PHYSICAL REVIEW VOLUME 170, NUMBER 2 10 JUNE 1968

Ultrasonic Attenuation and Elastic Constants for Uranium Dioxide*

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(Received 27 December 1967; revised manuscript received 25 March 1968)

Elastic-constant measurements for c_{11}, $c_{11}-c_{12}$, and c_{44} have been made over the temperature range of 4.2 to 300°K. Anomalies are found in all three elastic constants near the Néel point, but particularly large anomalies are seen for c_{44}. Ultrasonic attenuation measurements at 50 MHz for all three elastic constants are also given as a function of temperature. Both c_{11} and $c_{11}-c_{12}$ have small attenuations confined to the immediate vicinity of T_N. There is a very large attenuation associated with c_{44}, and the attenuation extends over a broad temperature range. c_{44} is seen to vary as T^{-1} in the paramagnetic region. This behavior has led to an analysis of c_{44} in the paramagnetic region, in terms of a coupling between elastic strains and the triplet ground state for the U^{4+} ion. The magnitude of the strain coupling parameter is deduced from the data to be 722 cm^{-1} per unit strain. Dynamical Jahn-Teller interactions are discussed as the source of this coupling. The attenuation for c_{44} is analyzed in terms of relaxation theory and it is shown that the relaxation time deduced varies exponentially with temperature, with relaxation times of the order of 10^{-11} sec. The c_{11}, the $c_{11}-c_{12}$, and part of the c_{44} data are discussed in relation to an Ising-model calculation of Garland and co-workers. Only qualitative statements can be made, but it seems reasonable that the c_{44} data reflect the angular dependence of the exchange energy, particularly of the U-O-U bond. The c_{11} and $c_{11}-c_{12}$ attenuation data below T_N are qualitatively in agreement with the Landau-Khalatnikov theory of relaxation by critical scattering from long-range order fluctuations. A relaxation time of 5×10^{-10} sec is estimated for relaxation due to long-range order fluctuations below T_N. There are no such fluctuations above T_N.

I. INTRODUCTION

URANIUM dioxide is a magnetic material whose low-temperature properties are the subject of much current interest. One might almost say that the more the material is studied the more confusing the picture becomes. A catalog of some experimental and theoretical results will illustrate this point.

UO_2 was first found from specific-heat[1] and magnetic susceptibility[2] measurements to undergo a paramagnetic-antiferromagnetic transition in the vicinity of 30°K. In the paramagnetic state the material is known to have the CaF_2 crystal structure. Henshaw and Brockhouse[3] did elastic neutron scattering measurements on a powdered specimen in the antiferromagnetic state, and determined that the ion had considerable $5f$ character with a magnetic moment of $2.1\mu_B$. They deduced [111] as the spin alignment direction. Later, Frazer *et al.*[4] and Willis and Taylor[5] repeated these measurements on single-crystal samples and identified the transition temperature as 30.8°K. These later studies suggested that the ordered state was a two-sublattice antiferromagnet consisting of ferromagnetic sheets perpendicular to [001] axes, with the sheets arranged antiferromagnetically. The spins lay in the sheets and were directed either along [100] or [110] directions, and the effective moment was between 1.7 and $1.8\mu_B$. It was pointed out that this value was only coincidentally close to the spin-only value of $2\mu_B$. Rather, the form-factor analysis suggested again a considerable $5f$ character with the free ion having a $^3H_4$ configuration. The crystal-field splitting presumably gives a ground state with considerable orbital degeneracy and a magnetic moment near the spin-only value. Interestingly, however, the transition was observed to be first-order in nature, with the magnetization dropping from 50% of its saturation value to zero in less than 0.03°K.

Hutchison and Candela[6] made susceptibility measurements on magnetically dilute ditetramethylammonium uranium hexachloride and found a temperature-independent susceptibility, in contrast to the temperature-dependent paramagnetism usually displayed by compounds containing the U^{4+} ion. They made a point-charge crystal-field calculation for this $^3H_4$ ion in O_h symmetry with eightfold coordination appropriate to their compound. (This is also the configuration of O^{2-} ions about U^{4+} in UO_2.) The ninefold degenerate $J=4$ state was found to split into a singlet (labeled Γ_1), a Γ_3 doublet, a Γ_4 triplet, and a Γ_5 triplet. Either Γ_1 or Γ_5 could be the ground state, depending on the ratio of fourth- to sixth-order terms in the crystal-field potential. A similar result was obtained by Lea, Leask, and Wolf[7] as part of a more general crystal-field calculation for the rare-earth ions. (One might expect the actinides to be roughly similar to the rare earths.)

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* Work supported by the U.S. Army Research Office (Durham) and the Advanced Research Projects Agency through the Northwestern University Materials Research Center.

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Rahman and Runciman[8] have recently made a crystal-field calculation specifically for UO_2, and found the Γ_5 state to lie lowest. Thus, even the ground state of the ion is not definitely established, although one might tend to lean toward the triplet.

The possibility of a singlet ground state was exploited by Blume[9] as the basis for an ingenious theory for the first-order transformation. In this model, the Γ_5 excited state is assumed to lie a small energy Δ above the singlet ground state. The exchange field is postulated to split the triplet sufficiently so that one of its members will lie below the singlet, thus giving a magnetic ground state which could produce the exchange field in the first place which would further split the triplet, etc. As the material is warmed, the temperature dependence of the magnetization would cause the triplet splitting to decrease; and when the bottom member of the triplet crossed the singlet the material would abruptly leave the ordered state. Blume needed $\Delta/k \approx 50°K$ to fit the measured sublattice magnetization. One feature of Blume's theory is that there is no need for a first-order volume change at the transition, in contrast to an earlier theory of Bean and Rodbell[10] based on exchange striction. The contrast between these two theories led us[11] to measure the temperature dependence of the thermal expansion coefficient for UO_2. We observed an abrupt length change of 20–30 ppm at the transition. The contraction was isotropic and suggested a volume change of 60–90 ppm. Such a value is at least a factor of 10 too small for the Bean and Rodbell mechanism to be operative in UO_2. Our measurements have been substantiated by Rodbell,[12] who measured the lattice parameter. Rodbell also found no tetragonal distortion at T_N, although it could possibly have been masked if the antiferromagnetic domains were of the order of 1000 Å in size. Thus, the length measurements do not eliminate the possibility of a singlet ground state.

One very powerful test of Blume's model would be far-infrared absorption measurements in the antiferromagnetic state. Such measurements have been done by Daniel,[13] Allen,[14,15] and Aring and Sievers.[16] Between them they have observed lines at the following frequencies (all in cm^{-1}): 17.5, 19.2, 19.5, 20.5, 23, 79, 99, 184, and 216. The 19.2, 19.5, 20.5, and 23 cm^{-1} lines appear to be impurity induced. The 79 and 99 cm^{-1} lines were identified by Daniel[13] as free-ion transitions between the bottom of the triplet and the singlet, and between the bottom and middle of the triplet, respectively. He applied Blume's model and deduced $\Delta/k = 30°K$ from his data. Aring and Sievers[16] pointed out that anisotropy in the transverse g value might allow such normally forbidden free-ion transitions to be observed. Allen[15] identifies these same two lines as being the two antiferromagnetic resonances expected for a two-sublattice antiferromagnet. He finds that the frequencies of both lines seem to shift with temperature as the magnetization does. He notes that these two lines agree with the frequencies of the modes measured at magnetic Bragg reflections by Cowley and Dolling.[17,18]

Allen attributes the 184 and 216 cm^{-1} lines to two phonon absorptions allowed by virtue of the strong phonon-magnon coupling known[19] to exist in UO_2. He notes that the lines occur at twice the zone boundary frequencies along [001] and [111] measured by Dolling, Cowley, and Woods.[20] (However, the agreement with the [001] TA phonons may not be quite as good if one uses the 9°K neutron data.[18]) Allen explains the remaining line, at 17.5 cm^{-1}, as either an electronic-dipole impurity mode or a magnetic-dipole transition generated by domain walls. The latter possibility seems especially reasonable if one considers the small domain sizes postulated by Rodbell.[12] This factor could also explain the sample dependence of the 17.5 cm^{-1} line.

This close agreement between infrared and inelastic neutron scattering data lends strong support to the assignment of the triplet as the ground state. The triplet ground state is assumed in the recent spin-wave theories of Allen,[15] and of Cowley and Dolling.[18] In Allen's theory the ground state of the antiferromagnetic state is presumed to arise from a competition between exchange energy and the energy from a cooperative Jahn–Teller interaction.

Our previous measurements[11] of the temperature dependence of the elastic constants for UO_2 showed unusual behavior. All elastic constants are reproduced in Figs. 1 and 2. c_{11} and $c_{11}-c_{12}$ are seen to behave as expected for an insulator except near T_N, where they change abruptly. c_{44}, however, changes continuously from room temperature down to the transition. We have now made ultrasonic attenuation measurements for waves appropriate to all three elastic constants. In this paper we discuss the elastic-constant and attenuation measurements together, particularly in the paramagnetic region. In this region we show that the dominant behavior of c_{44} can be explained in terms of a coupling between elastic strains and the triplet ground state of U^{4+}. c_{44} departs from the T^{-1} behavior predicted by this mechanism as one nears T_N, and it is shown that this deviation of c_{44}, as well as the gross behavior of c_{11} and $c_{11}-c_{12}$, can be explained in terms of the onset of the exchange interaction. This behavior is shown to be con-

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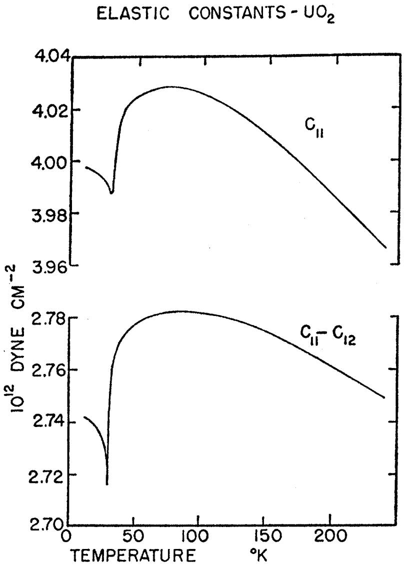

FIG. 1. c_{11} and $c_{11}-c_{12}$ versus temperature for UO_2. Note the rapid change near 30°K, and the relatively small percentage change in the elastic constants.

sistent with a two-dimensional Ising-model treatment for order-disorder transformations of thermodynamic first order developed by Garland *et al.* Lastly, the possibility that dynamical Jahn-Teller interactions are the source of the coupling which dominates c_{44} is considered, and it is seen that one cannot clearly reject or accept this possibility.

II. EXPERIMENTAL RESULTS

A. Elastic Constants

The details of the technique used in measuring the elastic constants as a function of temperature have been published elsewhere.[21] In brief, a pulse-echo technique is employed. The echoes which result from ultrasonic pulses that have traversed the UO_2 sample are summed at the receiver input along with the continuously decaying exponential voltage generated by a free-ringing quartz transducer maintained at room temperature. Thus, one observes the phase difference between the two inputs. As the temperature of the UO_2 is changed, the sound velocity also changes, resulting in a change in the phase difference. By observation of the phase difference as a function of temperature one obtains a measure of the temperature derivative of the sound velocity, and hence of the elastic constants. The method yields a precision for relative velocity changes of at least 0.1%, but gives no information on the absolute values of the elastic constants. We used the room-temperature values of Wachtman *et al.*[22] for all three elastic constants as a starting point, and obtained our final curves by integration of our experimental curves. The phase changes were monitored continuously as a function of temperature by feeding the receiver output and temperature readings to the axes of an X–Y recorder. Thus, the final curves are shown as continuous functions of temperature, even though they were obtained by integrating the experimental curves at certain temperature values and drawing a smooth curve through the results. The choice of these temperatures at which the data are integrated is perfectly arbitrary and is a function only of the patience one has in processing the data.

Since UO_2 crystallizes with the CaF_2 structure there are only three independent elastic constants. These are c_{11}, $c_{11}-c_{12}$, and c_{44}. c_{11} and $c_{11}-c_{12}$ are shown in Fig. 1 and were obtained from propagation of longitudinal waves along [100] and shear waves along [110] polarized along [1$\bar{1}$0], respectively. c_{44} is shown in Fig. 2 and was obtained by propagation of shear waves along [100] with any polarization, and along [110] polarized along [001]. Because of a high attenuation near T_N it was not possible to follow c_{44} through the transition. A check on the consistency of the data can be made by propagating longitudinal waves along [110]. This particular sound velocity is determined by the combination $c_{11}-c_{12}+2c_{44}$. The measured values of this velocity agreed with the calculated values to within experimental error. All velocities were corrected for thermal expansion, which was determined separately.[11] The elastic constants were determined at several frequencies between 20 MHz and 90 MHz, and were found to be frequency-independent. Unlike many measurements on UO_2 the elastic constants are sample-independent.

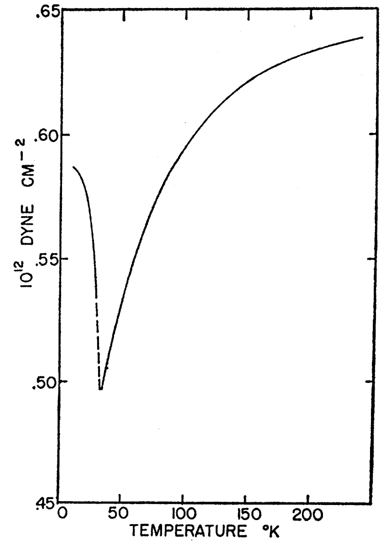

FIG. 2. c_{44} versus temperature for UO_2. Note the very large percentage change in this elastic constant. Note also that measurements cannot be made very near T_N because of high attenuation.

While all three elastic constants clearly show the

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influence of the phase transformation, the behavior of c_{44} is by far the most dramatic. Interestingly, the c_{44} data in the paramagnetic region can be shown to satisfy the following relation over a very broad temperature range:

$$(c_{44})_{\text{meas}} = 0.668\times10^{12}\ \text{dyn/cm}^2 - (7.3\times10^{12}/T)\ (\text{dyn deg/cm}^2), \quad (1)$$

where T is the temperature in °K. The uncertainty in both numbers is at most 5%, based on evaluation of all possible errors in the experiment. The c_{44} data are replotted versus $1/T$ in Fig. 3, where the solid line represents Eq. (1) and the dashed line represents the measured values of c_{44}. As can be seen in Fig. 3 the measured values of c_{44} fall on the curve given by Eq. (1) over the temperature range 200°K to about 65 or 70°K. Below this range the data always lie above the T^{-1} curve.

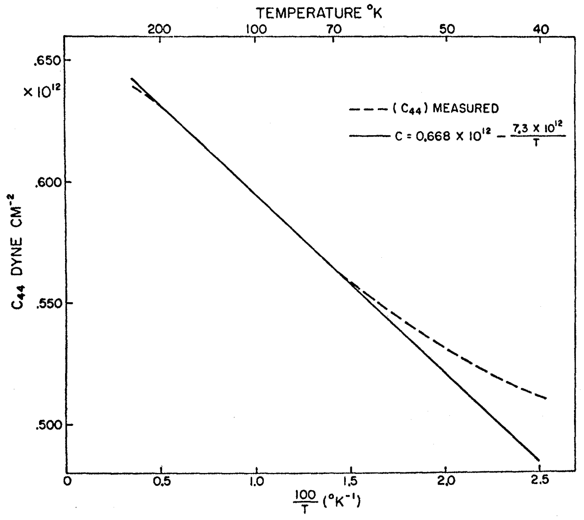

FIG. 3. Replot of c_{44} versus temperature for UO_2. An inverse temperature scale is used. The solid line is a T^{-1} straight line while the dashed line represents the data.

Equation (1) implies that c_{44} would vanish at a temperature of 10.92°K if the data were never to depart from the T^{-1} curve.

B. Ultrasonic Attenuation

In contrast to the elastic-constant behavior, the temperature dependence of the attenuation is sample-dependent. The attenuation appropriate to ultrasonic waves propagating at velocities given by c_{11} and $c_{11}-c_{12}$ is given in Fig. 4. Only a small temperature range is covered since outside this range the attenuation is constant. The constant background was subtracted out to obtain the data of Fig. 4. The attenuation was monitored continuously as a function of temperature on an $X-Y$ recorder. Each point in Fig. 4 is an average of several runs, and the data were obtained at 50 MHz. We note that the attenuation peaks are small in magnitude and perhaps discontinuous through the transition.

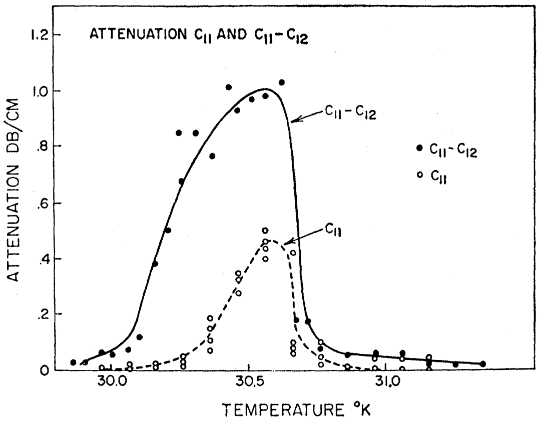

FIG. 4. Attenuation of 50-MHz ultrasonic waves in UO_2. Solid line is "eyeball fit" to the data for propagation at velocity given by $c_{11}-c_{12}$. Dashed line is same for c_{11}. A constant background attenuation has been subtracted out.

Our samples were so large, however, that it is difficult to have the entire sample at the same temperature, and thus we cannot verify the possibility that the peaks in Fig. 4 are discontinuous near T_N. The peaks are clearly skewed toward the antiferromagnetic side.

The attenuation data for shear waves propagating with a velocity determined by c_{44} are given in Fig. 5, where the various symbols represent different samples. Attenuation data were taken at 50 MHz. Since it is difficult to make all the necessary corrections properly (such as those due to bond losses and diffraction) the curves are arbitrarily normalized to coincide at 43°K. It is clear that three of the samples have attenuation values which are more or less in agreement, but one sample is very different. We shall consider the data only for those samples which agree. There are two very obvious features in Fig. 5. (1) The attenuation is a factor of 20–30 greater than that seen in Fig. 4. Thus, there must be a large loss mechanism associated with c_{44}. (2) The attenuation is spread over a much broader range of

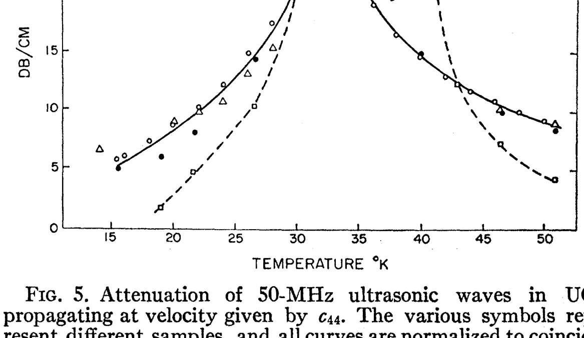

FIG. 5. Attenuation of 50-MHz ultrasonic waves in UO_2 propagating at velocity given by c_{44}. The various symbols represent different samples, and all curves are normalized to coincide at 43°K.

temperature; only near 70°K does the attenuation drop to the constant background.

The attenuation and elastic-constant data taken together suggest the following constraints on an interpretation of the data in the paramagnetic region. We must search for a mechanism which causes a softening of c_{44} at temperatures well above T_N and which predicts a T^{-1} dependence for c_{44}. At these high temperatures the mechanism should be lossless since there is no high-temperature attenuation except for a constant background. Below approximately 70°K, one of three conditions must hold. The mechanism operative at high temperatures causes c_{44} to depart from the T^{-1} behavior and causes a large loss. Alternatively, a second mechanism comes into play near T_N which causes changes in all three elastic constants. This second mechanism would govern the over-all behavior of c_{11} and $c_{11}-c_{12}$, as well as the difference between the measured c_{44} and the value of c_{44} predicted from the T^{-1} curve. This second mechanism could then be responsible for all the attenuation observed, although it must give a stronger attenuation for shear waves propagating at velocity $v^2=c_{44}/\rho$. Thirdly, the departure of c_{44} from T^{-1} behavior is caused by one mechanism, and the loss by another. At this time we shall not attempt a detailed explanation for the elastic constants or attenuation in the antiferromagnetic region.

C. Hysteresis

The neutron diffraction measurements,[4,5] which established the first-order character of the transition in UO_2, showed no evidence of hysteresis in the magnetization. Some hysteresis is always expected for a first-order transition, and the implication which must be drawn from the neutron data is that any barrier energies involved in the transition must be less than the temperature resolution of their experiments ($\sim 3\times 10^{-2}$°K). However, all our measurements show a small hysteresis. Length change, elastic constant, and attenuation are all not exactly repeatable as one warms or cools through the transition. The amount of hysteresis is a function of the time it takes to pass through the transition, but with a time of about 3 h taken to pass from 29 to 32°K an irreducible hysteresis of about 0.10°K was observed. We feel that our absolute temperature is known at least this accurately. It is not clear whether this effect is real or simply an artifact of our large sample sizes ($\sim$2–10 cm^3). In some cases the elastic constant, our most sensitive indicator, was observed to vary in steps, as if the sample were making the transition a small region at a time.

D. Magnetic Field and Stress Effects

The temperature dependence of c_{44} and of the attenuation of sound waves associated with c_{44} were studied at 50 MHz as a function of magnetic field up to fields of 35 kG. Because of the dimensions of the solenoidal magnet it was only possible to have the field oriented along the direction of sound propagation. No effect whatever on c_{44}, its attenuation, or the position of T_N was observed.

Because of the strong coupling between lattice and spins known to exist in UO_2, both c_{44} and the attenuation associated with c_{44} were studied as a function of applied external stress over the range 4.2 to 50°K. Stresses of up to 175 kG/cm^2 were applied. Ultrasonic waves were propagated along [100] with the stress applied along [110] in order to give a static shear strain. No effect could be observed in the behavior of c_{44} or the attenuation appropriate to it. Similarly, for longitudinal waves there were no observed effects. Longitudinal waves have a low enough attenuation that they can be observed all the way through the transition. No shifts in T_N were observed. At the highest stresses the echo train became nonexponential, implying that the crystal faces had become nonparallel. Such behavior limited the maximum stress which we could apply. Both the applied magnetic field and the applied stress, at their maximum values, give energy splittings equivalent to approximately 4°K.

III. THEORY

In this section we outline the relevant concepts which we feel are necessary for a coherent explanation of our data. Elastic strain coupling between ultrasonic waves and an ion with a degenerate electronic ground state will be discussed first. It is necessary to extend previous theory to include collective effects since each unit cell in UO_2 contains an ion of uranium. The arguments are made specific for a possible Jahn-Teller interaction, and some *ab initio* theoretical difficulties for U^{4+} are indicated. In addition, as seen in the preceding section, the acoustic losses and elastic constant changes for UO_2 are quite large, and these experimental facts require a more detailed examination of earlier theory. Lastly (and obviously), it is necessary to take account of cooperative effects, both in terms of magnetic exchange and strain coupling to the U^{4+} ground-state triplet.

A. Quasistatic Coupling with Elastic Strain

Let us consider the general problem of a system of energy levels which can couple to an external strain. For simplicity let the levels be degenerate in the absence of a strain, although this is not necessary, and let the energy be E_0. There are N_0 ions in the crystal. Under an applied strain, these energy levels will shift in energy with some rising above E_0 by energies $\alpha_2\epsilon$, $\alpha_4\epsilon$, $\alpha_6\epsilon$, $\cdots$, and some dropping below E_0 by energies $\alpha_1\epsilon$, $\alpha_3\epsilon$, $\alpha_5\epsilon$, $\cdots$. Here ϵ is the value of the strain. Some levels may even remain at E_0 in the presence of strain, whence $\alpha_i=0$. After application of the strain, if one waits a long time for equilibrium (quasistatic assumption), then there are n_1 uranium ions with energy $E_0-\alpha_1\epsilon$, n_3 with energy $E_0-\alpha_3\epsilon$, $\cdots$, n_2 with energy $E_0+\alpha_2\epsilon$, etc. We allow for degeneracy even under strain by not requiring all α_i to be different.

Then, at temperature T, the ith level will on the average contain n_i ions, where

$$n_i=(N_0/z)\exp(-\alpha_i\epsilon/kT)\exp(-E_0/kT) \tag{2}$$

and

$$z=\sum_{j=1}^{P}\exp(-\alpha_j\epsilon/kT)\exp(-E_0/kT).$$

P is the total number of levels and α_i can be positive and negative. The total energy of the system is

$$V=\sum_{i=1}^{P}E_in_i$$

$$=\frac{\sum_{i=1}^{P}N_0\exp(-\alpha_i\epsilon/kT)\exp(-E_0/kT)(\alpha_i\epsilon+E_0)}{\sum_{j=1}^{P}\exp(-\alpha_j\epsilon/kT)\exp(-E_0/kT)} \tag{3}$$

or

$$V=\frac{N_0\epsilon\sum_{i=1}^{P}\alpha_i\exp(-\alpha_i\epsilon/kT)}{\sum_{j=1}^{P}\exp(-\alpha_j\epsilon/kT)}+N_0E_0. \tag{4}$$

But N_0E_0 is just the total energy before application of the strain. Thus, the change in total energy due to the strain is

$$\Delta V=\frac{N_0\epsilon\sum_{i=1}^{P}\alpha_i\exp(-\alpha_i\epsilon/kT)}{\sum_{j=1}^{P}\exp(-\alpha_j\epsilon/kT)}. \tag{5}$$

For ultrasonic waves the associated strain is small ($\sim 10^{-6}$). As we shall see, α_i is also small enough so that $\alpha_i\epsilon \ll kT$ over the temperature range of interest. Thus, we can write

$$\Delta V\approx\frac{N_0\epsilon\sum_{i=1}^{P}\alpha_i(1-\alpha_i\epsilon/kT)}{\sum_{j=1}^{P}(1-\alpha_j\epsilon/kT)} \tag{6}$$

or

$$\Delta V\approx N_0\frac{\epsilon}{P}\sum_{i=1}^{P}\alpha_i-\frac{N_0\epsilon^2}{kTP}\sum_{i=1}^{P}(\alpha_i)^2+\frac{N_0\epsilon^2}{kTP^2}\sum_{i=1}^{P}\sum_{j=1}^{P}\alpha_i\alpha_j. \tag{7}$$

If we use the conventional definitions

$$\frac{1}{P}\sum_{i=1}^{P}\alpha_i\equiv\langle\alpha\rangle, \tag{8a}$$

$$\frac{1}{P}\sum_{i=1}^{P}(\alpha_i^2)\equiv\langle\alpha^2\rangle, \tag{8b}$$

$$\frac{1}{P^2}\sum_{i=1}^{P}\sum_{j=1}^{P}\alpha_i\alpha_j=\langle\alpha\rangle^2, \tag{8c}$$

then

$$\Delta V=N_0\epsilon\langle\alpha\rangle-(N_0\epsilon^2/kT)\{\langle\alpha^2\rangle-\langle\alpha\rangle^2\}. \tag{9}$$

Equation (9) is the change in total elastic energy per unit volume due to a static strain ϵ. If the system obeyed perturbation theory, then both $\langle\alpha\rangle$ and $\langle\alpha\rangle^2$ would be zero, and ΔV would be quadratic in strain. Since we are dealing with elastic energy we can define a "strain-ion elastic constant" by the relation

$$c^{\mathrm{S-I}}=d^2(\Delta V)/d\epsilon^2$$

or

$$c^{\mathrm{S-I}}=-(2N_0/kT)\{\langle\alpha^2\rangle-\langle\alpha\rangle^2\}. \tag{10}$$

This identification is legitimate since the energy change due to the interaction is quadratic in strain for small strains, as is the elastic energy. Equation (10) can be interpreted as the (negative) contribution to the elastic constant provided by the reduction in energy associated with a coupling between strains and the electronic energy levels. In our case we identify the appropriate elastic constant as c_{44}, and obtain

$$c_{44}^{\mathrm{S-I}}=-(2N_0/kT)\langle\alpha^2\rangle. \tag{11}$$

Now let us ask what might be the particular source of the coupling between strains and U^{4+} ions in UO$_2$. If the electronic ground state is in fact a triplet, which exists in the cubic symmetry of CaF$_2$ structure, then one is led to consider Jahn-Teller interactions.

The theorem of Jahn and Teller[23] states that a nonlinear molecule possessing an electronically degenerate ground state is unstable with respect to a configuration with lower symmetry which relieves the degeneracy (unless the ground state is a Kramers doublet). Van Vleck[24] pointed out that the molecule will undergo a static distortion to the lower symmetry if the electrons are sufficiently strongly coupled to the relevant vibrations of the complex. On the other hand, if the coupling is weak or if the zero-point energy for the vibrations of the complex exceeds any barriers separating equivalent configurations, then no distortion occurs.[25] Rather, the molecule has a complicated motion consisting of cou-

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[25] W. Moffitt and A. D. Liehr, Phys. Rev. **106**, 1195 (1957).

pled electrons and vibrational modes; this phenomenon is the so-called dynamical Jahn-Teller effect.[26]

An evaluation of the contribution made to the elastic energy by Jahn-Teller distortions has been made for Mn^{3+} in YIG and Ni^{3+} in Al_2O_3 by Sturge and coworkers.[27,28] Their treatment was simplified greatly by the fact that Mn^{3+} and Ni^{3+} have electronic ground states with E_g symmetry, and in the stated hosts have sixfold octahedral coordination. As shown by Van Vleck,[24] and later by Öpik and Pryce,[29] there are six relevant even-parity distortions of the six neighboring ions, of which only two can couple to the ion in question. These distortions (i.e., vibrations of the ions away from equilibrium) are labeled Q_2 and Q_3. Thus, in order to solve for the Jahn-Teller splitting energy, one must evaluate only a 2×2 determinant. There are then two energy branches in Q_2–Q_3 space, which when plotted versus Q_2, appear as intersecting parabolas. When one introduces Q_3, rotational symmetry about the energy axis obtains, and the resultant energy surface is the well-known "Mexican hat" potential. Inclusion of higher-order displacement terms into the potential yields the result that three relative minima exist in this energy surface, evenly spaced around the energy axis. These minima move in energy with applied strain, and it is this motion of the minima which allows a coupling to ultrasonic waves, as studied by Sturge and coworkers. In their work, the various α_i appropriate to our Eqs. (8) and (11) can be deduced from the data since one knows in advance how to relate one α_i to another.

The situation is considerably more complicated for the U^{4+} ion in UO_2. With a triplet ground state of Γ_5 symmetry (we use the Bethe notation for electronic symmetries), then of the 27 normal modes of vibration possible for the complex of U^{4+} and eight surrounding oxygen ions, only a single E_g mode and two T_{2g} modes can be coupled to the triplet.[15] However, since the T_{2g} modes are triply degenerate and the E_g mode is doubly degenerate, one must solve a rather larger determinant to obtain the energy surface. The fact that only c_{44} is involved for UO_2 would eliminate E_g, but one would still need a seven-dimensional space to plot the energy surface. The problem has received some general consideration by Liehr,[26] and it is not clear how many minima would exist in this surface, nor how they would move with strain. So if one wishes to interpret the strain coupling in UO_2 in terms of Jahn-Teller interactions, then the best he can do is apply Eq. (11) to his data and determine an average value for the strain coupling parameter.

B. Dynamical Effects

Now consider that the strain in the preceding section is not static but is time-dependent. Then, if there is a lifetime τ associated with the thermal redistribution, or there is a barrier between energy states, at some frequency the ions will begin to have difficulty following the oscillating strain. If this oscillating strain is provided by an ultrasonic wave then the wave will be attenuated. At the same time, not as many ions will be able to move to the lower energy configurations as could move under a static strain. Thus, both the elastic constant and the attenuation will depend on the frequency of the wave. We calculate the explicit dependence here. One method of making the calculation was used by Sturge *et al.*,[28] but their calculation contains implicit assumptions which restrict it to cases where both the attenuation and elastic-constant changes are small. Our data violate both possibilities. Instead, we consider a generalization of a method given by Pomerantz,[30] only we write all equations in terms of elastic stiffness constants directly, rather than in terms of compliance constants. Our results, in the limit of small attenuation and small elastic-constant change, go over to those of Sturge *et al.*[28] and of Pomerantz.[30]

Assume a stress is applied to a crystal containing ions with energy levels which couple to strain. Then, n_0 ions would change over to a lower energy configuration if enough time were available. Let n be the instantaneous number of ions which have made the change in the time allowed. If the stress is F and the strain is X, we may write

$$F=c_1X+gn, \qquad (12)$$

where c_1 is the conventional elastic constant and g is the proportionality constant which relates n to the component of strain. The first term in Eq. (12) follows from conventional elasticity theory and the second term follows from Eq. (9), where it is seen that the strain coupling energy is quadratic in the strain. Thus, the stress is linear in the instantaneous strain, which itself is linear in the instantaneous number of ions which have changed their energy. Thus, we also have

$$n_0=bX, \qquad (13)$$

where b is a constant.

We now make the critical assumption (which determines the outcome of the calculation) that n approaches n_0 in the following way:

$$dn/dt=-(1/\tau)(n-n_0). \qquad (14)$$

τ is the relaxation time, which will in general be temperature-dependent, as will c_1 and the product gb. If

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[26] For a complete list of references the reader is referred to F. S. Ham, Phys. Rev. **138**, A1727 (1965); A. D. Liehr, J. Phys. Chem. **67**, 389 (1963); **67**, 471 (1963).

[27] E. M. Gyory, R. C. LeCraw, and M. D. Sturge, J. Appl. Phys. **37**, 1303 (1966).

[28] M. D. Sturge, J. T. Krause, E. M. Gyorgy, R. C. LeCraw, and F. R. Merritt, Phys. Rev. **155**, 218 (1967).

[29] U. Öpik and M. H. L. Pryce, Proc. Roy. Soc. (London) **A238**, 425 (1957).

[30] M. Pomerantz, Proc. IEEE **53**, 1438 (1965).

one combines Eqs. (12)–(14) one obtains

$$F+\tau dF/dt=c_1X+bgX+c_1\tau dx/dt. \qquad (15)$$

Equation (15) is analogous to Pomerantz's Eq. (1), but everything is reversed since we have used stiffness constants rather than compliances.[30] We will thus be able to handle arbitrarily large changes in elastic constant and loss.

If both F and X vary as $e^{-i\omega t}$, Eq. (15) becomes

$$F=X_0\left\{\frac{c_1+bg+c_1\omega^2\tau^2}{1+\omega^2\tau^2}+\frac{i\omega\tau bg}{1+\omega^2\tau^2}\right\}. \qquad (16)$$

The loss experienced when such a system is driven at frequency ω is given by the quality factor

$$|Q^{-1}|=\frac{\mathrm{Im}(F/X_0)}{\mathrm{Re}(F/X_0)}$$

$$=\frac{|bg|}{[c_1+bg/(1+\omega^2\tau^2)]}\frac{\omega\tau}{1+\omega^2\tau^2}. \qquad (17)$$

With the conventional relation between attenuation and Q, $A=(4.343\omega/v_SQ)$ dB/cm, where v_S is the velocity of sound, we obtain

$$A=\frac{4.343}{v_S}\frac{|bg|}{[c_1+bg/(1+\omega^2\tau^2)]}\frac{\omega^2\tau}{1+\omega^2\tau^2}. \qquad (18)$$

We now identify c_1 as the conventional elastic constant, designated by $c_{44}{}^0$, and bg as the strain-ion elastic constant from the previous section, designated by $c_{44}{}^{S-I}$ We recall that $c_{44}{}^{S-I}$ is negative and include the minus sign at once; thus,

$$A=\frac{4.343}{v_S}\frac{c_{44}{}^{S-I}}{c_{44}{}^0-c_{44}{}^{S-I}}\frac{\omega^2\tau}{1+\omega^2\tau^2}. \qquad (19)$$

We note that Eq. (19) has the elastic-constant terms inverted from Eq. (8) of Pomerantz.[30] This inversion is crucial when the data are analyzed. Pomerantz's Eq. (8) cannot be used when the elastic-constant changes are large, whereas our Eq. (19) can be used. When the explicit temperature dependence of $c_{44}{}^{S-I}$ is included in Eq. (19), it replaces Eq. (3) of Sturge *et al.*,[28] which also is not applicable when the elastic-constant changes are large.

The real part of Eq. (16) also gives the effective elastic constant for waves traveling in this solid:

$$c_{44}{}^{\mathrm{eff}}=c_{44}{}^0-c_{44}{}^{S-I}/(1+\omega^2\tau^2). \qquad (20)$$

Equation (20) is only strictly valid when one can completely ignore any loss effects or any effects due to coupling of the ions. A more correct relation is derived in the next section.

Equations (19) and (20) can thus be interpreted as reflecting the influence of the difficulty which the ions have in following the oscillating strain. This difficulty arises because there is a lifetime associated with the thermal redistribution due to an energy barrier between the various energy minima, and the ions need a time lapse before they can appear as contributors to the elastic constant. The attenuation arises because the ions are not in phase with the wave.

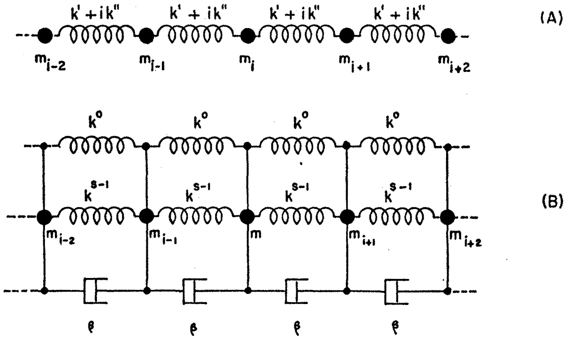

FIG. 6. (A) Highly schematic linear chain model for UO$_2$, showing coupling between ions with springs having real and imaginary parts to the spring constant. (B) Somewhat less schematic linear chain showing "ordinary elastic spring," strain-ion spring, and loss device.

If there is an energy barrier between the energy levels of height V_0, then at high temperatures the loss is due to the difficulty the ions have in hopping over the barrier. In this case τ is determined by[28]

$$\tau^{-1}=2\nu_0\exp(-V_0/kT), \qquad (21)$$

where ν_0 is the "attempt frequency." On the other hand, one would expect a power-law dependence for τ if the lifetime were due to, say, a Raman process.

C. Linear Chain Model

The arguments of the preceding section were implicitly made for a crystal containing a single ion coupled to strain. We have not yet considered interactions between such ions. But in UO$_2$ $\frac{1}{3}$ of the ions in the crystal are involved in this effect: each U^{4+} is coupled to all other U^{4+} through the oxygen ions. Thus, for UO$_2$ it is necessary to consider collective effects. We do so in anticipation that collective effects will be negligible in our case since the ultrasonic waves used had such long wavelengths ($\sim10^5$ units cells). At these wavelengths, all the elastic wave can do is count the U^{4+} ions it encompasses, but it clearly cannot resolve couplings of a collective nature. However, the collective effects could be observable by other experimental techniques.

We construct a linear chain model to represent UO$_2$, and in so doing are guided by the results of the previous two sections. Let us consider a linear chain of ions of mass M, where M is the reduced mass of the UO$_2$ unit cell. We ignore any optical branch possibilities. Let these ions be coupled by lossy springs, as shown schematically in Fig. 6(a). The springs in this chain have a complex spring constant, whose real and imaginary parts are given by analogy to Eq. (16):

$$k'=k^0-k^{\mathrm{S-I}}/(1+\omega^2\tau^2), \tag{22a}$$

$$k''=\omega\tau k^{\mathrm{S-I}}/(1+\omega^2k^2). \tag{22b}$$

That is, the real part of the spring constant is given by an "elastic" force constant k^0 and a "strain-ion" force constant $k^{\mathrm{S-I}}$ while the imaginary part of the spring constant is proportional to $k^{\mathrm{S-I}}$. A specific mechanical model is shown in Fig. 6(b). The springs are in parallel because of Eq. (22a), as well as the energy arguments leading to Eq. (11). The dashpots supply a damping force of $-B(\dot{x}_i-\dot{x}_{i-1})$, where $\dot{x}_i$ is the velocity of ion i. The dependence of B on $k^{\mathrm{S-I}}$ guarantees that the dashpots will only be in the system when the strain-ion springs are in the system, and the damping of a wave will only be large when the strain-ion contributions are large.

The dispersion relation for such a chain is no mystery, and one can see a schematic picture in Fig. 11.2 of Brillouin's book.[31] If one assumes propagation of a wave of the form

$$\psi=\psi_0e^{-q'x}e^{i(qx-\omega t)},$$

one obtains the following relations between q and ω, i.e., the dispersion relation:

$$\omega^2=(2k'/M)(1-\cos qa\cosh q'a)$$
$$+(2k''/M)(\sin qa\sinh q''a). \tag{23}$$

Here a is the equilibrium separation between ions. The $\cosh q'a$ term in Eq. (23) represents the collective-loss effects in the dispersion relation. In the limits $q'a\ll1$ (low attenuation) and $qa\ll1$ (long wavelengths), Eq. (23) reduces to

$$\omega^2=(k'/M)q^2a^2,$$

after the $\cos qa$ term has been expanded to second order. This limit gives a wave velocity for shear waves identical to that predicted from Eq. (2). Thus, at long wavelengths and small loss per unit cell one does not observe collective behavior in the elastic constants.

One might remark, however, that at temperatures near 35°K, where the measured ultrasonic attenuation becomes large, the collective strain-ion effects in Eq. (23) should become noticeable in the [100] TA dispersion curves observed by inelastic neutron scattering. In particular, this branch would not approach the zone boundary with zero slope, and the [100] TA zone-boundary frequency would be temperature-dependent. The slope of the TA branch near $k=0$ would be strongly temperature-dependent, varying as T^{-1}.

The damping constant q' obtained by solving for the imaginary part of the dispersion relation, using the chain of Fig. 6(b), gives back Eq. (19) exactly.

D. Cooperative Effects

As one nears the transition temperature it is necessary to take cooperative effects into account. Fortunately, for UO_2 the transition is first order and there can be no critical scattering of sound waves by long-range fluctuations in magnetization above T_N. The two cooperative effects which must be considered are the exchange interaction leading to the magnetic ordering and any cooperative strain-ion interactions. We shall not treat the latter mechanism at all.

One method for handling the influence of magnetic exchange on elastic constants and ultrasonic attenuation has been developed by Garland and co-workers.[32] They have considered a two-dimensional Ising model for a system of spins located on mass particles in a compressible lattice. Their treatment is limited to the case where the coupling between spins and lattice is weak, in order that the spin contributions can be handled separately from the lattice contributions. Such an assumption is clearly incorrect for UO_2, but we shall nevertheless examine whether any qualitative comments can be made for UO_2.

Their work shows that such a lattice becomes unstable near its critical point and undergoes a first-order transition. They were able to derive the Ising contributions to the constant area temperature dependence of the elastic constants. Lastly, they applied their theory, in a three-dimensional form, to their data near the phase transition of NH_4Cl, which undergoes a quasiferromagnetic transformation in which neighboring NH_4^+ ions align parallel. They have also studied the analogous transition for NH_4Br, which is quasiantiferromagnetic, but have stated that their theory does not apply there.

Garland's theoretical treatment was carried out for a simple two-dimensional cubic lattice, which is solvable, in contrast to the three-dimensional fcc lattice for UO_2.

Their chief results obtained by carrying the two-dimensional solution over to three dimensions by analogy are as follows:

$$\tfrac{1}{2}(c_{11}-c_{12})=\tfrac{1}{2}(c_{11}{}^0-c_{12}{}^0)-mG(0,H)-nU_I(0,H)/NJ, \tag{24a}$$

$$c_{44}=c_{44}{}^0-lU_I(0,H)/NJ, \tag{24b}$$

$$c_{11}-\tfrac{4}{3}(c_{11}-c_{12})=\frac{1}{\beta_0{}^T}-\frac{vT}{J^2}\frac{c_I(0,H)}{N}\left(\frac{dJ}{dv}\right)^2$$
$$+\frac{v}{J}\frac{U_I(0,H)}{N}\left(\frac{d^2J}{dv^2}\right). \tag{24c}$$

$H\equiv J/kT$, J is the exchange energy, v is the unit cell volume, $\beta_0{}^T$ is the isothermal bulk compressibility far above the transition, and $c_{11}{}^0$, $c_{12}{}^0$, and $c_{44}{}^0$ are the regular elastic constants excluding Ising interactions. $c_I(0,H)$

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[31] L. Brillouin, *Wave Propagation In Periodic Structures* (Dover Publications, Inc., New York, 1953), p. 39.

[32] C. W. Garland and R. Renard, J. Chem. Phys. **44**, 1120 (1966); R. Renard and C. W. Garland, *ibid.* **44**, 1125 (1966); C. W. Garland and R. Renard, *ibid.* **44**, 1130 (1966); C. W. Garland and C. F. Yarnell, *ibid.* **44**, 3678 (1966); **44**, 1112 (1966).

and $U_I(0, H)$ are the configurational heat capacity per spin and Ising internal energy per spin. $G(0, H)$ is a function of H, and is essentially zero below $H=2.269$, and unity above this value of H. The functions c, U, and G are all functions of H and are evaluated at zero displacement when derivatives of H are involved in the functions. m, n, and l are given by

$$m=(4vJ)^{-1}[(\partial J/\partial\epsilon_{||})_0-(\partial J/\partial\epsilon_{\perp})_0]^2, \qquad (24\text{d})$$

$$n=-\frac{1}{4v}\left[\left(\frac{\partial^2 J}{\partial\epsilon_{||}{}^2}\right)_0-2\left(\frac{\partial^2 J}{\partial\epsilon_{||}\partial\epsilon_{\perp}}\right)_0+\left(\frac{\partial^2 J}{\partial\epsilon_{\perp}{}^2}\right)_0\right.$$
$$\left.+\left(\frac{\partial J}{\partial\epsilon_{||}}\right)_0+\left(\frac{\partial J}{\partial\epsilon_{\perp}}\right)_0\right], \qquad (24\text{e})$$

$$l=\frac{1}{v}\left[\left(\frac{\partial^2 J}{\partial\theta^2}\right)_0+\frac{1}{2}\left\{\left(\frac{\partial J}{\partial\epsilon_{||}}\right)_0+\left(\frac{\partial J}{\partial\epsilon_{\perp}}\right)_0\right\}\right]. \qquad (24\text{f})$$

In these equations, derivatives denoted by $\epsilon_{||}$ are taken with respect to elongations parallel to a line joining the ions between which one is calculating the exchange energy, while $\epsilon_{\perp}$ denotes derivatives with respect to elongations perpendicular to this line. θ is the angle between axes of the unit cell when a shear strain is imposed.

Under the assumptions of the Garland theory, the principal behavior of the elastic constants ought to be as follows: $c_{11}-c_{12}$ is governed by the Ising internal energy and by the "separation dependence" of the exchange integral, that is, by the way the exchange energy varies with separation of the ions parallel or perpendicular to the line joining them. c_{11} alone is governed by the Ising specific heat, the square of the exchange energy, and the volume dependence of the exchange energy. c_{44} is governed by the Ising internal energy and the "angular dependence" of the exchange energy, that is, by the way the exchange energy varies with the angle between axes of the unit cell. In UO_2 this angular dependence could also be the U–O–U angle.

Garland and Jones[33] have reviewed the possible temperature and frequency dependences one might expect for the ultrasonic attenuation near a critical point, due to dynamic relaxation effects. Their basic result is

$$A=[(c^{\infty}-c^0)/2v_sc][\omega^2\tau_{sv}/(1+\omega^2\tau_{sv}{}^2)]. \qquad (25)$$

In this equation c^{∞} is the infinite-frequency elastic constant, c^0 is the zero-frequency elastic constant, c is the measured elastic constant, and v_s is the sound velocity. The proper subscripts must be added to specify which particular elastic constant is causing the attenuation. τ_{sv} is a relaxation time appropriate to sound waves, that is, the adiabatic rather than the constant temperature and volume relaxation time τ_{TV}. The two relaxation times are related by

$$(\tau_{sv})^{-1}=(\tau_{TV})^{-1}+(fT/c_v{}^{\infty})(\partial S/\partial\xi)^2{}_{T,V}, \qquad (26)$$

where f is a rate constant, $c_v{}^{\infty}$ is the infinite-frequency specific heat, S is the entropy, and ξ is an internal variable which characterizes the system at given temperature and volume.

The significant physics here is to try and decide what is an appropriate relaxation time. The Landau-Khalatnikov theory[34] predicts a relaxation time, associated with the long-range order parameter η, of the form

$$\begin{aligned}\tau&\propto 1/(T_N-T), &&\text{for } T<T_N\\ \tau&=\infty &&\text{for } T>T_N.\end{aligned} \qquad (27)$$

The result was augmented by Yakovlev and Velichkina,[35] who considered relaxation through the long-range order parameter η below T_N, but also considered relaxation above T_N due to fluctuations of η about its zero value. They obtained

$$\begin{aligned}\tau^+&=A_N{}^+/(T-T_N),\\ \tau^-&=A_N{}^-/(T-T_N),\end{aligned} \qquad (28)$$

for the relaxation times above and below T_N, respectively. A^+ and A^- are constants which depend on the material, but $A^+/A^-=2$. Tanaka, Meijer, and Berry[36] introduced a second relaxation due to the short-range order parameter, which they assumed was a slowly varying function of temperature. They then obtained Eq. (28) for the relaxation due to the long-range order, after assuming the long- and short-range order relaxations are uncoupled.

Garland and Jones[33] have also reviewed some more complicated models which involve both long- and short-range order relaxations. One expects in general that the short-range order parameter relaxation time τ_1 will converge to the same definite value as T_N is approached from either side. τ_2, due to long-range order, should tend to infinity as T approaches T_N from either side. If, however, the transition is first order then τ_2 should have a discontinuous change between two finite values at T_N. They analyzed their attenuation data for NH_4Cl using

$$\tau_{sv}{}^{-1}=(|T-T_N|)/A+B, \qquad (29)$$

where A has different values above and below T_N, and B is a constant which includes the second term in Eq. (26). Garland and Yarnell[32] used a more complicated, but basically similar, argument for a reanalysis of the NH_4Cl data.

Thus, for cooperative effects due to the magnetic exchange interaction one expects changes in the elastic constants and attenuation. The elastic-constant changes might allow one to deduce information about the directional and volume dependence of the exchange energy. Fluctuations in both order parameters should

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[33] C. W. Garland and J. S. Jones, J. Chem. Phys. **42**, 4194 (1965).

[34] L. D. Landau and L. M. Khalatnikov, Dokl. Akad. Nauk SSSR **96**, 469 (1954).

[35] I. A. Yakovlev and T. S. Velichkina, Usp. Fiz. Nauk **63**, 411 (1957) [English transl.: Soviet Phys.—Usp. **63**, 522 (1957)].

[36] T. Tanaka, P. H. E. Meijer, and J. H. Barry, J. Chem. Phys. **37**, 1937 (1962).

lead to attenuation. One has a feeling for the attenuation due to long-range order fluctuations. However, the short-range order picture is not so clear.

IV. ANALYSIS OF DATA AND DISCUSSION

Let us restate our fundamental assumption, namely that the ground state of U^{4+} in UO_2 is a triplet, or Γ_5 state. The singlet state is high enough in energy above the triplet so that it has no influence below room temperature. With this assumption a more or less consistent interpretation of our data can be reached. However, if we assume that the singlet is the ground state, then we are unable to fit all the experimental facts together. Whether such inability is due to lack of imagination or to essential physics is a matter for other experiments to decide.

A. 1/T Behavior of Elastic Constants

The most straightforward step is an analysis of c_{44} in terms of the strain-ion interaction. Under this assumption the empirical curve, Eq. (1), which fits the c_{44} data above 70°K, is directly relatable to Eqs. (20) and (11), which were derived under the assumption of such an interaction. If Eq. (11) is substituted into Eq. (20) we obtain

$$c_{44}^{\text{eff}}=c_{44}^{0}-(2N_0/kT)[\langle\alpha^2\rangle/(1+\omega^2\tau^2)]. \qquad (30)$$

Equation (30) is directly comparable to Eq. (1), leading to the following identification:

$$\frac{2N_0}{kT}\frac{\langle\alpha^2\rangle}{1+\omega^2\tau^2}=\frac{7.3\times10^{12}}{T}\frac{\text{dyn deg}}{\text{cm}^2}.$$

As is shown below, τ is low enough so that at the frequencies used (~20–90 MHz) $\omega\tau\ll1$ always. Thus, we obtain

$$N_0\langle\alpha^2\rangle=\tfrac{1}{2}(7.3\times10^{12}k)\,(\text{dyn deg/cm}^2).$$

Since N_0 can be computed from Avagadro's number and the density known to be 2.45×10^{22} U^{4+} ions per cm^3, we have

$$\langle\alpha^2\rangle=2.05\times10^{-26}\ \text{erg}^2. \qquad (31)$$

In turn, the rms value for α is 722 cm^{-1} per unit strain. The uncertainty in α is about 5%, due to the uncertainty in slope in Eq. (1). This value can be compared with the value of 21 200 cm^{-1} for Ni^{3+} in Al_2O_3 deduced by Sturge *et al.*,[28] where we have reexpressed their value for α in terms of our rms definition for α. Sturge *et al.* attributed the strain-ion coupling explicitly to a Jahn-Teller interaction. These two values are quite different, but it must be remembered that Ni^{3+} is a *d* ion while U^{4+} is an *f* ion. Presumably, the *f* electrons are much more shielded by outer electrons than are *d* electrons. It is interesting, however, that even though the α value for U^{4+} is only 1/30 that for Ni^{3+}, the elastic constant for UO_2, c_{44}, is observed to change about 20% while the corresponding elastic-constant change for Ni^{3+} in Al_2O_3 was only about 0.002%. The reason for this apparent contradiction is obvious: $33\frac{1}{3}\%$ of the ions in UO_2 are U^{4+}, while Sturge *et al.* used a concentration of 0.004% Ni^{3+}.

In the above analysis it was assumed that $\omega\tau\ll1$ at all temperatures. It was not necessary to do this as the same value for α would still have been obtained. Indeed, one might consider using Eq. (31b) in the following way: As seen in Fig. 3, the measured c_{44} falls above the T^{-1} curve for temperatures below approximately 70°K. One might argue that the difference between the measured curve and the T^{-1} curve is simply due to the influence of τ. The ions would begin experiencing difficulty in following the ultrasonic wave, and thus the elastic constant would stop decreasing as rapidly. One could thus deduce τ by fitting Eq. (31b) to the measured c_{44} data. This approach has one serious difficulty which we can illustrate by an example. At 40°K, the difference between the measured c_{44} curve and the T^{-1} curve is 0.027×10^{12} dyn cm^{-2}. One thus deduces that $\tau=7.6\times10^{-9}$ sec at 40°K, at an ultrasonic frequency of 50 MHz. With this (assumed) known value of τ one can in turn use Eq. (19) to calculate the attenuation expected at 40°K. The calculated attenuation is 4×10^6 dB/cm, and is to be compared with the measured value of 15 dB/cm. Clearly, the c_{44} departure from T^{-1} dependence and the attenuation associated with c_{44} cannot both be due to the same mechanism. Since attenuation even approximately as large as the predicted value has not been observed we must conclude at once that the departure of c_{44} from T^{-1} behavior is not due to the difficulty the ions experience in following the oscillating strain. Another mechanism must be found for this particular behavior. The above arguments are invalid with a singlet ground state since all temperature dependences would be much more complicated.

B. Applied Stress

Our method of applying a uniaxial stress was intended to produce a shear strain, although it was recognized at the outset that at best only a component of such a strain would be obtained. However, assuming that the stress of 175 kg/cm^2 did in fact cause a shear strain governed only by c_{44}, we would expect the strain to be $\epsilon\sim3\times10^{-3}$, and using the value of $\alpha_{\text{rms}}=722$ cm^{-1} per unit strain we find that the splitting of the energy levels would be ~2 cm^{-1}, or ~3°K. This is not an insignificant amount. However, for a strain to affect the elastic constant, the strain splitting must be of the order of kT, which is clearly not true at 35°K.

C. Ultrasonic Attenuation Associated with c_{44}

We now examine what can be deduced from the attenuation associated with c_{44} in terms of the temperature dependence of a relaxation time. It is interesting that Sturge *et al.*[28] were faced with a dilemma similar to ours; their elastic-constant changes were not commensurate with their attenuation values. They handled the problem by assuming that most of the Ni^{3+} ions, all of which contributed to the elastic constant, did not contribute to the loss. They cited independent evidence for the possibility that Ni^{3+} existed in Al_2O_3 in more than one type. We cannot make a similar assumption since we have no reason to suspect that any one U^{4+} ion differs from any other. Under the assumption that the attenuation is given by a strain-ion loss we can deduce from the data the temperature dependence of a relaxation time. There must be an elastic-constant change associated with this attenuation if one believes in the Kramers-Kronig relations. However, given the values of τ deduced below, one can compute the associated Δc_{44}. The result is far smaller than the measured difference between c_{44} and the T^{-1} curve, and thus is buried in the experimental difference. Presumably, if the extra elastic-constant-change mechanism postulated in Sec. IV A did not exist, then one could observe the strain-ion change in c_{44}. We recognize that our postulate of one mechanism giving departure from the strain-ion elastic-constant curve, and the barrier hopping giving the loss, cannot be proved. All we can do is render it plausible.

The c_{44} attenuation data, shown in Fig. 5, have been analyzed in terms of Eq. (19). There is one subtle point involved in this equation. The elastic constants are given in the equation specifically. $c_{44}{}^{S-I}$ is known at any temperature simply by plugging the known $\langle\alpha^2\rangle$ into Eq. (11). $c_{44}{}^0-c_{44}{}^{S-I}$ can in turn be computed from Eq. (20), using $\omega^2\tau^2\ll1$. However, there is some question as to what one should use for v_s. One might adopt the point of view that since Eq. (19) gives the attenuation due to the strain-ion mechanism, one should use $[(c_{44}{}^0-c_{44}{}^{S-I})/\rho]^{1/2}$ for v_s. However, the relation between attenuation and quality factor, which introduces v_s, implicitly contains the assumption that one should use the measured sound velocity. We shall follow this idea and use $[c_{44}{}^{\text{meas}}/\rho]^{1/2}$ for v_s. If our approach is wrong, the changes in our deduced values for τ are easy to make; no changes in temperature dependence are involved. Ordinarily, of course, this is not a point of practical importance since the elastic constants do not usually vary as markedly as here.

Within this framework, the attenuation appropriate to c_{44} was analyzed by use of Eq. (19) at 50 MHz over the temperature range 35–60°K. As seen in Fig. 5, below 35°K the attenuation is out of sight, and above 60°K the attenuation is essentially down to background. The temperature dependence of the values of τ which were deduced is demonstrated in Fig. 7, in which $\log_{10}\tau$ is plotted versus T^{-1}. As can be seen, the values for τ are represented quite well by a straight line on such a plot, and τ is of the order of 10^{-11} sec. The line in Fig. 7 can be represented by

$$\tau^{-1}=4.2\times10^{11}\exp(-70.5/T). \tag{32}$$

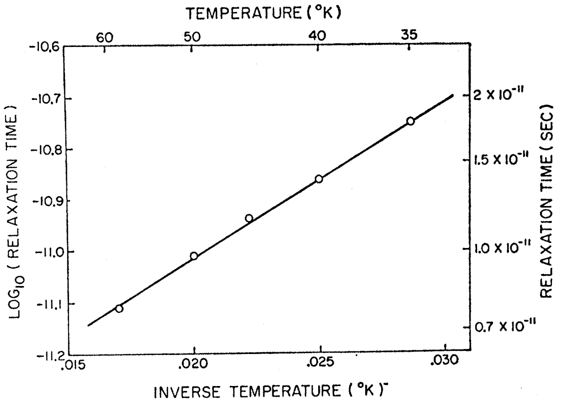

FIG. 7. Log_{10} of relaxation time deduced from Fig. 5 versus inverse temperature. Procedure is described in text.

Equation (32) is of the same form as Eq. (21) and might lead one to identify the deduced relaxation times as being due to hopping over a barrier. If the attenuation is indeed due to a Jahn-Teller mechanism, then such an exponential behavior is what one expects in a high-temperature limit. If we make the formal identification between Eqs. (21) and (32), we obtain for the barrier height V_0/k a value of 70.5°K. Similarly, the attempt frequency ν_0 has the value 2.1×10^{11} sec^{-1}. These values might be compared to those of Sturge *et al.*[28] for Ni^{3+} in Al_2O_3. Their values were $V_0/k=127$°K and $\nu_0=10^{13}$ sec^{-1}. Our value for the barrier height is not unreasonable, but our value for the attempt frequency seems quite low. One would expect the attempt frequency to be of the order of lattice vibrational frequencies in this temperature range, i.e., of the order of 10^{12} sec^{-1}. Our low value for the attempt frequency is one objection we have to the identification of the attenuation for c_{44} as being due to a Jahn-Teller mechanism.

Thus, we are in the following position: The T^{-1} behavior for c_{44} could be explainable without close inspection on the basis of a quasistatic Jahn-Teller interaction. The departure of c_{44} from T^{-1} behavior near T_n does not seem explainable on the basis of relaxation effects associated with the Jahn-Teller interaction. The attenuation appropriate for c_{44} does indeed seem to have the proper analytic behavior for Jahn-Teller relaxation with reasonable relaxation times and a correct barrier height but a low attempt frequency. However, as shown by Ham,[26] one can relate the lowering in energy produced by a Jahn-Teller interaction to the coupling parameter which measures the way the minima in the surface move with strain. The exact numerical factors are, of course, a bit uncertain. However, if one uses Ham's relation [just above his Eq. (3.5)], and uses as a vibrational frequency of the Jahn-Teller complex of U^{4+} and eight oxygens our low value for the attempt frequency above, one obtains a Jahn-Teller energy of about 90 cm^{-1}, or about 130°K. This number is uncertain because the exact numerical factor is not known for the triplet in eightfold cubic coordination. But we have used a frequency which is probably on the low side, giving us an overestimate of the Jahn-Teller energy. If the Jahn-Teller energy for U^{4+} in UO_2, deduced from our value of α, is really the order of 130°K, then in the temperature range of interest to us (70–220°K) it is clearly not possible to have a quasistatic Jahn-Teller effect. The system could never settle down in any of the minima.

Thus, the Jahn-Teller effect is an interesting possibility as an explanation for the strain-ion coupling in UO_2, above T_n, but there is a bit of peril in invoking it. However, one must still explain the exponential temperature dependence of the relaxation time. If it is not barrier-hopping, then what is it? The crystal-field calculations[8] state that the next electronic state is as least 2000°K above the ground state, so an Orbach process cannot be invoked to explain the observed exponential factor of 70.5°K.

D. Cooperative Effects

If the difference between c_{44}^{meas} and the T^{-1} curve is not due to strain-ion relaxation effects, and if the attenuation for c_{44} is also not due to such relaxation, then how much ground might one hope to make by considering cooperative behavior? We do not consider cooperative strain-ion interactions simply because we can find no unambiguous way to handle them. The obvious possible inclusion is cooperative effects due to magnetic exchange, since both elastic-constant and attenuation difficulties only arise as T_N is approached.

The first step would be to reexamine c_{44} after subtracting c_{44}^{S-I} out of the measured data. This procedure would presumably give the contribution to the elastic constant due to ordinary elastic behavior plus magnetic exchange. Examination of Figs. 2 and 3 shows that the effect of removing the strain-ion contribution to c_{44} is to give an elastic constant which varies with temperature hardly at all above 70°K. Then the elastic constant begins to rise and jumps up as one passes through T_N. Thus, c_{44} with c^{S-I} taken out, and Fig. 1 can be compared to the data for the elastic constants of NH_4Cl, mentioned earlier, which also has a volume contraction at its transition. Our c_{11} and reprocessed c_{44} qualitatively resemble the NH_4Cl data, while $c_{11}-c_{12}$ does not.

One would like to compare in detail our elastic-constant data with Eqs. (24a)–(24f) in an attempt to extract some microscopic information. However, it is dangerous to push such comparisons too far as these equations were derived by Garland and co-workers for a two-dimensional square Ising lattice with weak coupling between lattice and spins. UO_2 has the fluorite structure with strong coupling between lattice and spins, and strong strain-ion interactions as well. We shall confine ourselves to qualitative comments.

Examination of Fig. 1 shows that near T_N, c_{11} resembles qualitatively the λ-like specific-heat curve, only inverted. Surprisingly, so also does $c_{11}-c_{12}$. Equations (24a) and (24c)–(24e) suggest the following comments: c_{11} is governed near T_N chiefly by the specific heat. This would suggest that the volume dependence of the exchange energy is small compared with the specific-heat term. This suggestion is not unreasonable since the volume contraction for UO_2 at T_N is so small. $c_{11}-c_{12}$ is rather puzzling. This particular elastic constant should not depend on the specific heat, but the Ising internal energy should not show a λ-like behavior. It does not seem likely that the directional derivatives of the exchange energy, given by Eq. (24e), will change sign at T_N. This elastic constant does not seem to fit in with the Ising-model calculations. c_{44}, however, does. Equation (24b) should be governed by c_{44}^0 as one goes away from T_N in the paramagnetic region. The Ising energy U_I should start out small and increase with decreasing temperature. Since the Ising energy eventually becomes constant far below T_N, one expects c_{44} to level off, as indeed it does in Fig. 2. The very rapid change in c_{44} as one passes through T_N, which persists even after subtraction of c^{S-I}, should probably not be attributed to the volume dependence of the exchange energy, since we assumed this quantity to be negligible in analyzing c_{11}. Rather, it seems more likely that the quantity l, given by Eq. (24f), supplies the rapid change through T_N. In order to be consistent with c_{11}, one must identify the dominant contributor as being the angular dependence of the exchange energy. This seems especially appropriate for UO_2 because one expects marked superexchange through the U–O–U bonds, and this feature should exist as an effective exchange which is dependent on bond angle. Actually, of course, any elastic wave will cause fluctuations in the U–O–U bond angle. But if the exchange energy is linear in this angle, then only c_{44} will be strongly sensitive to this angle through the term $\partial^2 J/\partial\theta^2$.

The preceding analysis of exchange contribution to the elastic constants is certainly speculative. It is particularly speculative when one considers that the exchange contribution may in reality include cooperative strain-ion interactions as well. One can make similar comments about the attenuation. As seen in Fig. 4, the attenuation associated with c_{11} and $c_{11}-c_{12}$ is small. The attenuation falls off quite rapidly as one leaves T_N toward higher temperatures, and less rapidly as one moves to lower temperatures. Qualitatively, this behavior is consistent with the Landau-Khalatnikov theory described by Eq. (27), with the proviso that infinities are not observed near T_N. Thus, Fig. 4 could be taken to be a measure of long-range order fluctuations in UO_2 as one approaches T_N from below. By use of Eq. (25) and the c_{11} and $c_{11}-c_{12}$ elastic-constant data, one can estimate a relaxation time of about 5×10^{-10} sec for long-range order fluctuations. There would then be no such fluctuations above T_N (agreeing with neutron scattering data[4]).

The attenuation appropriate for c_{44} cannot be related to the Ising-model calculations. First, the attenuation is too large near T_N by a factor of at least 5. Secondly, the measured attenuation does not have a temperature dependence anything like Eqs. (27)-(29). The measured attenuation is probably a sum of both the strain-ion relaxation and magnetic exchange relaxation. If one subtracts a few (3 or 4) dB/cm from the measured attenuation at 35°K, and progressively less as one goes to higher temperatures, one would get a curve which is probably closer to the truth for strain-ion interactions in UO_2. The few dB subtracted away would be attributed to the magnetic exchange interaction. The effect of such a subtraction would be to reduce τ a bit near T_N, but not at all when one is far from T_N. The slope of the line in Fig. 7 would be reduced and one would obtain a value for V_0/k which is smaller than our value of 70.5°K. A slight reduction would also occur in the attempt frequency.

There is one final observation of interest. It is possible to fit the elastic-constant data for c_{44} above approximately 95°K with the following relation:

$$c_{44}^{\text{meas}} = 0.660\times10^{12}\ (\text{dyn/cm}^2) - (0.515\times10^{13}\ \text{dyn cm deg})/(T-24.1^\circ\text{K}). \quad (33)$$

The data below 95°K lie above the curve. When only a T^{-1} curve was used the data fell above the curve for temperatures below 65 or 70°K. Equation (33) is suggestive of a naive way to account for cooperative strain-ion interactions in UO_2. Just as the bulk susceptibility for a ferromagnet is describable by a $1/(T-T_c)$ law in the paramagnetic state, so, too, could one understand Eq. (33) as being a crude way of accounting for ferromagnetic cooperative strain-ion interactions above some "transition temperature." Equation (33) suggests that if the c_{44} data never departed from the Curie-Weiss–like behavior, c_{44} would become zero at 31.91°K. This temperature is above the Néel temperature for UO_2 and suggests that Eq. (33) may not be unreal. In Allen's theory[15] the ordered state for UO_2 comes about from competition between magnetic exchange and cooperative Jahn-Teller interactions. The exchange in a sense wins because the ordered state is an antiferromagnet. Also, in this simple picture the magnetic exchange interaction, as seen by the departure of c_{44} from Eq. (33) below 100°K, would appear to persist almost to 100°K. This feature would also be in agreement with the discrepancy between the specific heat calculated from neutron scattering data and the measured specific heat. The neutron curve lies below the measured curve up to about 100°K, suggesting the presence of considerable entropy well above T_N.[37]

V. SUMMARY

(1) The elastic constants, c_{11}, $c_{11}-c_{12}$, and c_{44} have been measured between room temperature and liquid-helium temperature for UO_2. Anomalies are found in all three cases, but particularly for c_{44}.

(2) The ultrasonic attenuation at 50 MHz has also been measured for waves appropriate to all three elastic constants. The attenuation for c_{11} and $c_{11}-c_{12}$ is small and confined to the immediate vicinity of T_N, while the attenuation for c_{44} is spread over a broad temperature range.

(3) A coupling between strains and the triplet ground state of the U^{4+} ion is invoked as a mechanism for explaining the gross behavior of c_{44} and its attenuation. Strain-ion splitting energies of 722 cm^{-1} per unit strain are deduced from the data. The attenuation is seen to be explained by a relaxation time which varies exponentially with temperature, with an exponential factor of 70.5°K.

(4) The elastic behavior of c_{11}, $c_{11}-c_{12}$, and part of c_{44} is attributed to magnetic exchange interactions. Only qualitative comments can be made in comparing our data to the Ising-model theory of Garland and coworkers. However, it is possible that c_{44} displays the angular dependence of the exchange energy.

Note added in manuscript. After most of this paper had been prepared we became aware of the magnetic susceptibility measurements on ThO_2 doped with U^{4+} presented by Comly.[38] His work also seems to require the presence of a triplet ground state. The idea of expressing c_{44}^{meas} in the form of Eq. (33) grew out of conversations with Dr. Comly.

ACKNOWLEDGMENTS

Our largest debt of gratitude is to Dr. H. J. Anderson of Batelle Northwest, who supplied us with many excellent and large single crystals of UO_2. We also profited from discussions with Dr. S. J. Allen, Jr., Dr. J. Comly, Dr. G. Dolling, Dr. F. S. Ham, and Dr. D. S. Rodbell. The authors are indebted to Dr. J. Marcus for the generous loan of his equipment.

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