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Frequency and temperature dependence of conduction-electron spin resonance in a highly enhanced-susceptibility metal: $TiBe_2$

D. Shaltiel, D. Ioshpe,* A. Grayevsky, V. Zevin, and J. L. Smith†
Racah Institute of Physics, Hebrew University, Jerusalem 91904, Israel
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The conduction-electron spin resonance of the highly enhanced-susceptibility metal $TiBe_2$ was investigated in the large frequency range of 0.2–36 Gc/sec at temperatures below 25 K. Subtracting demagnetization broadening, the linewidth increases linearly with frequency up to 10 Gc/sec; it increases more than linearly at 36 Gc/sec. The results are discussed in relation to the g-value anisotropy of the conduction electrons on the Fermi surface. Observed deviation from the Elliot relation below 20 K may arise from paramagnon relaxation.

Conduction-electron spin resonance (CESR) in metals has been investigated for the last thirty years, mainly in elemental metals such as Li, Na, Al, and Cu.[1] The linewidth in these metals increases with the increase of the impurity content as it increases the spin scattering of the conduction electrons.[1] It is therefore necessary to use metals with impurities in the ppm level in order to observe their CESR, even at helium temperatures. Pd is an exception, as its linewidth is relatively narrow even at higher impurity concentrations.[2] This results from the enhancement of the conduction-electron susceptibility which reduces the linewidth by the enhancement factor.[3] CESR in alloys or intermetallic compounds, which so far was not possible to obtain with a purity comparable to pure metals, can therefore be observed only in intermetallic compounds with extremely enhanced susceptibilities.

$TiBe_2$ has a strong Curie-like paramagnetic temperature-dependent susceptibility with a shallow maximum at 10 K [$\chi(10\,\mathrm{K}) \simeq 8.3\times10^{-3}$ emu/mole Oe].[4] Its high density of states obtained from specific heat,[5] its nonlinear behavior of the susceptibility at high magnetic fields[6] and the observation of the CESR implies[7] that it is an enhanced susceptibility metal. Band-structure calculations confirmed the high density of states at the Fermi surface and estimated an enhancement factor larger than 50 in its susceptibility.[8] To the best of our knowledge, it has the highest paramagnetic d-band susceptibility in any metal observed so far. CESR was observed in this compound at X-band microwave frequencies, with strong signals from liquid helium to room temperature.[7,9] The g value was 1.983 ± 0.005 and it was temperature independent. The linewidth increased strongly with the temperature and varied almost linearly with the resistivity between 20 to 250 K.

Little is known about the CESR properties of enhanced susceptibilities metals, such as the effect of impurities on the intrinsic zero-temperature linewidth and relaxation mechanisms at low temperatures. Another problem is related to the anisotropy of the g value of the conduction electrons in the Fermi surface.[10] This anisotropy tends to broaden the resonance linewidths, but motional narrowing, as well as many-body interactions, has an opposite trend and narrows the line. To study this effect, one can investigate the frequency dependence of the CESR as a function of temperature.[11]

We have therefore investigated the CESR frequency dependence of $TiBe_2$ in order to study the properties of an enhanced susceptibility metal. We report here this dependence from 0.2 to 36 Gc/sec. This is the first time that the CESR is investigated in such a large frequency range and that the frequency was varied continuously from 0.2 to 8 GHz.

Two $TiBe_2$ samples were used with a residual resistivity ratio (RRR) of 55 and 110, prepared at the Hebrew University and Los Alamos National Laboratory, respectively. The spectrum at about 9 and 36 Gc/sec was measured with Varian spectrometers. A homemade spectrometer was used to measure the spectrum from 200 to 8000 Mc. It consists of a set of variable frequency generators connected to a two-way 20-dB directional coupler, followed by a coaxial line that terminated with a single coil, where the sample was introduced.

The $TiBe_2$ powder sample consists of particles whose size is 50 ± 20 μm. To improve the thermal contact with the sample we used a cup sample holder made of a quartz single crystal and mixed our sample with quartz powder.[12]

The resonance line was detected at frequencies as low as 200 Mc. It was possible to observe the line even at lower frequencies; however, since the tail of the line was at negative fields, we did not attempt to go lower. The resonance line could be closely fitted to a Lorentzian line with Dysonian shape. The linewidths as a function of frequency for the RRR 55 sample at 4.1 K and for the RRR 110 sample at 4.1 and 1.6 K are shown in Fig. 1. It shows that the linewidth increases linearly with the frequency and the slopes obtained by least squares are almost equal for the two samples. However, for the same temperature, the higher RRR sample has a smaller linewidth when extrapolated to zero frequency. In addition to the results of the 110 RRR up to 10 Gc/sec at 4.1 K, the inset in Fig. 1 also shows the results at 35.6 Gc/sec, at the same temperature. The linewidth at 35.6 Gc/sec is 65 G, larger than the linear extrapolated value obtained from the lower frequency measurements.

Figure 2 gives the g value as a function of the frequency. It is constant between 9.3 Gc/sec and 1.5 Gc/sec and equal to 1.983 ± 0.005; its value at 35.6 Gc/sec is 1.986 ± 0.003. Thus the g value is almost constant in this

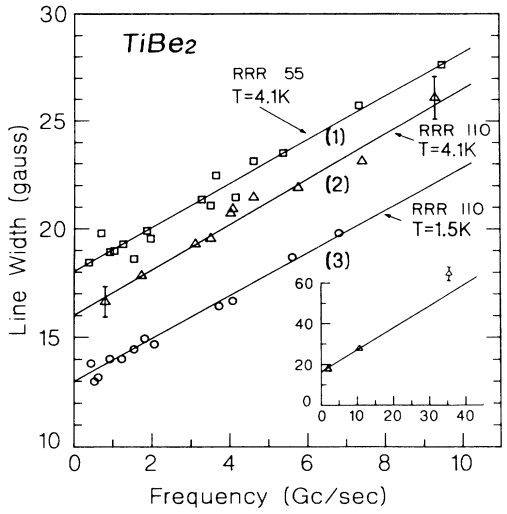

FIG. 1. Linewidth as a function of the frequency for the 55 and 110 RRR samples at 4.1 K and for the 110 RRR sample at 1.5 K, between 0.5 and 10 Gc/sec. The inset shows the linewidth of the RRR 110 sample at 4.1 K between 0.5 and 10 Gc/sec, together with the measurement at 35.6 Gc/sec; the straight line is extrapolated from the low-frequency results.

large frequency range. The slight decrease of g below 1.5 Gc/sec may be erroneous due to the increase in the error of g; this error is inversely proportional to the resonance field and, hence, to the frequency.

Figure 3 shows the low-temperature dependence of the linewidth for the 110 RRR sample at 9.3 Gc/sec. For comparison, the figure shows the measurements of the 55 and the 15 RRR samples reported earlier.[7,9] In the 55 and 110 RRR samples the linewidth increases with the temperature and can be presented as a guide to the eye by two straight lines that intersect between 10 to 20 K. Similar behavior has been observed for lower frequencies in both samples, as can be seen in the inset of Fig. 3 that shows, as an example, the temperature behavior of the linewidth of the 110 RRR sample at 0.595 Gc/sec.

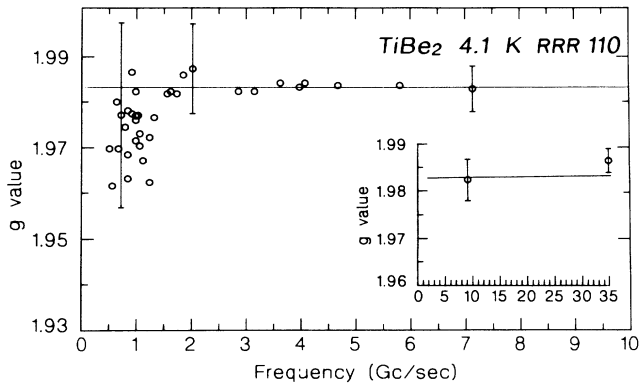

FIG. 2. g value as a function of frequency of the 110 RRR sample at 4.1 K between 0.5 and 10 Gc/sec. The inset includes the result at 35.6 Gc/sec.

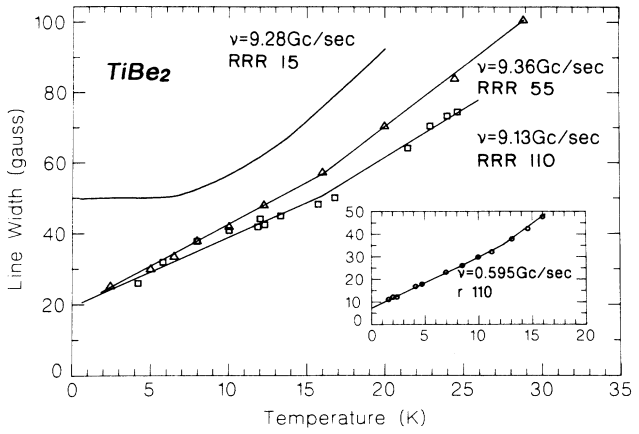

FIG. 3. Linewidth as a function of temperature as X band for the 15, 55, and the 110 RRR samples. The results of the 15 and 55 RRR samples are from earlier publications (Refs. 7 and 9, respectively). The inset show the linewidth at 0.595 Gc/sec for the RRR 110 sample.

Analysis of the linewidth as a function of the resistivity, where the temperature is the implicit parameter for the 55 RRR, sample is presented by two straight lines intersecting around 20 K (Fig. 4 taken from Ref. 9).

The experimental results in $TiBe_2$ can be summarized as follows.

(1) The g value is 1.986 ± 0.003 at 35.6 Gc/sec and it is constant and equal to 1.983 ± 0.005 for the large range of frequencies 10 to 1 Gc/sec and probably even at lower frequencies. It is not affected by the sample resistivity.

(2) In the helium-temperature region, at constant temperature the linewidth increases linearly with the frequency up to 10 Gc/sec. The slope of the linewidth versus frequency does not depend on the resistivity or the temperature. However, the higher the RRR the lower the linewidth for constant temperature and frequency. The linewidth of the 110 RRR sample at 35.6 Gc/sec at 4.1 K is larger than the linear extrapolation from measurements up to 10 Gc/sec. Single particles between 0.7 and 0.1 mm in size show, at X band and 4.1 K, a linewidth not smaller

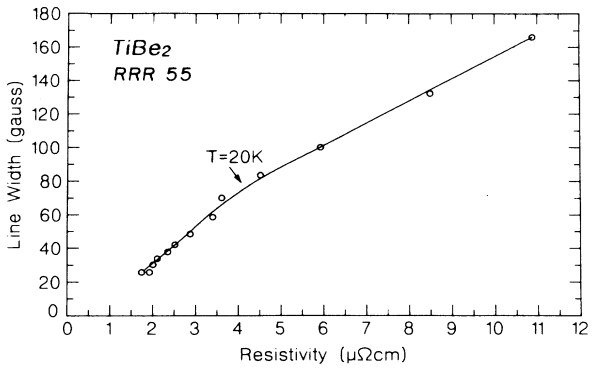

FIG. 4. Linewidth as a function of the resistivity for the 55 RRR sample, the temperature being the implicit parameter. The results are from an earlier publication (Ref. 9).

than 21 G compared to the powder sample, whose linewidth was 26 G.

(3) The temperature dependence of the linewidth for the large temperature range from 10 up to 250 K was found, in an earlier work, to be approximately linear with the resistivity.[9] However, in the low-temperature region we observe that the simple linearity between linewidth and resistivity is not maintained.

A contribution to the frequency dependence of the linewidth arises from demagnetization effects. The maximum spread in the position of the resonance line due to demagnetization for elongated needles, in different directions, is $3\pi M$ (M is the demagnetization). In the measurements of the frequency dependence of the linewidth, powder samples have been used that had a distribution in size as well as in shape. Drain[13] has calculated the demagnetization broadening, assuming spheroids of an axial ratio of 2, and including effects due to closely packed spheres. The size distribution of the particles in the $TiBe_2$ 110 RRR sample was 50 ± 20 μm and their shape, though not regular, had a distribution of length to width ratio around 2. Using the susceptibility $\chi = 9.7 \times 10^{-3}$ emu/mole and the density of 3.3 G/cm^3 Drain's calculation gives a broadening of 5 G at an external field of 3.5 kG. An upper limit for demagnetization contribution to the linewidth is also obtained from the increase of the NMR linewidth with magnetic field of 5.6 G at 3.5 kG (Ref. 14) in agreement with our results. A similar value is obtained from measurements on single particles. In a single particle of regular shape, the demagnetizing field is homogeneous and therefore its contribution to the linewidth should be zero, and only the line position should shift. The measurements were carried out at 4.1 K on the X-band spectrometer whose sensitivity was adequate to measure a 50 μg particle with a signal to noise better than 100 to 1. The sensitivity of the other spectrometers was much lower to enable such a measurement. In two nonelongated particles of irregular shape whose size was 0.25 and 0.1 mm, the linewidth was 22 ± 1 G and the line position was 0 ± 0.5 independent of their orientation with the magnetic field. This indicates a homogeneous demagnetization field or that motional narrowing averages existing inhomogeneities. Taking 21 G as the linewidth of a single particle with homogeneous demagnetization field compared to 26 G obtained in powders, we again obtain an increase of 5 G at 3500 G which amounts to 0.5 G/Gc sec. As the total increase in the linewidth is 1 G/Gc sec we conclude after subtracting the demagnetization contribution, that there is an intrinsic increase in the linewidth of 0.5 G/Gc sec.

An increase of the linewidth with frequency, at constant temperature was reported for elemental Cu, Ag, and Al.[11] It was suggested that the mechanism for this frequency dependence arises from the g-value anisotropy of the conduction electrons at the Fermi surface. This anisotropy may broaden the linewidth due to the spread in the g value $\langle dg \rangle$ of the conduction electrons at different k states. Simple motional narrowing should decrease this broadening. An additional narrowing process rises from electron-electron interaction. Fredkin and Freedman have calculated the frequency dependence of these two processes.[10] Their results show that for simple metals the linewidth increases as the square of the frequency, as observed in Cu.[11] In an enhanced susceptibility metal they found that the linewidth is further narrowed by the enhancement factor. In Al, where a linear increase of the linewidth was observed, the effects of pockets and ridges on the Fermi surface were added to explain this linearity.[15] For $TiBe_2$, using an enhancement of 50, the contribution to the linewidth obtained, using the calculation of Fredkin and Freedman and assuming large $\langle dg \rangle (=0.2)$ and $x = 10^{-14}$ sec (Ref. 7), gives negligible contribution to the linewidth compared to that deduced from our results for the measured frequency range. Thus additional theoretical work is indicated that will explain the linear increase of 0.5 G/GHz up to 10 GHz and the deviation from linearity at 35.6 GHz where an even larger increase was observed. The variation of the linewidth with temperature or resistivity at low temperatures given in Figs. 3 and 4, respectively, needs some clarification. As shown in an earlier work, the overall temperature dependence of the linewidth, up to 250 K, is linear with the resistivity.[9] This agrees with the Elliot relation,[1] which states that the coupling of the spin system to the lattice is via the spin-orbit coupling, and therefore the spin relaxation of the conduction electrons is proportional to the momentum relaxation, divided by the square of the g shift. Thus the linewidth should be proportional to the resistivity.[7] The slope of the linewidth versus the resistivity up to 20 K is larger than above 20 K (Fig. 4). It indicates an additional relaxation process at the lower-temperature range. A possible mechanism for this process may be due to paramagnon fluctuations that arise from the large enhancement of the spin susceptibility in $TiBe_2$.[16]

The extrapolated linewidth to zero temperature $DH(T=0)$ at constant frequency does not show marked difference between the 55 and the 110 RRR samples, but it is remarkably smaller than that of the 15 RRR sample (Fig. 3). Impurity scattering may explain the larger $DH(T=0)$ for the 15 RRR sample, but it does not explain the almost equal linewidths for the other two samples.

In conclusion, this is an experimental work which, for the first time, has investigated in detail the frequency dependence of the ESR linewidth of the conduction electrons, in a highly enhanced-susceptibility metal. CESR in $TiBe_2$ can be used as a link between the two extreme cases of CESR and ferromagnetic resonance (FMR). CESR in elements such as Na or Ag, deals with conduction electrons where the electron-electron interaction is weak. In contrast, FMR of $3d$ metals like Fe or Ni investigates the resonance of strongly coupled d electrons that are coupled via s-d interaction to the s electrons. The study of the CESR of a paramagnetic metal, such as $TiBe_2$, that is on the verge of becoming ferromagnetic,[17] can yield information on basic mechanisms of relaxation and other phenomena in FMR that are obscured due to other effects.

There is need of further experimental and theoretical work to clarify the various points discussed above.

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*Present address: Gilo, Block 63/12, Jerusalem 93384, Israel.
†Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

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