THE
REVIEW OF SCIENTIFIC
INSTRUMENTS

VOLUME 41, NUMBER 5 MAY 1970

Magnetic Susceptibility Measurements with a Tunnel Diode Oscillator*

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(Received 14 November 1969; and in final form, 12 January 1970)

A tunnel diode oscillator is described which has been successfully used for paramagnetic susceptibility measurements at frequencies from 3 to 55 MHz, at temperatures from 1.2 to 77 K, and at magnetic fields up to 18 kG. In appropriate cases, such measurements may be used to infer magnetic specific heats and spin–lattice relaxation times.

INTRODUCTION

MOST magnetic susceptibility experiments at kilohertz and megahertz frequencies have used marginal vacuum tube oscillators with self-resonant parallel LC tank circuits, for which a good approximation to the frequency is

$$\omega \approx 1/(LC)^{\frac{1}{2}}. \tag{1}$$

When a magnetic sample is inserted into the oscillator tank coil, there is a small increase in coil inductance ΔL, which is proportional to the real part χ' of the complex magnetic susceptibility

$$\chi = \chi' - i\chi''. \tag{2}$$

If $\Delta L/L \ll 1$, then from Eq. (1)

$$\Delta\omega_m/\omega \approx -\Delta L/2L = -2\pi F\chi', \tag{3}$$

where $\Delta\omega_m$ is the change in frequency and F is the filling factor of the magnetic sample in the tank coil. Thus, $\chi'(\omega,H,T)$ of a magnetic compound may be found from measurements of $\Delta\omega_m$ for a suitable range of values of ω, H, and T. A review of techniques used for such susceptibility experiments has been given by Gorter.[1]

For susceptibility experiments at liquid helium temperatures, the oscillator tank coil is generally cooled together with the sample and it is connected to the rest of the oscillator at room temperature by a coaxial or parallel wire transmission line, which is usually 60–100 cm long. The transmission line is an integral part of the tank circuit and the inductance L_t of the transmission line adds directly to the coil inductance L. For this case, Eq. (1) becomes

$$\omega = 1/[(L+L_t)C]^{\frac{1}{2}}, \tag{4}$$

and Eq. (3) becomes

$$\Delta\omega_m/\omega \approx -2\pi F\chi'\Delta L/(L+L_t). \tag{5}$$

Typically, L_t is about 2 μH and the highest frequency which can be obtained is about 15–20 MHz. Also, to get frequencies over 10 MHz, the coil inductance L must be smaller than about 2 μH and, for this case, $\Delta\omega_m$ is less than one-half the value which would occur if the transmission line inductance L_t was zero.

The above limitations on ω and $\Delta\omega_m$ caused by the transmission line inductance are eliminated by using the tunnel diode oscillator described in the next section with which susceptibility experiments at frequencies up to at least 60 MHz are possible. Moreover, the values of χ' are more accurate than those found with a vacuum tube oscillator in comparable experiments, not only because the frequency shifts $\Delta\omega_m$ are larger but also because the tunnel diode oscillator is inherently more stable. Our version of the tunnel diode oscillator has only five high frequency circuit elements and yet stable oscillation can be achieved for a wide range of the oscillator circuit parameters from liquid helium temperatures to above room temperature and in magnetic fields up to at least 18 kG. Also, the high frequency portion of the oscillator will fit into a volume of less than 5 cc and only an additional dc power supply is required at room temperature. As in any susceptibility measurement involving a self-inductance, this method measures only one component of an anisotropic susceptibility tensor at a time, but it is in principle possible to

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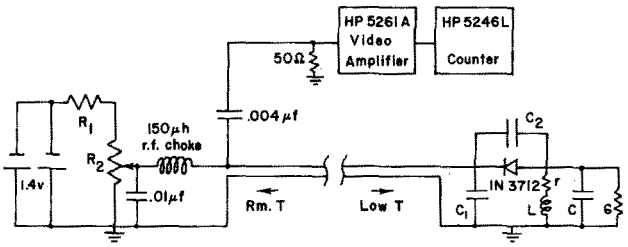

FIG. 1. The forward tunnel diode oscillator (TDO) used for susceptibility experiments.

rotate the sample inside the coil to determine other components. A possible alternative scheme using an oscillator with its tank coil outside the tail of the cryostat was rejected because of the greater inconvenience of using such a system in conjunction with large magnetic fields.

I. TUNNEL DIODE OSCILLATOR

Recently, oscillators using back tunnel diodes have been used for liquid helium experiments[2] below 1 K, principally because power dissipation into the helium bath is small. Back diodes, however, have a small negative conductance ($10^{-5}-10^{-4}$ mho) and stable oscillation is achieved with a back diode oscillator only if a high Q oscillator circuit is used. In practice, stable oscillation is not achieved above liquid nitrogen temperatures.

For magnetic susceptibility experiments above 1 K the power dissipation of the oscillator into the cryogenic liquid is not a serious limitation, and in order to obtain a large frequency and temperature range of operation we have built a new tunnel diode oscillator using a forward tunnel diode. An alternative approach would be to use a field effect transistor,[3] but so far this possibility does not seem to have been explored for our type of application.

The forward tunnel diode oscillator, henceforth referred to as the TDO, is shown in Fig. 1 and is similar to previous designs.[2,4] A germanium IN3712 diode is used, which at 300 K has the V–I characteristic shown in Fig. 2. The maximum negative conductance g_d of the diode is about -0.02 mho, which is over a factor of 100 larger than for the previously used back diodes.[2] The diode capacitance C_d is about 10 pF. C_1, C_2, and C in Fig. 1 are Aerovox silver mica capacitors, and the batteries used for biasing are Duracell 1.4 V mercury cells. For the tank coil with inductance L, both hand wound copper wire coils on Lucite forms and LRC Electronics metal-deposited-on-glass standard inductors have been used successfully. The Q of the parallel LC tank circuit is typically 100–150, for which the parallel conductance G of the tank circuit is about 10^{-4} mho and the series resistance r is about 1 Ω.

Experimentally the TDO oscillates stably over the entire temperature range from 1 to 300 K. To initiate oscillation, the dc biasing circuit is tuned until the dc load line no longer intersects the low voltage positive resistance region of the diode, as shown in Fig. 2. Then the bias voltage V_b jumps to the negative resistance region of the diode and self-sustaining nearly sinusoidal oscillations begin.

The steady state condition for oscillation is that the average value per cycle of the power supplied by the diode must be equal to the power dissipated in the rest of the circuit. To achieve this condition, the average value per cycle of the diode negative conductance g_d must be equal to the parallel conductance of the tank circuit G. With our relatively high Q tank circuit G was much smaller (of the order of 100 times) than the maximum value of g_d, and large nonlinear voltage oscillations were therefore required to reduce the average value of g_d. In practice, the steady state ac voltage across the tank circuit, which is approximately equal and opposite to the voltage across the diode, was as large as 400 mV peak to peak at 300 K and 600 mV at 4.2 K, with voltage swings extending into the positive resistance region for part of each cycle.[5] Under these conditions the diode must clearly be treated as a nonlinear circuit element in any detailed analysis of the oscillation characteristics of the TDO. On the other hand, the nonlinear response is only of minor importance in our particular application, since a frequency counter measures only the fundamental frequency, and the change in this will still be proportional to ΔL as in Eq. (3), if $\Delta L/L$ is small.

The values of various circuit elements of the TDO are not critical for initiating and maintaining stable oscillation. Instead, the magnitude of the ac voltage at steady state simply varies as the circuit parameters are varied in order to maintain the condition $\bar{g}_d \sim -G$. The circuit oscillates stably for wide ranges of C_1, C_2, L, C, R_1, and R_2. Typical values are $C_1=500$–1500 pF, $C_2=5$–30 pF, $L=0.3$–3 μH, $C=20$–500 pF, $R_1=200$–800 Ω, and $R_2=500$–3000 Ω. The tank capacitance C and tank inductance L have been varied independently to give frequencies from 1.5 to 60 MHz. A wider frequency range is probably possible, but the extension to lower frequencies is more readily achieved by reverting to back diodes with which stable oscillations down to 400 kHz have already been obtained.[6]

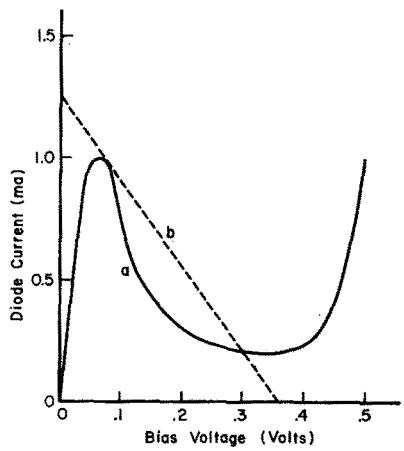

FIG. 2. (a) V–I characteristic of the IN3712 tunnel diode, (b) typical dc load line at the initiation of stable oscillation of the TDO.

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Once the TDO begins oscillating, the bias voltage V_b may be varied over most of the negative conductance range of the diode and, despite the nonlinear behavior of the TDO, we find empirically[7] that a good approximation to the oscillator frequency is the simple tank circuit frequency

$$\omega=(L\{C+C_1(C_2+C_d)/[C_1+C_2+C_d]\})^{-\frac{1}{2}}. \qquad (6)$$

An interesting characteristic of the TDO is that the frequency ω goes through a maximum as a function of bias voltage, examples of which are shown in Fig. 3. The dependence of the frequency on bias voltage becomes less severe as C or C_2 is increased, which indicates from Eq. (6) that the above effect may be caused by a variation of the diode capacitance C_d as the bias voltage is varied.

Susceptibility experiments were carried out for a range of bias voltages within ± 50 mV of the value at which the frequency peaks and it was found that the average susceptibility results were independent of bias voltage, within experimental error. However, operating the TDO closer to the frequency peak minimizes frequency fluctuations that occur during the measurements, and for this condition the accuracy of susceptibility estimates is maximized. Moreover, for this condition the frequency of the oscillator is least sensitive to losses introduced by any out of phase component χ'' of the susceptibility, so that the method can be used to measure χ' even when relaxation effects are significant.

To relate the measured frequency shifts to χ' we find empirically that Eq. (3), which is consistent with Eq. (6), is a good approximation since $\Delta L/L$ is always very much less than 1. The absolute accuracy of the susceptibility measurements is generally no better than about $\pm 5\%$ but the relative accuracy is much better ($\sim\pm 1\%$), as will be discussed in the next section where we consider details of the method and some of the important corrections.

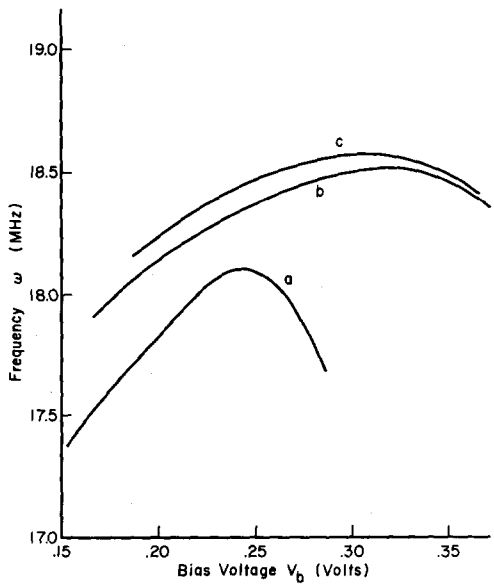

FIG. 3. Typical bias voltage dependence of the TDO oscillation frequency for (a) 300 K, (b) 77 K, and (c) 4.2 K.

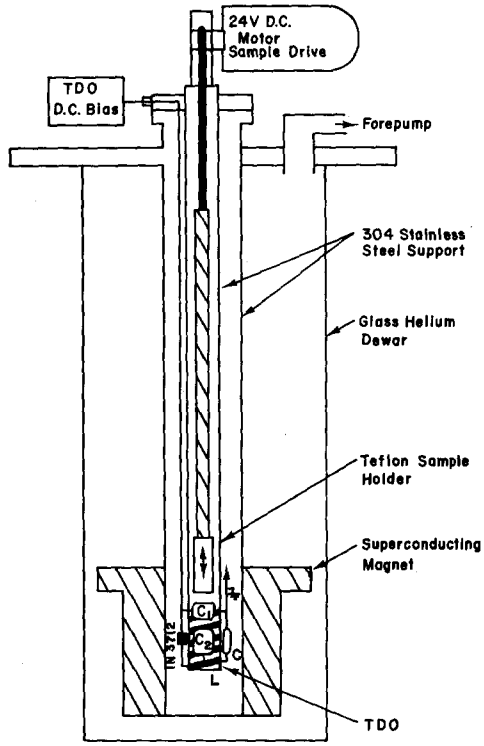

FIG. 4. The magnetic susceptibility apparatus with the TDO in the helium Dewar. The bore of our superconducting magnet was 3.2 cm.

II. SUSCEPTIBILITY EXPERIMENTS

The TDO described above has been used to measure the real part of the differential paramagnetic susceptibility $\chi'(\omega,H,T)$ of single crystals of $CeCl_3$,[8] $CeBr_3$[9] $GdCl_3$,[10] and cerium ethyl sulfate,[11] which are all low dielectric loss insulators. In each case the longitudinal component χ'_{zz} of the general susceptibility tensor was isolated by virtue of arranging the ac magnetic field parallel to the axis of quantization of the magnetic compound, which was also parallel to the externally applied dc magnetic field. From such measurements one may estimate magnetic specific heats C_M[12,13] and spin–lattice relaxation times τ_{sl}.[14,15] Relaxation times are found from the frequency dependence of χ' and specific heats are found from the field dependence of χ'.[1,12] For such applications, suitably wide ranges of frequency and applied magnetic fields are clearly required.

Our susceptibility apparatus is shown schematically in Fig. 4. The over-all ranges of the controlled variables used in our experiments were 3 MHz$\leq\omega\leq$55 MHz, 1.2 K $\leq T\leq$77 K, and $0\leq H\leq$18 kG. Although the oscillator is capable of a wider frequency range, the errors in χ' become greater at the frequency extremes and we therefore limited the frequencies used in the present series of experiments.

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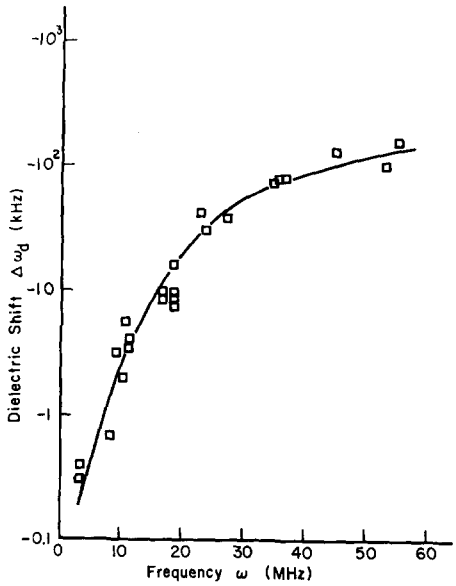

FIG. 5. Frequency dependence of the dielectric frequency shift for the TDO. Scatter in the values of the shift at a given frequency represents the effect of using different oscillator coils and different magnetic samples in the susceptibility experiments.

The dc magnetic field H was produced by a Magnion CF 10-125-500C superconducting magnet which must be cooled with liquid helium. For susceptibility experiments at helium temperatures, the oscillator and magnetic sample were both immersed directly in the helium which could be pumped down to 1.2 K in the usual way. However, for experiments at liquid hydrogen or liquid nitrogen temperatures, the oscillator, sample, and cryogenic liquid must be isolated from the liquid helium cooling the magnet. This was accomplished by using a simple double wall stainless steel Dewar which fits into the magnet.

In our apparatus, the high frequency components of the TDO were connected to the bias circuit by a parallel copper wire transmission line (No. 40 AWG wire) which was about 90 cm long. The capacitor C_1 was chosen to be much larger than C_2 and C_d so that during oscillation only a very small ac voltage was generated across the transmission line. For this case, the transmission line is effectively only a dc connector and is not an integral part of the TDO tank circuit. In particular, the transmission line inductance L_t does then not limit the frequency, as it does for vacuum tube oscillators.

To obtain the susceptibility χ', one must measure the frequency ω_i with the magnetic sample in the oscillator tank coil and the frequency ω_0 with the coil empty. The sample was moved in and out of the coil by the dc motor shown in Fig. 4, and the frequencies were measured with a Hewlett–Packard 5246L digital counter which was accurate to ± 1 cycle out of 50 MHz. The small ac voltage generated across the capacitor C_1 was coupled capacitively to the counter, as shown in Fig. 1.

The measured frequency shifts $\omega_i - \omega_0$ contain not only the magnetic shift $\Delta\omega_m$ given by Eq. (3), but also an additional and frequently comparable dielectric contribution $\Delta\omega_d$ which is caused by changes in stray capacities when the sample is moved in and out of the oscillator coil. Thus, the total frequency shift is

$$\omega_i - \omega_0 = \Delta\omega_m + \Delta\omega_d, \tag{7}$$

and to estimate $\Delta\omega_m$ an accurate estimate of the dielectric correction is required.

The origin of $\Delta\omega_d$ must generally be quite complicated but it is basically due to capacitive shielding effects between oscillator components and the metal parts of the cryostat and magnet support.[1] As the tank capacitance C is reduced to obtain higher frequencies, stray capacities become more important and $\Delta\omega_d$ increases dramatically, as shown in Fig. 5. However, $\Delta\omega_d$ at a given frequency appeared to be independent of the magnetic sample used and in fact $\Delta\omega_d$ was about the same when the sample holder was empty, or when a diamagnetic sample was used.

Fortunately, these effects are also independent of temperature and magnetic field in contrast to the magnetic shifts, and this provides a ready means for estimating the relative contributions in any particular case.

If, as is the case for many magnetic compounds, χ' decreases rapidly when a dc magnetic field is applied, $\Delta\omega_m$ may be made negligible by applying a suitably large field, and $\Delta\omega_d$ can be measured directly.[8,9] For some compounds, the field dependence of χ' is not so pronounced, but its variation is known theoretically so that $\Delta\omega_d$ may be estimated by numerical methods.[10] In principle one can also use the known temperature dependence of χ' in zero field to estimate $\Delta\omega_d$, assuming it to be temperature independent, or one can measure the frequency shift produced by a nonmagnetic dummy sample, but in practice neither of these methods is as accurate as using the field dependence.[10,16]

The accuracy with which one can measure the experimental frequency shift $\omega_i - \omega_0$ depends on several factors. When our TDO came to a steady state there was little short term fluctuation in the measured frequency. Thus at room temperature and at 77 K the TDO frequency was constant to about one part in 10^6 (± 5 cycles out of 10 MHz) over a period of several minutes. However, when the TDO was put directly in liquid helium, the frequency fluctuations were about 10 times larger, of the order of one part in 10^5. This appeared to be caused by helium bubbles in the coil which cause fluctuations in the stray capacity of the coil.[1] This was substantiated by the disappearance of these larger fluctuations when the helium bath was cooled below the λ point.

The dynamic operation of moving the sample in and out of the coil in order to determine the frequency difference $\omega_i - \omega_0$ caused even larger uncertainties in the frequency

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measurements than the quiescent fluctuations discussed above. Upon moving the sample, mechanical and/or thermal transients in the frequency occurred which have a time constant on the order of 1 min. For a vacuum tube oscillator which we used in earlier experiments[8] transients of this type were larger still, especially for liquid helium experiments, but could be substantially reduced by enclosing the oscillator transmission line in a vacuum jacket. This indicates the transients for that particular oscillator were primarily thermal in origin. However, the same procedure for the TDO left the transients unaffected, which is not really surprising since the transmission lines are primarily dc feeds in that case. Thus, the transients in the TDO appear to be caused primarily by mechanical rather than thermal variations. Combining the steady state fluctuations with the dynamic transients gave frequency measurements accurate to no worse than one part in 10^4 (± 500 cycles out of 10 MHz), but no better than two parts in 10^5. Thus, if the magnetic shift $\Delta\omega_m$ is such that $\Delta\omega_m/\omega \geq 10^{-3}$, reasonable estimates of $\Delta\omega_m$ can be obtained using the TDO. In practice, shifts of this size could be obtained from samples of the order of 1 cc in volume having a susceptibility of about 0.001 emu/cc.

One way of improving the accuracy in experiments in which only the field dependence of χ' is of interest (such as in measurements of C_M) is to measure ω_i as a function of the field without moving the sample, determining ω_0 only at the beginning and end of the field sweep and assuming that ω_0 is independent of field. This assumption may readily be checked by a separate field sweep with the sample out of the oscillator coil. This procedure eliminates transient effects but it requires a fairly good temperature control since χ' is generally a strong function of T.

For several experiments, we tried to determine the experimental validity of Eq. (3) by comparing absolute estimates of χ' and the filling factor F with the corresponding values of $\Delta\omega_m/\omega$. In all cases, there were systematic differences of about 5%, in addition to the above experimental errors. However, in experiments to find magnetic specific heats and relaxation times one needs only relative values of the susceptibilities,[12] so that one can write

$$\chi'(\omega,H_1,T_1)/\chi'(\omega,H_2,T_2) = \Delta\omega_m(\omega,H_1,T_1)/\Delta\omega_m(\omega,H_2,T_2) \quad (8)$$

to a good approximation, independently of the proportionality constants in Eq. (3) or Eq. (6). The only condition, which is always valid for paramagnetic samples, is that $\Delta L/L$ should not be too large, as discussed earlier.[7]

In practice the ratio of frequency shifts can generally be measured to better than 1%, and if the magnetic specific heat is not too large, a similar accuracy can be achieved in the determination of C_M. This is considerably better than the accuracy which can usually be achieved by inferring C_M from the total specific heat measured calorimetrically, since this generally contains a very much larger lattice contribution. Results of specific heat and relaxation time determinations using our TDO are reported elsewhere.[8–11]

ACKNOWLEDGMENTS

We would like to thank R. J. Blume, P. Kindlmann, H. Meyer, and R. G. Wheeler for valuable discussions, C. Sneider and D. Carpenter for building and designing parts of the apparatus, and S. Mroczkowski for growing crystals used in the experiments.

* Work supported in part by the U.S. Atomic Energy Commission.

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[5] The ac voltage changes with temperature because the diode current at bias voltages over 350 mV, which is mainly due to thermal excitation, decreases as the temperature decreases, to give a larger voltage range over which the diode conductance is negative.

[6] A. Skjeltorp (private communication).

[7] To attempt to justify this result, other than empirically, we carried out a computer simulation of the TDO oscillation characteristics using an IBM 1620 ECAP program. The results show that one should expect a few percent deviation in ω and $\Delta\omega_m$ compared to values one would calculate from Eqs. (6) and (3). However, the computer analysis indicates further that for $0<\Delta L/L\lesssim 0.02$, the approximation that $\Delta\omega$ is proportional to ΔL and hence to χ' should be valid to within $\pm 0.5\%$, which is less than the errors in our susceptibility experiments.

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[13] The method of using susceptibility measurements for determining C_M has an important advantage over direct calorimetric experiments when C_M is much smaller than the lattice specific heat C_L. With the direct method, one always measures C_M+C_L. However, with the susceptibility method, one can obtain C_M directly from the field dependence of χ' without having to make any correction for C_L. For example, in our experiments on $GdCl_3$ we have successfully determined C_M at 77 K to an accuracy of $\pm 3\%$ even though C_L is more than a thousand times larger than C_M (see Ref. 10).

[14] Spin–lattice relaxation time estimates based on susceptibility measurements are not intrinsically more accurate than comparable measurements with pulse resonance methods. However, for magnetic crystals in which a phonon bottleneck may obscure the true spin–lattice relaxation time τ_{sl}, the susceptibility method is capable of yielding τ_{sl} directly,[11] whereas the pulse resonance method is not.

[15] For a summary of the results of pulse resonance experiments and a discussion of the phonon bottleneck problem, see C. D. Jeffries, *Dynamic Nuclear Orientation* (Interscience Publishers, Inc., New York, 1963).

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