b)]. A few experiments conducted on n-type InSb and InAs (purity unknown) revealed that the hardness of their surfaces is also sensitive to light, but to a much smaller degree than that of germanium or silicon [Fig. 1 (c)].

The effect seems to be sensitive to the surface preparation, etchants, and the time and temperature of etching. However, not enough experiments were conducted to establish even a qualitative relationship between these variables. All germanium, InSb, and InAs samples in the experiment described above were etched with standard CP-4 solution, and the silicon crystals with a mixture of 75 HNO$_3$ and 25 HCl, by volume.

It is impossible at the present time to offer a detailed theory of this effect. The mechanism of the change of hardness with light must definitely be related to the energy states associated with dislocations. These, as has been pointed out at the beginning of this paper, are affected by the carrier distribution within the crystal. As the effect seems to be limited to a thin surface layer, which changes with impurity content (Figs. 2 and 3), it may be that this layer is identical with the space-charge layer[4] existing near the surface of semiconductors. Both infrared and ultraviolet light may alter the energy of dislocations in that layer and thus induce changes in its plastic properties, the former by changing carrier concentration within that layer and the latter by affecting surface electrons. However, on this basis, it is difficult to understand the similarity of the behavior of p- and n-type semiconductors. Another possible direction in which an explanation of this phenomenon should be sought would be to explore the effect of light on impurity atoms pinning down dislocations.[5] Such atoms could be ionized by light and become less effective in immobilizing dislocations. Again the effect of ultraviolet radiation would be difficult to fit into this scheme. It appears that more extensive experimental work is necessary before an adequate explanation can be advanced.

The authors are indebted to Dr. C. Mullin, Professor of Physics, University of Notre Dame, for many helpful discussions and to the Minneapolis Honeywell Research Center, for a supply of germanium single crystals.

[4] J. Bardeen, Phys. Rev. **71**, 717 (1947).
[5] Suggested by Dr. F. Seitz.

Magnetic Analysis of the Uranium-Oxygen System*

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Magnetic susceptibility measurements have been carried out on the uranium-oxygen system in the composition range of UO$_2$ to UO$_{2.67}$. The existence of an antiferromagnetic transition at compositions close to stoichiometric UO$_2$ which had been previously reported by the authors has been confirmed. The data make it possible to define clearly the phase limits of the UO$_2$ and U$_3$O$_8$ structures and to determine unambiguously that the excess oxygen ions in the nonstoichiometric salts occupy interstitial positions in the lattice.

I. INTRODUCTION

ALTHOUGH UO$_2$ and U$_3$O$_8$ are stable stoichiometric chemical compounds, it is well known that as much as 75% oxygen may dissolve in uranium and in the process several phases may form at various concentrations of oxygen. While the crystal structures of the various phases appear to be known, it is not known just how the oxygen goes into the lattice and precisely at what compositions the new phases appear. Since these points are of some importance in the technology of the oxides of uranium, it is desirable to ascertain whether oxygen goes into the system interstitially or by causing uranium ion vacancies in an expanded lattice.

This investigation was undertaken with the intention of ascertaining by the techniques of magnetic analysis the following points:

1. Does the oxygen go into the lattice interstitially

or does it cause uranium ion vacancies to be formed? It has been shown by the authors[1] that UO_2 undergoes a transition to an antiferromagnetic state at 28°K. This means that there is an exchange interaction between the uranium ions either directly or by means of a super-exchange mechanism through the oxygen atoms. As will be pointed out below, magnetic susceptibility data as a function of temperature can yield significant information on the neighborhood of the uranium atoms.

2. As oxygen enters the lattice, the valence of some of the U^{4+} ions must change to either U^{5+} or U^{6+} in order to preserve electrical neutrality. It is not clear, however, from chemical considerations which of these two alternatives is the equilibrium form. The magnetic moment per uranium atom as a function of composition should give this information.

3. What are the solubility limits of the various phases formed? A sharp indication of phase changes should be obtained from plots of susceptibility at constant temperature *versus* composition.

4. Is any UH_3 formed in the uranium oxide? This should be detectable magnetically since the UH_3 is ferromagnetic with a Curie point of approximately 175°K.

Measurements of the magnetic susceptibility of materials UO_x, where x varies from 1.84 to 2.67, have been carried out by Dawson and Lister[2] in the temperature range between liquid O_2 and 570°K. However, it appeared reasonable to repeat the work, extending the measurements down to liquid helium temperatures, for the following reasons: (a) Dawson and Lister's work was carried out on small samples of the order of 2 to 10 mg. Their measurements were at but one field and hence no correction for ferromagnetic impurities was possible. Their data showed considerable scatter. Their analysis was carried out by fitting a straight line on a least-squares basis (without considering the possibility of real curvature) to a plot of inverse susceptibility *versus* temperature. The chemical analysis of their samples was by means of increase in weight during oxidation. Their samples are the same samples on which the most complete x-ray data are available; hence, if magnetic analysis shows their composition to be in error, the x-ray data need to be reconsidered. (b). The discovery of an anomaly in the specific heat of UO_2 at 28°K by Jones, Gordon, and Long[3] led to the hypothesis that it is associated with a magnetic transition. This has been confirmed recently by the authors who have measured the magnetic susceptibility through the transition point down to 2°K on a sample from the same batch as the one in which the anomaly was observed. The transition appears to be to an antiferromagnetic state. The effect on this transition of deviations from the stoichiometric compound UO_2 appeared worthy of investigation.

[1] A. Arrott and J. E. Goldman, Phys. Rev. **99**, 1641(A) (1955).
[2] J. Dawson and M. Lister, J. Chem. Soc. p. 2177 (1950).
[3] Jones, Gordon, and Long, J. Chem. Phys. **20**, 695 (1950).

The most direct approach to determining whether the lattice defects under consideration are vacancies or interstitials is to compare the x-ray lattice parameters with measured densities. Though this has been attempted with the uranium-oxygen system, sufficiently accurate density measurements have not been obtained. The major difficulty is the porosity of the material leading to an apparent change in density with particle size.

II. SIGNIFICANCE OF SUSCEPTIBILITY *VERSUS* TEMPERATURE CURVES

In an antiferromagnetic material, the susceptibility per gram, χ, is related to the absolute temperature by the relation

$$\chi = C/(T+\theta), \tag{1}$$

where C and θ are both constants and

$$C = Ng^2\beta^2 J(J+1)/3k,$$

as in paramagnetic materials. Here N is the number of magnetic ions per gram, g is the gyromagnetic ratio, β the Bohr magneton, J the total angular momentum, and k is Boltzmann's constant. In the generalized Weiss-Néel molecular field treatment of antiferromagnetism, θ has the value $[J(J+1)/3k]\sum\pi_i Z_i A_i$, where Z_i is the number of interacting magnetic neighbors of a given ion in a given sublattice, A_i is the exchange interaction, and π_i is a factor which depends on the number of sublattices into which the lattice is divided. In this treatment it is assumed that the lattice may be broken down into several sublattices and the effective field acting on the ions of any sublattice consists of a contribution from each of the other sublattices in addition to the applied field.

A plot of $1/\chi$ *versus* T gives as its slope $d(T)/d(1/\chi)=C$. If it is assumed to a first approximation that only the spin contributes to the angular momentum and that g is close to 2, the valence of the magnetic ion can be obtained quite readily from this slope. The value of $1/\chi$ at $T=0$ as found from extrapolation from higher temperatures where Eq. (1) is valid is given by

$$\left(\frac{1}{\chi}\right)_{T=0} = \frac{\theta}{C} = \frac{\sum\pi_i Z_i A_i}{Ng^2\beta^2},$$

and is a measure of the average exchange interaction per pair of magnetic ions.

When this expression is applied to the UO_x system it will be shown below that (1) the variation with composition of C will be different for the case of U^{6+} ions replacing U^{4+} ions than for U^{5+} ions replacing U^{4+} ions, but will not depend on whether a model of interstitial oxygens or of uranium vacancies is used; and (2) the variations of θ/C with composition will be roughly independent of which valence states are assumed for the uranium ions but will be critically dependent on whether the oxygens go in interstitially or not.

In the expression for the susceptibility per gram, two quantities change on increasing the oxygen content. These are N, the number of magnetic ions per gram, and Z, the number of magnetic nearest neighbors. The number of magnetic ions per gram in the case of U^{6+} replacing U^{4+} goes as $N = N_0(3-x)/(238+16x)$, where N_0 is Avogadro's number and x is the oxygen/uranium ratio. (The denominator varies by but 3% from UO_2 to U_3O_8.) The number of magnetic nearest neighbors varies as $\bar{Z} = \bar{Z}_0(3-x)$ for oxygen entering the lattice interstitually and as $\bar{Z} = \bar{Z}_0(3-x)(2/x)$ for uranium leaving the lattice and causing vacancies. The factor $2/x$ gives the fraction of uranium sites vacant. As the factor $\bar{Z}/N$ appears in the ratio θ/C, the dependence of θ/C on composition should go as $\bar{A}$, the average exchange integral, for the case of interstitials, and as $2\bar{A}/x$ for the case of vacancies. In the case of vacancies, $\bar{A}$ should be roughly independent of composition as the interaction between any pair of U^{4+} ions is through oxygen atoms and the oxygen lattice is undisturbed.

For interstitials, however, the interactions between next-nearest neighbors is greatly increased. The only interstitial site in the CaF_2 lattice large enough to accommodate an oxygen ion is located at the $(0,\frac{1}{2},0)$ lattice positions giving $180°$ $U-O-U$ bonds. This arrangement is most favorable for a strong superexchange effect. Hence, as the O/U ratio is increased, the interaction parameter θ/C should be expected to increase if the interstitial model is correct and decrease if the vacancy model is correct.

In the molecular-field treatment that leads to the above results, it is assumed that the interactions of one ion with its neighbors are proportional to the net moments of sublattices of the various neighbors. As long as only one type of magnetic ion is present, such an approximation does not seem unreasonable. The use of the effective-field formulation for an assembly of mixed moments appears to involve an extra degree of deviation from an exact treatment of the system. The most crude way of taking the interaction into account is to make the further assumption that the U^{5+} ions, if they are present in the lattice, are distributed at random and that their presence merely decreases the effective moment in each sublattice. In this case the above results are unaltered except that

$$\frac{1}{\chi} = \frac{3kT}{N_A g_A{}^2 \beta^2 J_A(J_A+1) + N_B g_B{}^2 \beta^2 J_B(J_B+1)} + \frac{\sum \pi_i Z_i A_i}{N_A g_A{}^2 \beta^2 + N_B g_B{}^2 \beta^2},$$

where subscripts A and B refer to the different species of moments. Here all the above arguments about the variation of interaction parameter with composition hold so long as $g_A{}^2$ is of the same order as $g_B{}^2$. The slope of the $1/\chi$ versus T curve, however, will vary with composition differently than for the combination of U^{6+} and U^{4+} ions. As a function of x, the constant C becomes

$$C = \frac{N_0}{238+16x}\left(\frac{\beta^2}{3k}\right)$$

$$\times [g_A{}^2(5-2x)J_A(J_A+1) + g_B{}^2(2x-4)J_B(J_B+1)].$$

If we assume $g_A{}^2 = g_B{}^2$ and free spins with no orbital contribution to the moments, then as $J_A = 1$ and $J_B = \frac{1}{2}$ we have

$$C = \frac{N_0}{238+16x}\left(\frac{\beta^2}{3k}\right)[g_A{}^2 J_A(J_A+1)\tfrac{1}{4}(14-5x)],$$

so that the slope as a function of composition for U^{5+} ions should go as $\frac{1}{4}(14-5x)$ which compares with $(3+x)$ for U^{6+} ions.

The above relations for $1/\chi$ are linear in T, and it is for such simple cases that the analysis of this variation of the parameters C and θ/C as a function of composition have been treated above. However, the curves observed in these experiments, as in many other experiments, are not linear. Curvatures can arise for many reasons, some of which we enumerate here: (a) A mixture of two phases, both with magnetic ions, would give

$$\frac{1}{\chi} = \frac{T+\theta_1+\theta_2+\theta_1\theta_2/T}{\alpha C_1+(1-\alpha)C_2+[\alpha C_1\theta_2+(1+\alpha)C_2\theta_1]/T},$$

where α is the fraction of one phase. (b) Different moments on individual magnetic sublattices, such as would arise from preference of ions of one valence for a particular sublattice and those of another valence for another sublattice, would lead to a hyperbolic $1/\chi$ vs temperature relation with a transition to ferromagnetism at lower temperatures. (c) The linearity of the molecular field treatment arises from the use of averages for local interactions. The validity of this averaging is open to question in some cases. (d) The presence of temperature-independent contributions to the susceptibility would give $1/(\chi-\chi_0) = (T+\theta)/C$.

EXPERIMENTAL RESULTS

The method of measurement is to place a cylindrical sample in a uniform field and then to restore the uniformity of the field by passing a suitable current through a fine solenoid wound on the surface of the sample.[4] The uniformity of the field is detected by moving the sample with its solenoid with respect to two fixed detector coils connected in series opposition. The sample moves from within one detector coil to within the other. The two detector coils are used to discriminate against field fluctuations. The apparatus is designed to permit motion of the sample in a horizontal direction at the bottom of a three-walled metal Dewar of the Henry and Dolecek design.[5] Measurements are made in a liquid bath only at liquid-helium temperatures where vapor-pressure thermometry was

[4] A. Arrott and J. E. Goldman, Rev. Sci. Instr. **28**, 99 (1957).
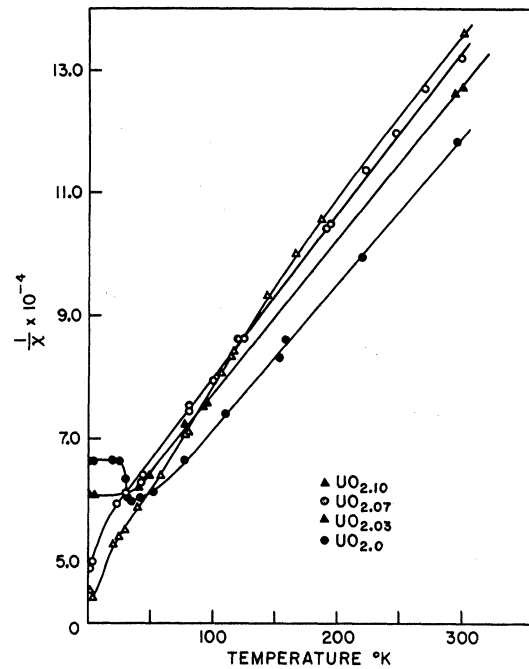[5] W. Henry and R. Dolecek, Rev. Sci. Instr. **21**, 496 (1950).

TABLE I. Chemical composition (O/U atomic ratio) of the samples used in this investigation.

Sample	Before compacting	Chemical analysis
JGL UO_2	no analysis	
MCW UO_2	2.00	2.03
NOH-20	1.96	2.07
MO-11	2.10	2.10
MO-13	2.20	2.20–2.23
MO-14	2.30	2.30–2.33
MO-15	2.40	2.40
MO-16	2.50	2.53
MO-17	2.60	2.58–2.59
U_3O_8	no analysis	

used. At all other temperatures the atmosphere is helium gas and, though the temperature is not controlled, the drift is slow enough to permit reasonable equilibrium to be established within the sample during the measurement. The temperature of the sample is determined from the resistance of the fine copper solenoid wound on the surface of the sample. The resistance-temperature relation used is that of Dauphinee and Preston-Thomas[6] corrected for the residual resistivity as determined at 4.2°K for each coil used.

Chemical analysis by means of oxygen take-up during preparation and by analysis for uranium after firing were carried out by the Westinghouse Atomic Power Division which supplied the samples. The analyses are shown in Table I. Preparation of good samples appears to be not without its difficulties. An indication of this is that the sample analyzed at $UO_{2.07}$ was the result of a deliberate attempt to produce an oxygen-deficient UO_2 specimen. As most of the analysis of the magnetic data presented here depends on knowledge of the compositions of the samples, the effectiveness of the analysis is greatly diminished when the compositions are in doubt as they are here. In addition, a number of these samples are not homogeneous. In particular, the $UO_{2.20}$ sample showed the presence of the U_3O_8 structure by x-ray techniques which would be insensitive to less than 10% U_3O_8 phase. The probable lack of homogenity and the uncertainty in the chemical analysis make all but the most general conclusions open to question.

At room temperatures and liquid nitrogen temperatures measurements of magnetizations were made in fields of 3, 7, and 12 kilogauss; at liquid helium temperatures measurements were made in fields of 0.003, 0.3, 3, 7, and 12 kilogauss; and at a number of intermediate temperatures magnetizations were determined in fields of 7 kilogauss. The magnetic isotherms at liquid helium temperatures all showed small hysteresis. This hysteresis is presumably associated with antiferromagnetism,[7] except in the case of U_3O_8 where the effect was very small and could be due to ferromagnetic impurity. The data at liquid-nitrogen and room temperatures, when plotted as M vs H, could be fitted with a straight

[6] T. Dauphinee and H. Preston-Thomas, Rev. Sci. Instr. **25**, 884 (1948).
[7] Y. Y. Li, Phys. Rev. **101**, 1450 (1956).

FIG. 1. Inverse susceptibility *versus* temperature of UO_x; $2.0 \leq x \leq 2.1$.

line through the three points, but the straight line does not go through the origin. Originally this was interpreted as due to small amounts of ferromagnetic impurities, but it was later found that the fluxmeter used was in error in a nonlinear manner. These corrections for the fluxmeter errors are somewhat in doubt, though it appears to be sufficient to limit the ferromagnetic impurity effects to within experimental error. The uncertainty in the fields may be as large as 2%. The susceptibilities may be in error as much as 3%. The inverse susceptibilities are plotted *versus* temperature in Figs. 1–3. These values are corrected for the diamagnetism of the U core and O atom as this effect becomes as large as 10% in the case of U_3O_8 at room temperature.

The susceptibilities at some definite temperatures have been determined by extrapolation using the inverse susceptibility *versus* temperature curves. Curves of susceptibility (uncorrected for diamagnetism) at constant temperature *versus* composition are shown in Fig. 4.

DISCUSSION OF RESULTS

The analysis given in the first part of this paper shows that two questions may be resolved from a study of inverse susceptibility *versus* temperature for the range of composition from $x=2$ to $x=2.67$. First, determining whether or not the interaction parameter, θ/C, increases or decreases with increasing oxygen content should distinguish between the presence of uranium vacancies or oxygen interstitials. This question, we believe, is rather well decided in favor of the interstitial model as will be shown below. Secondly, the change in the slope of the curves with composition
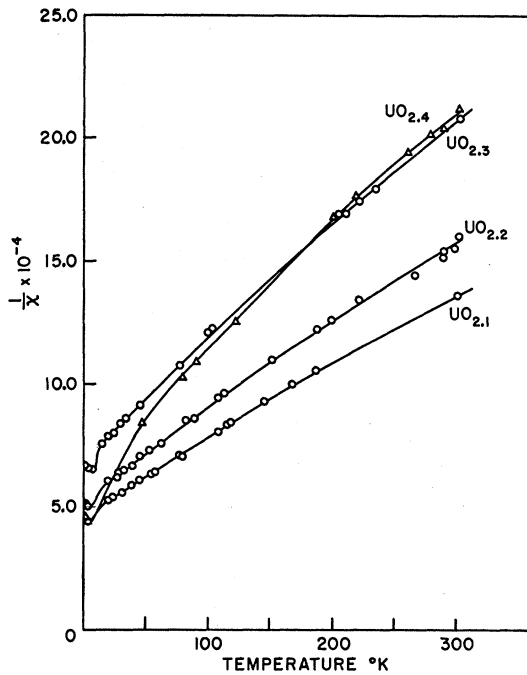
FIG. 2. Inverse susceptibility *versus* temperature
of UO_x; $2.1 \leq x \leq 2.4$.

should distinguish between a model where U^{5+} ions replace U^{4+} ions and a model where U^{6+} ions replace U^{4+} ions. This question is not at all well resolved on the basis of the data obtained. The curvature of the $1/\chi$ *versus* T plots leaves the average spin state of the uranium atoms in great doubt. This curvature most
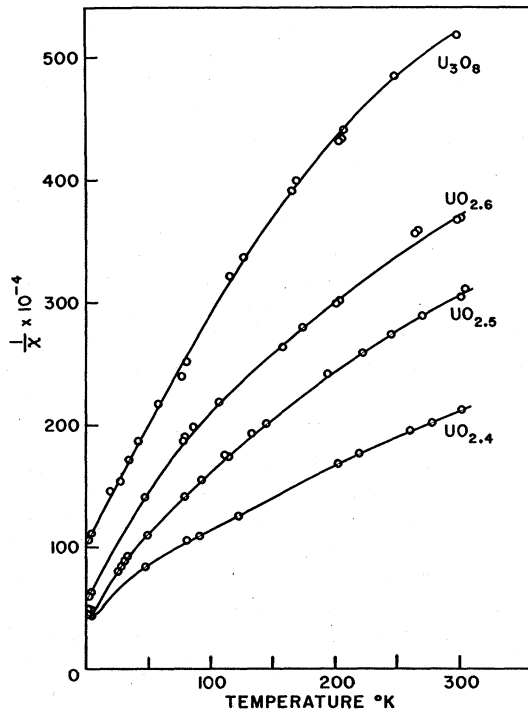
likely arises from gross inhomogeneity (not just a range of compositions, but actually mixture of phases) but may also be an intrinsic magnetic property of the system. Any attempt to explain the curvature from the inclusion of a term independent of temperature in the susceptibility leads to values of the average spin state a factor of 3 lower than that to be expected on any model. The possibility of nearly overlapping $5d$ and $4f$ states which would add a statistical term to the temperature dependence, cannot be ruled out.

Though the data do not fit well to a Curie-Weiss law, an interpretation of the data in terms of the parameters C and θ/C is possible if they are evaluated at fixed temperatures. This has been done arbitrarily by considering straight-line fits to the data between 50°K and 100°K, 200°K, and 200°K and 300°K. The values of C and θ/C obtained in this way are shown in Figs. 5 and 6.

The general increase of θ/C with increasing oxygen content is interpreted as an increase in the average exchange between pairs of uranium atoms through intervening oxygen atoms. Thus, this is taken as strong evidence for the entrance of oxygen into the UO_2 lattice in interstitial positions.

The behavior of the constant C as a function of composition does not permit a decision in favor of either the model in which U^{6+} replace U^{4+} ions or that in which U^{5+} ions replace U^{4+} ions. The fact that the model in which U^{5+} ions are present predicts curvature in the inverse susceptibility *versus* temperature plots and that such curvature occurs experimentally might lend support to that model. It must be noted that this model

FIG. 3. Inverse susceptibility *versus* temperature
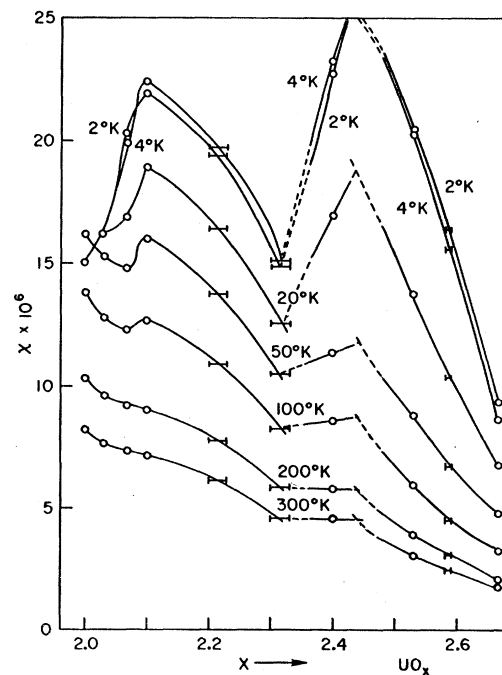of UO_x; $2.4 \leq x \leq 2.67$.

FIG. 4. Susceptibility *versus* composition at various temperatures
for the uranium-oxygen system.

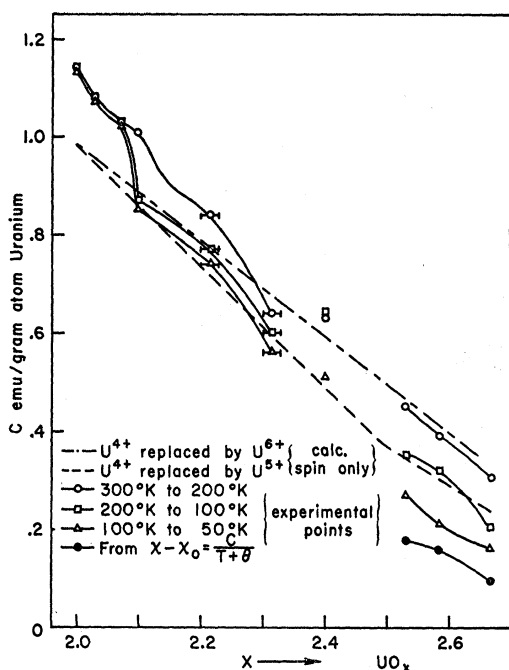FIG. 5. Variation of effective magnetic moment squared with composition.

FIG. 6. Variation of effective exchange parameter with composition.

does not lead to curvature in the higher oxygen range where only U^{5+} and U^{6+} ions would be present. Yet curvature exists for these compositions.

The deviations of the values of C from the spin-only values for composition near UO_2 indicate incomplete quenching of the orbital angular momentum. The values of C approach the spin-only values with increasing oxygen content at the same composition at which the cooperative phenomena disappear. This dependence on composition is consistent with the interstitial model for the oxygen atoms since in such a case the symmetry of the crystal field which the uranium ions see is altered.

A plot of susceptibility at constant temperature *versus* composition has long been recognized as a useful tool for phase analysis. In a single-phase region the variation of susceptibility at constant temperature with composition is in general unpredictable and almost never linear, particularly when contributions to the susceptibility of a Curie-Weiss type are present. The variation of C and θ may tend to be linear in composition but this could lead to nonlinear variations in χ. In a two-phase region the susceptibility must vary linearly with composition if the composition of the two phases remain fixed and only their relative abundance changes. If the susceptibility of a sufficient number of compositions are known, sharp indications of phase changes will be apparent from the magnetic analysis. If, however, the number of compositions are too limited, some reliance on x-ray data, for instance, is helpful. When this work was started, it was presumably well established that low-temperature oxidation of UO_2 retains the calcium fluoride structure over a range of composition extending toward $UO_{2.3}$, that there is a
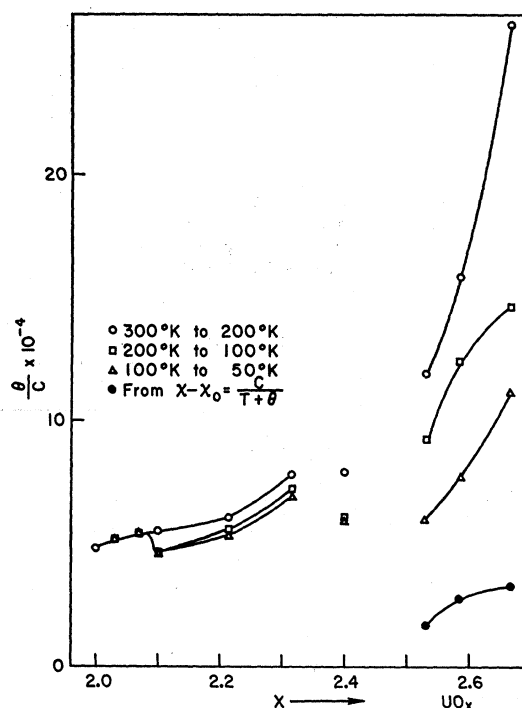
two-phase region around $UO_{2.4}$, and that the orthorhombic U_3O_8 structure extends down toward $UO_{2.5}$. The curves drawn between the points of Fig. 4 have been influenced somewhat by the above preconceptions. The resulting interpretation of the diagram is that the two-phase region extends from $UO_{2.315\pm0.015}$ to $UO_{2.43\pm0.01}$. The uncertainty in the phase limits is just the uncertainty in the chemical composition. The strange behavior in the $UO_{2.0}$ to $UO_{2.1}$ region is attributed to magnetic anomalies associated with the antiferromagnetic nature of UO_2. Recently it has been suggested[8] that oxidation of UO_2 proceeds by means of the formation of U_3O_7. The magnetic data presented here do not rule out this possibility if the data are interpreted in terms of a two-phase region lying between $UO_{2.1}$ and $UO_{2.33}$.

The magnetic anomalies to be associated with the antiferromagnetism of UO_2 appear to extend up to composition $UO_{2.07}$. In addition, all the samples except the two with the highest oxygen content showed some form of magnetic anomaly below 20°K. The anomalies were in the form of strong deviation of the points at 4°K from an extrapolation of the data from above 20°K, accompanied by a slight decrease in susceptibility between 4°K and 2°K and the appearance of slight hysteresis. If this is the result of inhomogeneity of the samples, it is an indication of the difficulty in preparing homogeneous samples as it would mean that a sample with a gross analysis of $UO_{2.53}$ still can contain some of the UO_2 phase.

[8] Gulbransen and Weissbart, Westinghouse Research Laboratories (private communications).