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CONDUCTION ELECTRON SPIN RELAXATION AT Li/Sb AND Li/Cu INTERFACES

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Résumé. — Nous présentons une étude systématique de la résonance de spin des électrons de conduction du lithium dans les systèmes Li/Sb et Li/Cu. Ceci permet la mesure de ε , probabilité de relaxation des électrons aux interfaces Li/Sb et Li/Cu. On trouve $\varepsilon_{\text{Li/Sb}} = (9 \pm 1) \times 10^{-5}$ à 77 K et 293 K, et $\varepsilon_{\text{Li/Cu}} = (8 \pm 1) \times 10^{-4}$ à température ambiante.

Abstract. — By systematic study of conduction electron spin resonance of Li coated with either Sb or Cu, we measure the spin flip probability ε at the interface Li/Sb and Li/Cu for conduction electrons. We determine $\varepsilon_{\text{Li/Sb}} = (9 \pm 1) \times 10^{-5}$ at 77 K and room temperature, and $\varepsilon_{\text{Li/Cu}} = (8 \pm 1) \times 10^{-4}$ at room temperature.

1. Introduction. — Following the first experiments on conduction electron spin resonance in metals [1], Dyson proposed that surface spin relaxation had to be taken into account [2]. He proposed characterizing this effect by means of a phenomenological spin flip probability ε . As for the case for bulk relaxation on impurities, defects or phonons, surface relaxation gives rise to a broadening of the resonance lines. However the broadening due to surface relaxation depends on the sample geometry and is largest for the thinnest samples, in analogy with the well known size dependent resistivity effect. A few attempts to determine the surface relaxation effects have been carried out on lithium [3] and sodium [4]. Results (expressed as Dyson's « ε ») differ somewhat with the authors, due to the smallness of the surface effect in these samples (ε ranging from 10^{-5} to 10^{-7}).

A much greater broadening was observed by Janossy and Monod [5], on aluminum slabs coated with zinc. These authors used the transmission technique to observe the resonance. In their interpretation, based upon Dyson's and Walker's model [2, 6], they assumed the bimetallic system to be equivalent to a slab of aluminum alone; zinc simply modified the boundary conditions *via* surface relaxation. This assumption allowed them to determine ε for the Al/Zn interface. The obtained value ($\varepsilon \simeq 0.03$) is much larger than values corresponding to metal/insulator interfaces [3, 4]. The question whether bulk relaxation

within the zinc layer had to be taken into account was then raised [5, 7]. Such a possibility has been investigated by other authors [8] working on the Li/Cu system. They introduced in the boundary conditions appropriate terms describing the coupling between the magnetizations of the two metals; these terms were superimposed on those describing surface relaxation of metals alone.

However, the problem of the nature of magnetization coupling at the interface of two metals remains largely unexplored so far, and its apparent temperature dependence [8] is not understood yet. We have thus undertaken a systematic study of bimetallic interfaces by electron spin resonance. Two types of interface with Li metal have been investigated : 1) Li/Sb; 2) Li/Cu. In each case the resonance of the Li metal is compared with uncoated Li. The behaviour of the two samples is shown to be quite different, suggesting an important difference in their interfacial properties.

2. Samples and apparatus. — Samples were prepared by thermal evaporation in a 10^{-6} torr vacuum system. The antimony (or copper) layer was first deposited upon a kapton film [11]; the lithium layer was deposited immediately afterwards in order to avoid a contamination of the interface. Thicknesses were determined by means of a quartz monitor. After evaporation, lithium was protected from oxidization

by *in situ* polymerization of gaseous styrene on the whole sample surface. Clean and easy to handle lithium films were thus obtained; they were kept in quartz tubes filled with anhydrous vaseline oil. We could thus obtain reproducible results from sample to sample, without ageing effect at least up to a month.

ESR spectra were obtained by means of a homodyne spectrometer, using a TE₁₀₂ rectangular cavity at 9 520 MHz operating at nitrogen and room temperature.

3. Li/Sb samples. — A major difficulty in preparing a suitable interface for surface spin relaxation studies lies in the possibility of atomic interdiffusion at the interface. We have chosen the Li/Sb system as it was shown by Asik *et al.* [10] that no detectable broadening of Li ESR by Sb impurity occurs even after melting. However it should be remembered that Li might form intermetallic compounds with Sb. Indeed we have some evidence by attacking the Li film with ethyl alcohol that the Sb layer in contact with it is also removed.

We have prepared a series of Li/Sb samples with antimony thicknesses (d_{Sb}) ranging from zero to 1 000 Å and lithium thicknesses (d_{Li}) ranging from 0.5 to 4 μm. We have observed Li ESR signals in all cases. The lineshape is in good agreement with the Dyson lineshape calculated by Pifer and Magno [9]. It is characterized by four parameters A , B_1 , B_2 , and $\overline{\Delta B}$ (Fig. 1). Using [9] it is possible to calculate the linewidth ΔB from the measurement of $\overline{\Delta B}$ and the ratio A/B_2 . Two types of measurements have been performed in order to separate the surface spin

FIG. 1. — Analysis of the Dysonian character of CESR lines in Li/Sb and Li/Cu samples at 293 K and 9 520 MHz (● Li/Sb; ▲ Li/Cu thin samples; △ Li/Cu thick samples; — Dyson's theory). See Ref [9].

relaxation rate from the *a priori* unavoidable contribution from diffusion or random impurities introduced during (or after) the coating process: we have studied the Li ESR linewidth for a fixed Sb thickness (300 Å) as a function of Li thickness (Fig. 2) and also

FIG. 2. — Broadening of CESR lines of Li/Sb and Li/Cu as a function of d_{Li}^{-1} at 9 520 MHz ($d_{\text{Sb}} = d_{\text{Cu}} = 300$ Å; □ Li/Sb at 293 K; ○ Li/Sb at 77 K; ▲ Li/Cu at 293 K thin samples; △ Li/Cu at 293 K thick samples).

at fixed Li thickness (2 μm) and variable Sb thickness (Fig. 3). As the bulk uncoated Li has an intrinsic linewidth of 1 gauss independent of deposition on the sample holder and polystyrene protection, we have subtracted this bulk linewidth from the measured linewidths in figures 2 and 3. It appears that, as expected for surface spin relaxation, the linewidth increment is independent of Sb thickness (Fig. 3)

FIG. 3. — Broadening of CESR lines of Li/Sb as a function of d_{Sb} at 293 K and 9 520 MHz ($d_{\text{Li}} = 2$ μm).

and linearly proportional to the inverse of Li thickness (Fig. 2). The slope is determined to be 6.0 ± 0.5 gauss/μm⁻¹ of Li thickness, independent of temperature at 77 K and room temperature. Furthermore the analysis of the Li CESR intensity (determined as the product of the corrected signal height and the square of the linewidth) appears on figure 4 and is approximately independent of Sb coating.

We interpret the Li/Sb result as being a clean case of conduction electron spin surface relaxation. Indeed a

FIG. 4. — Intensity of resonance lines as a function of d_{Me} (O Li/Sb ; Δ Li/Cu) at 293 K and 9 520 MHz.

simple model [6] of surface spin relaxation predicts that the observed (derivative) signal is given by [9] :

$$\frac{dP}{dB} = \frac{d}{dB} \left(Z_0 \operatorname{Im} \frac{R}{i(\omega - \omega_0) + \Delta B/2} \right) \quad (1)$$

where $\Delta B = \frac{2}{\gamma} \left(\frac{1}{T_2} + \frac{\varepsilon v_F}{2d} \right)$ and where Z_0 and R are complex numbers, $1/T_2$ is the Li bulk relaxation rate, ε is Dyson's surface relaxation coefficient, v_F the Li Fermi velocity and d is the Li thickness. It is assumed that no surface relaxation occurs at the *outside* Li surface and that the spin mean free path is larger than either d or the skin depth. Formula (1) readily accounts for our observations. In particular it is possible to determine the coefficient ε from the measured slope ΔB versus d^{-1} of figure 2 :

$$\varepsilon_{Li/Sb} = (9 \pm 1) \times 10^{-5}$$

(independent of temperature). This dimensionless quantity is a measure of the spin flip probability for a single collision at the Sb/Li interface.

4. Li/Cu samples. — The study of lithium/copper samples, with copper thicknesses ranging from zero to 1 200 Å and lithium thicknesses ranging from 1 to 10 μm, revealed a number of anomalous features in the observed CESR signal. For a fixed Li thickness there is a large dispersion of the measured ΔB . At present it is not possible to identify the origin of this dispersion which is larger than the measurement uncertainty for either the linewidth or the thickness.

For the thinnest samples it is still possible to use the previous analysis [9] as is shown in figure 1 where the representative points (closed triangles) lie close to the theoretical curve. These results have been expressed on figure 2 with closed symbols. For the thickest Li samples the points lie outside the theoretical range in figure 1 (open triangles) but applying to ΔB a correction factor of 2.06 (infinite thickness correction) the corresponding points are represented on figure 2 by open triangles.

For a thickness of Li 2 μm and Cu 300 Å we have noticed a broadening of ΔB from 9 gauss to 22 gauss upon cooling from room temperature to 77 K. This observation is consistent with previous work on the same system [8]. The intensity of the Li CESR is shown in figure 4 to decrease with increasing thickness of Cu, with a large dispersion of the data. Finally upon dissolving Li by ethyl alcohol the Cu surface remains unaltered thus indicating no interface diffusion or compound formation.

We tentatively interpret the Li/Cu results in the same way as for the Li/Sb system. However the dispersion of the data indicates the possibility of partial interface coupling due for instance to oxidization. In this case the resulting linewidth increment is expected to be *smaller* than the maximum value characteristic of complete surface effect. In order to get a value for ε we retain only the maximum slope of a straightline through the origin of figure 2. We get a broadening of 53 gauss/μm⁻¹ corresponding to $\varepsilon = (8 \pm 1) \times 10^{-4}$. Extrapolated values from Magno and Pifer [8] would indicate a value of ε about two times larger for this system. For comparison at helium temperature Flesner and coworkers [8] find $\varepsilon(T = 4.2 \text{ K}) = 2.5 \times 10^{-3}$.

In conclusion we have shown that it is possible to describe the spin flip at Li/Sb and Li/Cu interface by a spin flip probability ε in both systems. This parameter is very sensitive to surface condition and appears to be characteristic of the surface material. How this parameter is related to intrinsic spin-orbit properties and electronic density of state of the surface layer is still in question as is also the origin of the unexpected temperature variation of ε for Li/Cu.

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References

- [1] FEHER, G. and KIP, A. F., *Phys. Rev.* **98** (1955) 337.
- [2] DYSON, F. J., *Phys. Rev.* **98** (1955) 349.
- [3] GEN, M. Ya. and PETINOV, V. I., *Sov. Phys. JETP* **21** (1965) 19.
ASAYAMA, K. and ODA, Y., *J. Phys. Soc. Jpn* **22** (1967) 937.
SAIKI, K., FUJITA, T., SHIMIZU, Y., SAKOH, S. and WADA, N., *J. Phys. Soc. Jpn* **32** (1972) 447.
- [4] PETINOV, V. I. and ARDASHEV, A. Yu., *Sov. Phys. Solid State* **11** (1969) 1.
VITOL, A. Ya., KHARAKHASH'YAN, E. G., CHERKASOV, F. G. and SHVARTS, K. K., *Sov. Phys. Solid State* **13** (1972) 1787.
- [5] WANG, S. K. and SCHUMACHER, R. T., *Phys. Rev.* **B 8** (1973) 4119 and erratum.
- [6] JANOSSY, A. and MONOD, P., *J. Phys. F* **3** (1973) 1752.
- [7] WALKER, M. B., *Phys. Lett.* **32A** (1970) 230.
WALKER, M. B., *Phys. Rev.* **B 3** (1971) 30.
- [8] JANOSSY, A. and CSERMAK, K., Report KFK1-74-17 to Hungarian Academy of Sciences, Budapest (1974).
- [9] MAGNO, R. and PIFER, J. H., *Phys. Rev.* **B 10** (1974) 3727.
- [10] FLESNER, L. D., FREDKIN, D. R. and SCHULTZ, S., *Solid State Commun.* **18** (1976) 207.
- [11] PIFER, J. H. and MAGNO, R., *Phys. Rev.* **B 3** (1971) 663.
- [12] ASIK, J. R., BALL, M. A. and SLICHTER, C. P., *Phys. Rev.* **181** (1969) 645.
- [13] Polyimide film from Du Pont de Nemours International SA.