Fermi-surface structure effects revealed by the observation of conduction-electron-spin resonance in Zn

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The first observation of conduction-electron-spin resonance (CESR) in polycrystalline high-purity Zn in the temperature range between 4.8 and 35 K is reported. The observed g value equals 2.0033 ± 0.0005, and the linewidth above 11 K increases with temperature, as expected from the normal electron-phonon interaction. The signal is explained as being due to the "lens" part of the Zn Fermi surface, advancing herewith a new type of interpretation of CESR data. The usual CESR signal coming from the main part of the Fermi surface is believed to be broadened beyond the detection limit due to magnetic breakdown effects interplaying with the complex Fermi surface. Similar features in Mg are discussed.

I. INTRODUCTION

In conduction-electron-spin resonance (CESR) the dominant relaxation mechanism for the conduction electrons is believed to be via spin-orbit (SO) coupling.[1,2] Via this mechanism, the interaction of the conduction electrons with the phonons, impurities (both physical and chemical), and the sample surface causes three different contributions to the total observed linewidth $\Delta B \simeq 1/\gamma T_2$, designated as $\Delta B_{\rm ph}$, $\Delta B_{\rm i}$, and $\Delta B_{\rm s}$, respectively; γ is the gyromagnetic ratio and T_2 is the transverse relaxation time. As explained by Yafet[2] one expects the SO interaction to increase rapidly with the atomic number Z of the metal, giving large linewidths to high-Z metals. $\Delta B_{\rm i}$ is assumed to be T independent. The electron-surface interaction linewidth $\Delta B_{\rm s}$ is proportional to ϵ, the spin disorientation probability at the sample surface, and is given by[3]

$$\Delta B_{\rm s} = \frac{\epsilon v_F (1 + B_0)}{2\gamma d (1-\epsilon)} \qquad (1)$$

for $d < \delta_e$, where v_F is the Fermi velocity, B_0 is the first Landau-Fermi-liquid parameter, d is the sample foil thickness, and $\delta_e = (2DT_2)^{1/2}$ is the spin depth, D being the diffusion constant. In recent papers[4] it is demonstrated that ϵ increases strongly with Z, probably as $\epsilon \simeq Z^4$. Further Yafet[2] has shown that $\Delta B_{\rm ph}$ has the same temperature dependence as the resistivity ρ which means that $\Delta B_{\rm ph} \sim T$ for $T > T_D$ and $\Delta B_{\rm ph} \sim T^5$ for $T < T_D$ where T_D is the Debye temperature. Recently, Monod and Beuneu[5] have discussed extensively the simple relations proposed by Elliott[1] and Yafet[2] given as

$$\Delta B_{\rm ph} \sim \left(\frac{\lambda}{\Delta E}\right)^2 \frac{1}{\gamma \tau} \ , \qquad (2a)$$

$$\Delta g \equiv (g - 2.002\,32) \sim \left(\frac{\lambda}{\Delta E}\right) \ , \qquad (2b)$$

where τ is the momentum collision time, λ is the SO splitting of the atomic state which is dominant for the contribution to the SO admixture into the conduction band, and ΔE is the energy separation from the conduction band to the nearest band with the same transformation properties. They show that relations (2) are very well followed by the metals of valence $V = 1$ except by Li for which metal one thinks that not the SO-interaction mechanism is dominant but instead the spin-current mechanism.[5,6] Other metals like Al, Mg, Be, and Pd of higher valence do not follow the linewidth scaling, which is explained by inferring band-structure effects breaking down the simple relations proposed in Eqs. (2). It is important here to note that the latter interpretation has set a minimum amount of linewidth for an ideal (i.e., free-electron) metal as shown by their Grüneisen-like plot of $\Delta B(\Delta E/\lambda)^2$ against T/T_D. Their interpretation indicates to be a possible criterion for tracing the origin of an eventually observed new CESR resonance in a metal not yet detected before.

Generally, the total linewidth ΔB is written as[7]

$$\Delta B = \Delta B_{\rm i} + \Delta B_{\rm s} + \Delta B_{\rm ph} + \Delta B_{\rm a} + \Delta B_{\rm f} \ . \qquad (3)$$

The term $\Delta B_{\rm a}$ is due to the existence of a g distribution over the Fermi surface (FS) and accordingly is called the g-anisotropy term; it depends on the observational frequency f. $\Delta B_{\rm f}$ is a contribution to the linewidth which seems to be linearly proportional to f and independent of temperature, of which one has not yet been able to trace the origin. Both $\Delta B_{\rm a}$ and $\Delta B_{\rm f}$ are negligible if f is low enough.

When measuring the rather weak magnetic resonance signals of conduction electrons in bulk metals, it is important to acquire as small linewidths as possible such that the resonance line is not broadened beyond the detection limit. Taking into account the parameters which determine the signal intensity[3] and in view of the SO interpretation elaborated upon above it appears a little bit surprising that one has, so far, not succeeded in observing CESR in Zn although it has been tried intensively.[8] Indeed referring to the observed CESR in Cu with $Z=29$ compared to $Z=30$ for Zn one should expect, relying upon the known free-atom SO coupling properties,[2,5] that CESR should be observable in Zn.

II. EXPERIMENTAL TECHNIQUE AND SAMPLE PREPARATION

The CESR in Zn was searched for by the use of a reflection type electron-spin-resonance spectrometer working at 20.90 GHz, having computer-aided signal-averaging facilities. The starting material was very pure (99.9999+%) polycrystalline[9] Zn with an as-received residual resistance ratio RRR defined as $(R_{273\text{K}}/R_{4.2\text{K}})$ of at least 35 000. From this material thin platelets were produced by sequentially cold rolling and etching, taking extreme care in preventing contaminations. The foils were given a final oxygen anneal[10] which resulted in Zn platelets with a thickness of $\pm$ 10 μm and a bulk RRR better than 7500. This thickness of the samples were selected to give an as favorable as possible signal-to-noise (SN) ratio. To make this estimate,[11] the ϵ of Zn was taken to be the same as that for Cu because of the very close Z values of these two metals.[4] Knowing however how important the surface treatment is in order to obtain a low ϵ value,[12] care has been taken to produce very clean, smooth, and shiny Zn surfaces which were obtained by a chemical etchant based on HCl and methanol. From the polycrystalline foils produced in this manner, samples were formed with as big a surface as possible by stacking Zn platelets insulated from each other by PTFE sheets. The total effective Zn surface of a typical sample was $\simeq 10\ \text{cm}^2$. Samples treated in this way gave a reproducible resonance signal which could be identified as CESR in Zn according to several tests described subsequently.

Samples were prepared also from less pure material (and accordingly with a lower RRR value) of different origin.[13] No signal could be produced from these samples although they were treated and prepared in exactly the same way as the ones from the very pure material which produced the signals. This statement already includes that the observed signal is not due to cavity background; careful "empty-cavity" measurements under precisely identical circumstances as in which the Zn measurements were carried out confirmed this conclusion.

III. EXPERIMENTAL RESULTS

Figure 1 shows observed signals of a 10.0 $\pm$ 0.6-μm-thick Zn foil at three different temperatures together with a g-marker signal ($g=2.002\,29$) from Li particles formed in neutron-irradiated LiF. A first point to notice is that the line shape is the one typical for a CESR reflection signal in the anomalous-skin-effect (ASE) region. Fitting of the theoretical line shapes, taken from Dyson's theory as adapted for the ASE region by Pifer and Magno[3,14]— which theory has been proven to describe the CESR in the ASE region adequately—to the best signals at low T gave an A/B value of 3.6 $\pm$ 0.3, in good agreement with theory. Due to the low SN ratio and the increasing ΔB as T increases, reasonable signals could only be detected below 35 K. A plot of signal intensity (referred to a Li signal) defined as $(\Delta B)^2$ times the signal height, against T is shown in Fig. 2(b). From this it is clear that the total signal intensity is constant over the T range studied in accordance with Pauli paramagnetism χ_p taking into account that the spin depth δ_e and the anomalous skin depth δ_A do not

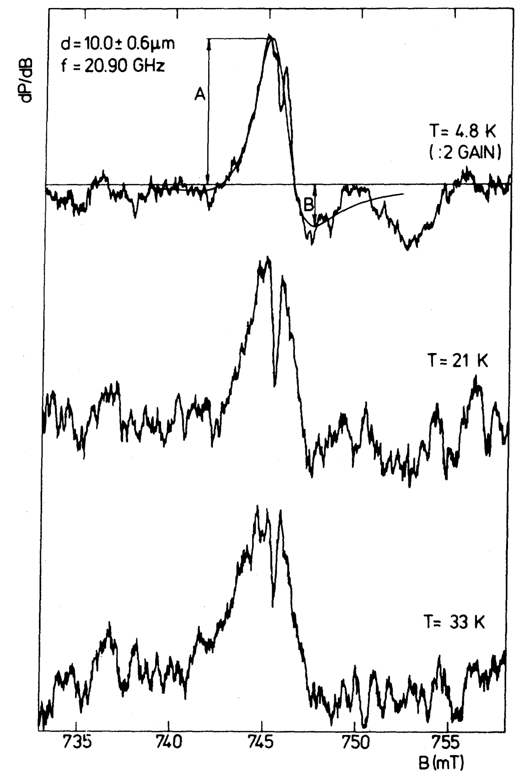

FIG. 1. Traces for the derivative of the power absorption in a stack of high-purity Zn slices at different temperatures measured by reflection technique. The signal is ascribed to CESR from the "lens" part of the Zn Fermi surface. A theoretical anomalous-skin-effect line shape for $\delta << d < \delta_e$ with $A/B=3.5$ is compared to the experimental signal at 4.8 K. The small signal near the top of the Zn signal is the CESR of Li particles in LiF ($g=2.00229$). The other small signal at the high-field side of Li is a weak paramagnetic background signal.

change significantly over the T range studied. To have a more quantitative idea of the signal intensity of the Zn resonance it has been compared with the Cu CESR signal by inserting a small Cu platelet of the same thickness as the Zn sample in the stack of Zn platelets and measuring both signals in the same field sweep. Taking into account the observed linewidths and sample surfaces of both metals, the Zn signal appears to be 32 ± 5 times weaker than the Cu CESR signal, over the whole T range studied. This result, of course, can explain previous failures in trying to observe CESR in Zn. Generally the measured susceptibility χ_m is related[15] to χ_p as $\chi_m = \chi_p(m^*/m)\ (1+B_0)^{-1}$ where m^*/m is the ratio of the electronic effective mass to the free-electron mass. Taking into account that $B_0 << 1$ and equating[16] m^*/m to 1.3 and 0.78 for Cu and Zn, respectively, one would not expect χ_m for Zn to be much lower than χ_m for Cu. We think the explanation for this must be sought in the FS pecularities of Zn as explained below.

A further point is illustrated in Fig. 2(a) where linewidths against T are plotted for two samples with thicknesses 8.5 ± 0.7 and 10.0 ± 0.6 μm, respectively, in the range $4.8 \leqslant T \leqslant 35$ K. This plot shows that the linewidth is constant below 11 K and increases with T for $T > 11$ K which we ascribe to the usual electron-phonon interaction. The Yafet relation, i.e., $\Delta B_{\text{ph}} \propto \rho_{\text{ph}}$, is fulfilled within the experimental scatter. However we think this finding is not very conclusive because the experimental accuracy is too low.

One also notices in Fig. 2(a) the constant difference in linewidth between samples of different thicknesses which we ascribe partly to surface relaxation[3] and which is convincing evidence for a CESR signal. Careful measurements of residual linewidths $\Delta B_{\text{res}} \equiv \Delta B\ (T < 10\text{ K})$ against thicknesses were carried out, thinning the samples after subsequent measurements, always on the "same" material. This allowed us to determine the ϵ value as being $\epsilon = (7 \pm 2) \times 10^{-4}$ which is very near to the Cu value,[4,12] as expected from the close Z values of both metals. The measured g value of the signal is T independent within the experimental error and is given by $g_{\text{Zn}} = 2.0033 \pm 0.0005$.

A final test for the assertion that this is indeed CESR is given by the $\Delta B(\Delta E/\lambda)^2$—against T/T_D plot. Using the scaling factors proposed by Monod and Beuneu, we compare our Zn data in Fig. 3 to

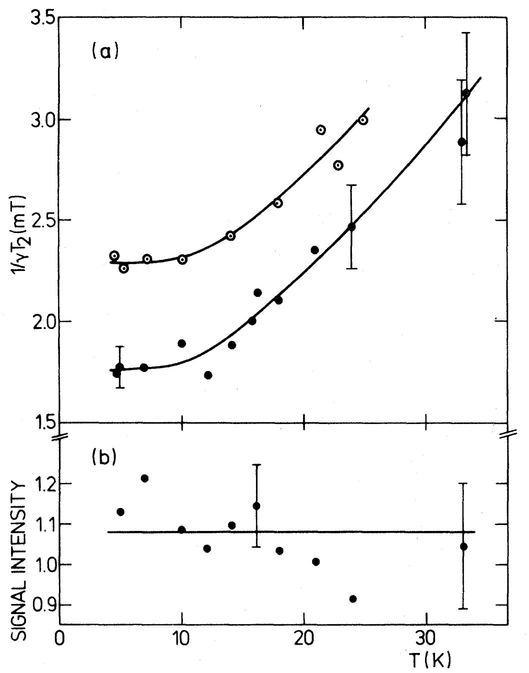

FIG. 2. (a) CESR linewidth as a function of T for two high-purity Zn foils measured at 20.90 GHz. The open and solid symbols represent data from 8.5- and 10-μm-thick foils, respectively. The signal intensity, defined as ΔB^2 times signal height and referenced to the CESR of Li, plotted against T for a 10-μm-thick foil is shown in (b).

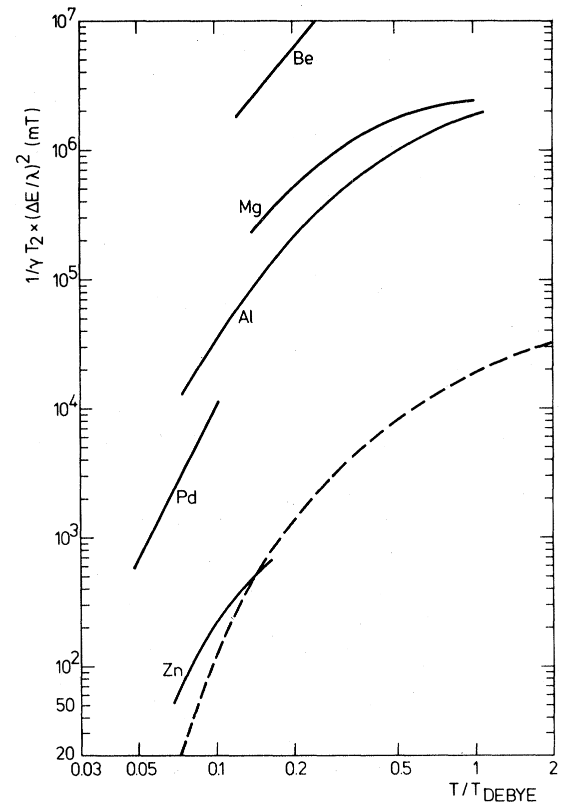

FIG. 3. Reduced linewidth due to electron-phonon interaction vs reduced T for several metals. The dashed curve is the average of all T-dependent data obtained on valence $V = 1$ metals (see Ref. 5). The CESR data of Zn obtained in this work are shown to follow closely the $V = 1$ metals. For the Mg and Al data, see Refs. 25 and 27, respectively.

their survey[5] of the CESR data of pure metals obtained before. Our data fit very well to the general behavior of the metals of valence 1 for which the simple theory is supposed to apply best and which exhibit the best free-electron-like behavior. The same conclusion is found in comparing[5] $(\Delta g)^2$ against $(\gamma T_2 \rho_{\rm ph})^{-1}$ at $T \simeq 0.7 T_D$. [Values of $(\Delta g)^2$ and $(\gamma T_2 \rho_{\rm ph})^{-1}$ are 10^{-6} and 7×10^6 mT Ω^{-1} cm^{-1}, respectively.]

IV. THEORETICAL INTERPRETATION

We believe that the properties mentioned above prove that we observed CESR in Zn. Although this is very interesting in itself, we think another important result lies in the answer to two questions revealed from the described analysis: first, why is the signal intensity in Zn so weak compared to other CESR signals of metals with comparable χ_p and, second, why does Zn show the "free-electron"-like behavior of the $V = 1$ metals while having an hcp structure with $V = 2$, which makes it comparable to Mg? The answer can be found in the complex structure of the FS of Zn. Although it is rather complicated, this FS is very well known.[17] In the usual hcp reduced zone scheme in $\vec{k}$ space, it is composed of four parts, i.e., the first-zone hole "caps," second-zone hole "monster," the third-zone electron "lens" centered at Γ, and "needles" centered at K where standard notation for the symmetry points has been used.

We ascribe the observed resonance in Zn to a CESR signal originating from the lens part of the FS only, which can be corroborated as follows. The third-zone electron lens is found to be very free-electron-like with a rather small g spread over the lens surface[17,18] leading to CESR properties similar to those of the other free-electron-like metals, as exposed, e.g., in Fig. 3. In connection with this, an averaged g value over the lens surface has been calculated. This was done using the SO interaction terms proposed by Stark and Falicov[17] for the FS calculation of Zn. The sign of the g shift as well as the order of magnitude agree with the small positive g shift recorded. A crude comparison of the intensity of the observed resonance to the intensity that one would observe if all the electrons of the FS contributed can be made by the ratio of the lens surface area S_L to the area $S_{\rm FS}$ of the whole FS. The dimensions[17] of the lens are given by $k^{\Gamma K} = k^{\Gamma M} = 8.685$ nm^{-1} and $k^{\Gamma A} = 2.68$ nm^{-1} for its major (in the basal plane perpendicular to the c axis) and minor semiaxis, respectively, while the Fermi wave vector is given by $k_F = 16.908$ nm^{-1}. This gives $S_L / S_{\rm FS} = (6.5)^{-1}$. Thus if we admit that χ_m(Zn) and χ_m(Cu) are comparable in size and if we also assume that the observed CESR in Cu originates from the complete FS then we can explain a reduction of the CESR intensity in Zn by a factor 6.5. As shown above, the m^* ratios can given another factor of 2 if, at least, one may admit that an m^* appropriate to the lens is given by the m^* observed for the entire FS, which is not unreasonable.[18] The remaining small additional weakening can easily be accounted for by variations in the surface impedance[19] at 21 GHz, which modify the anomalous skin depth and accordingly, the intensity. The main part of the Zn FS is formed by the second hole "monster" with a moderate g spread. One would expect that motional narrowing (MN) — either in the classical sense (if $\omega \tau_m \sigma_g / g \ll 1$ where σ_g is the rms g spread and τ_m is an electron collision time appropriate for MN) or via the cyclotron orbits ($\omega\tau > 1$) — would yield an observable resonance line from this "monster," as obtained, e.g., in the case of Mg which is another hcp metal with a FS similar to the Zn one. The reason for not observing this is found in magnetic breakdown (MB). Normally, at low T with only small-angle scatterings being present, different parts of the FS are not connected and during a spin lifetime T_2 an electron averages over the part of the FS to which it belongs. However this situation is changed in the presence of a magnetic field if MB occurs which can connect different parts of the FS. Indeed, this happens in our resonance field for the second-zone monster and the third-zone needles. Depending[20] on the angle θ between $\vec{B}$ and the c axis, the MB field parameter B_m for connection between the monster and the needles varies from 0.22 to 1 T for θ changing from $0°$ to $70°$. This gives for the probability for MB to occur in a certain direction for which B_m is, say 0.5 T, for an applied field of 0.75 T, already a value of $\exp(-B_m/B) = 0.5$. As such we may conclude that in our experiments we are in the MB region. Now the needles, being very small (cross-sectional[21] area perpendicular to the c axis of 0.015 nm^{-2}), have very large g factors (values up to 356 have been reported[22]) which cause the CESR line from the monster to be broadened very much, apparently beyond detection.

The proposed interpretation can also explain the strange behavior of the CESR in Mg at low and moderate T as Mg has a similar[23] FS as Zn. The linewidth, being broad at all field angles θ (10–50 mT at X band) is largest[24,25] when $\theta = 0°$ in which direction one really expects the MB to be most efficient. The fact that a CESR signal of usual intensity is seen in Mg can then be explained by a smaller g spread which applies for the needles (or "cigars" as they are called in Mg) which are bigger[23] in Mg than in Zn (cross-sectional area perpendicular to the c axis of 2.14 nm^{-2}). Moreover, in view of our Zn analysis, Mg should also show a CESR signal coming from the lens part of its FS similar to the Zn one. Careful measurements on 99.9999%-pure Mg samples[26] indeed showed a weak (20 ± 2 times weaker than Cu) signal with a linewidth of 12.5 ± 1 G and a g value of 2.006 ± 0.001 at 4.6 K, superimposed on the usual broad CESR resonance signal. When focusing ones attention on the detection of the usual broad Mg CESR line, it is evident that this small signal could have been easily overlooked in the past. We intend to carry out more accurate and extensive experiments about the last statement in the future.

V. SUMMARY

Strong evidence is given for the first observation of CESR in Zn via the reflection technique. The observed resonance line—with $g = 2.0033 \pm 0.0005$—shows most of the usual CESR behavior within the experimental error, e.g., Dysonian line shape, temperature-independent intensity which is in accordance with the Pauli paramagnetism of metals, a phonon contribution to the linewidth ΔB_{ph} which follows the Yafet relation (i.e., $\Delta B_{ph} \sim \rho_{ph}$), a surface-dependent part in the linewidth which varies with d^{-1} and which gives an ϵ value of $(7 \pm 2) \times 10^{-4}$, very near to the Cu value as expected.

Its weak signal intensity, i.e., 32 ± 5 times lower than Cu, which does not seem to cope with the expectations for CESR, and its free-electron-like behavior of the $V = 1$ metals lead to the interpretation that FS-structure effects are revealed by this observation in Zn. The signal is interpreted as being a CESR signal due to the electrons of the lens part of the FS only while magnetic breakdown effects cause the CESR signal, coming from the main part of the FS to be broadened beyond detection.

We realize that a substantial amount of experimental and theoretical work still needs to be done to work out precisely all the ideas proposed here. Obvious experiments to carry out in the near future will concern frequency-dependent measurements of g value and linewidth. It will be very interesting to find out whether the f-dependent term is also present in the Zn CESR linewidth and how it behaves. It is hoped that this will teach us more about the nature of this term.

It is our opinion that this observation of CESR in Zn which is attributed to originate from a part of the FS, can open new ways of interpreting CESR in metals, i.e., Mg, Be, Al.

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