ELECTRON PARAMAGNETIC RESONANCE IN FINELY DISPERSED LITHIUM

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A study was made of the effect of the particle size of lithium on the width and profile of a paramagnetic resonance line. It was discovered that the EPR line broadened almost 20-fold when the particle size was reduced from 6×10^{-5} to 6×10^{-6} cm. The probability of the spin flip of an electron on its collision with the surface of a particle was found. The value of the probability depended on the purity of the metal. At 77° K, an additional narrow line, ≈ 1 Oe wide, was observed for the finest lithium.

INTRODUCTION

IN metals whose paramagnetism is associated with the conduction electrons, the EPR line width is determined completely by the spin-lattice relaxation time T_{sl}. The spin-spin relaxation is unimportant because of the high electron velocities and the relatively weak spin-spin interaction, and therefore the longitudinal and transverse relaxation times are equal: $T_1 = T_2$.[1] When particle size of such a metal is reduced, an additional mechanism begins to act due to the scattering of electrons on the surface of the particles. Consequently, the relaxation time T_2 decreases. A theoretical treatment of the paramagnetic relaxation in fine metal particles was first given by Dyson.[2] He showed that

$$1/T_2 = 1/T_{sl} + 1/T_s, \qquad (1)$$

where T_s is the relaxation time governed by the collisions of electrons with the surface of a particle. For spherical metal particles, T_s is given by

$$T_s = {}^4\!/_3 r / \varepsilon v, \qquad (2)$$

where r is the particle radius, v is the electron velocity on the Fermi surface, and ϵ is the probability of spin flip on collision with the surface of a particle.

The reduction in T_2 because of the electron collisions with the surface was observed first for sodium and lithium particles having a size of 5 μ.[3] However, the line broadening due to T_s was so small that it was within the experimental error. Schumacher and Vehse[4] observed the disappearance of the EPR line of very fine sodium particles, for which the nuclear resonance signal was observed. This was explained by the broadening of

the paramagnetic absorption line because of the small value of the time T_s for such fine particles. On the other hand, Garif'yanov[5] observed narrowing of the EPR line of lithium (95% pure) when the particle size was reduced from 50 to 0.1 μ. The results of Feher and Kip[3] and those of Schumacher and Vehse[4] are in qualitative agreement with the theory, but those of Garif'yanov[5] contradict the theory. All this made it impossible to compare accurately the theory with experiment.

More detailed experimental investigations of the electron relaxation in fine metal particles have, so far, met with the following difficulties: a) finely dispersed metals were obtained mainly by ultrasonic pulverization in molten paraffin wax and therefore the particle size extended over a wide range, the particles were not spherical, and the defects, produced in the particles by strong deformation, altered the electron relaxation times; b) the methods of preparing fine metal particles made it impossible to determine sufficiently accurately the particle size; c) in some cases the metals used were insufficiently pure. Our method of preparing finely dispersed metals overcame, to a great extent, all these difficulties.

In the present work, we investigated the influence of the size of spherical lithium particles on the width and profile of the paramagnetic resonance line. The average particle size varied from 6×10^{-5} to 6×10^{-6} cm.

PREPARATION OF THE SAMPLES

The initial material was lithium containing 0.015% K, 0.03% Na, 0.0001% Fe, and less than 0.0002% of other impurities. Technical lithium (98% pure) was also used in order to determine

the effectiveness of the refinement of lithium in
the process of preparing the sample, and the in-
fluence of impurities on the probability of the spin
flip of an electron on its collision with the surface.

Finely dispersed lithium was prepared by the
aerosol method, similar to that described in [6].
An aerosol, formed in an evaporator, was carried
away by a stream of inert gas and collected by
passing it through molten paraffin wax or a fabric
filter. In the former case, the samples were ob-
tained in the form of suspensions of lithium parti-
cles in paraffin; in the latter, in the form of a
powder collected in a sealed glass ampoule filled
with an inert gas. Additional refinement of the
lithium took place during the evaporation process.
For this purpose, the aerosol, containing, in the
first minutes after preparation a large amount of
volatile impurities, bypassed the filters. The re-
fractory impurities collected in the residue of the
drop being evaporated. The average lithium par-
ticle size was varied by using gases of different
molecular weights (argon, helium) and by vary-
ing the velocity of the gas stream passing through
the evaporator. To investigate the degree of dis-
persion of the particles, a collodion film was
placed for several seconds in the aerosol stream
and then this film was photographed in an electron
microscope. The degree of dispersion was deter-
mined by measuring and counting the particles in
the photographs, such as that shown in Fig. 1. The

particle size distributions obtained in this way
were always similar to that shown in Fig. 2. It is
evident from Fig. 1 that the particles were
spherical.

The electron paramagnetic resonance spectra
were recorded at 300 and 77° K with standard
apparatus of the ÉPR-2 type using high-frequency
(9350 Mc) modulation.

RESULTS AND DISCUSSION

Figure 3 shows the dependence of the line
width, determined from the maxima of the deriva-
tive of the absorption line, on the average particle
size. Curve I corresponds to samples prepared
from lithium containing less than 0.05% impurities,
while curve II represents technical lithium (98%
Li). The average particle size was determined
from the distribution curve given in Fig. 2 using
the formula $d_{av} = (\Sigma n_i d_i^3 / \Sigma n_i)^{1/3}$. In the less
pure lithium, the electrons suffer multiple colli-
sions with the impurity atoms before reaching the
surface of a particle. Therefore, the time between
electron collisions with the surface becomes

FIG. 1. Photograph of lithium particles prepared in argon.
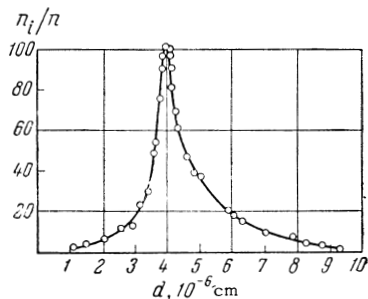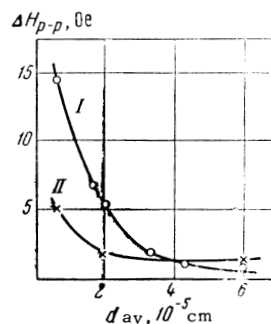Magnification 10^4.

FIG. 2. Size distribution of lithium particles. Preparation
conditions: helium gas; stream velocity 10 times greater than
in the case represented by Fig. 1 (n_i is the number of particles
of diameter d_i; n is the total number of particles.

FIG. 3. Dependence of ΔH_{p-p} on the average lithium par-
ticle diameter; H_{p-p} is the distance between the maxima of
the derivative of the absorption line. Curve I represents sam-
ples made from 99.95% pure lithium; curve II represents sam-
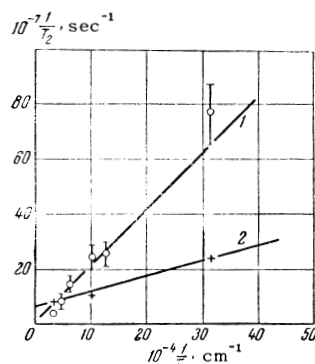ples prepared from technical lithium.

FIG. 4. Dependence of $1/T_2$ on $1/r$: curve I represents sam-
ples made from 99.95% pure lithium; curve II represents sam-
ples prepared from technical lithium.

longer and the relaxation governed by these colli-
sions correspondingly decreases. Using this, it is
easy to explain why Garif'yanov[5] did not observe
any line broadening at all in highly impure lithium
when the particle size was varied to 10^{-5} cm.

To determine the probability of the spin flip of
an electron on its collision with the surface and to
find the spin-lattice relaxation time, we plotted
the dependence of $1/T_2$ on $1/r$ (Fig. 4). The
spin relaxation time T_2 was determined in ac-
cordance with Dyson's work[1] as the quantity
inversely proportional to the paramagnetic reso-
nance line width ΔH; ΔH was found by calculating
the second moment of the absorption curve. Fig-
ure 4 shows that this dependence is linear, which
is in good agreement with the theoretical expres-
sion, obtained from Eqs. (1) and (2):

$$1/T_2 = 1/T_{sl} + \tfrac{3}{4}\,\varepsilon v/r.$$

We determined the quantities ϵ^{I} and ϵ^{II} from
the slopes of the straight lines I and II, and T_{sl}^{I}
and T_{sl}^{II}, from the intercepts of these lines on the
ordinate. Since, for lithium, $v = 1.3 \times 10^8$ cm/sec,
we found that $\epsilon^{I} = 2 \times 10^{-5}$, and $\epsilon^{II} = 7 \times 10^{-6}$; and,
correspondingly, that $T_{sl}^{II} = 1.6 \times 10^{-8}$ sec, and
T_{sl}^{I} was somewhat greater than 10^{-7} sec. The
value of ϵ^{I} was in good agreement with the esti-
mates of Feher and Kip.[3] They showed that the
spin-lattice relaxation time T_{sl} of lithium was
determined mainly by the relaxation on impurities.
They obtained $T_{sl} = 2 \times 10^{-8}$ sec for 99.9% pure
lithium. A comparison of this value with T_{sl}^{II}
$= 1.6 \times 10^{-8}$ sec showed that the impurity content
of technical lithium was reduced from 2% to 0.1%
in the process of preparing the sample.

Measurements at 77° K showed that the EPR
line broadened on cooling for all particle sizes.
The broadening was considerably weaker for sam-
ples prepared from technical lithium. Since the
broadening involved, mainly, an increase of the
absorption curve "wings," it was difficult to ob-
tain quantitative estimates.

Finally, we must consider a very interesting
effect, which also depended on the particle size
and on temperature, and appeared only in the
finest lithium powder obtained in our experiments.
Apart from the broad line, whose intensity was
independent of temperature, we observed at 77° K
a narrow signal whose g-factor was identical with
the g-factor of the conduction electrons (Fig. 5).
The width of the signal was ≈ 1 Oe. In recording
this signal, all precautions were taken to avoid
introducing paramagnetic impurities into the sam-
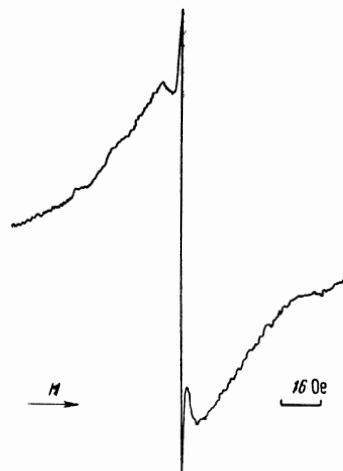ples. Ampoules in which the samples were placed

FIG. 5. Trace of the derivative of the absorption line of
finely dispersed lithium; $d_{av} = 6 \times 10^{-6}$ cm, $T = 77°$K.

were checked for the presence of such impurities,
and we used glass or polyethylene ampoules which
did not give a signal with $g = 2$. The signal was
not affected by substituting the powder samples
with the suspensions of lithium in paraffin. The
disappearance of the narrow signal simultaneously
with the broad line when the lithium oxidized
showed that the oxides could not be responsible
for its appearance. Repeated cooling of the sam-
ples to 77° K and subsequent heating to 300° K, or
annealing for a fortnight at room temperature,
had no influence on the intensity of this signal.
The narrow signal was not observed in samples
prepared from technical lithium.

We have not yet been able to explain this effect
within the framework of the existing theories. To
find the cause of the appearance of the narrow line,
it is necessary to carry out additional investiga-
tions of fine particles at lower temperatures.

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and I. F. Shchegolev for discussing the results.

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