CONDUCTION ELECTRON SPIN RESONANCE IN SMALL PARTICLES SUSPENDED IN SOLID MATRIX

J.-P. Borel, J.-L. Millet

► To cite this version:

J.-P. Borel, J.-L. Millet. CONDUCTION ELECTRON SPIN RESONANCE IN SMALL PARTICLES
SUSPENDED IN SOLID MATRIX. Journal de Physique Colloques, 1977, 38 (C2), pp.C2-115-C2-119.
10.1051/jphyscol:1977223 . jpa-00217062

HAL Id: jpa-00217062

<https://hal.science/jpa-00217062>

Submitted on 1 Jan 1977

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

CONDUCTION ELECTRON SPIN RESONANCE IN SMALL PARTICLES SUSPENDED IN SOLID MATRIX (*)

J.-P. BOREL and J.-L. MILLET

Laboratoire de Physique Expérimentale
Ecole Polytechnique Fédérale de Lausanne
CH-1007 Lausanne, Switzerland

Résumé. — De petites particules de lithium dispersées dans des matrices de CO_2 et de xénon ont été étudiées par R.P.E. Dans le cas du CO_2 on constate une influence importante de la matrice sur la forme du signal ainsi que sur sa position et sa largeur (ce qui n'est pas observé dans le cas du xénon).

Les échantillons contenant des particules de l'ordre de 1 000 Å ont une susceptibilité indépendante de la température, par contre, pour des particules plus petites (environ 30 Å par exemple) on a trouvé l'existence d'un domaine de température où se produit un passage de la susceptibilité de Pauli et une susceptibilité variant sensiblement comme $1/T$. Ce fait est conforme à des prévisions théoriques.

Abstract. — Small particles of lithium dispersed in matrices of CO_2 and xenon have been investigated using E.P.R. techniques. For the case of Li in a CO_2 matrix we have found that interactions associated with the matrix material affect both the line-width and the position of the resonance transitions. Such effects are not observed when a xenon matrix is employed. Samples for which the particle size exceeded 1 000 Å were characterized by a magnetic susceptibility which was independent of temperature. For smaller particles (e.g. 30 Å), however, a transition temperature region was found in which the susceptibility changes from a Pauli susceptibility to one which varies as $1/T$. These results are in agreement with previous theoretical predictions.

1. Introduction. — Previous work has indicated that the energy-level spectrum associated with conduction electrons in a very small metallic particle should be discrete. There are a number of interesting consequences which can arise from such a discrete energy-level structure, and effects of this type are generally termed *quantum size effects*. These effects have been discussed previously by a number of authors [1-5] who have shown that, in particular, when the mean-separation δ between two neighbouring energy levels is greater than kT , the behaviour of the magnetic susceptibility as a function of temperature will be very different depending on the parity of the ensemble of conduction electrons. Specifically, for an odd number of electrons at low temperature, one should observe a susceptibility which accurately follows the $1/T$ dependence of the Curie law. For an even number of electrons, depending on the assumptions which are made regarding the distribution of the electronic energy levels, one may observe a susceptibility which either approaches zero as the temperature goes to zero, or which maintains a value close to that of the bulk material to very low temperature.

When the mean-square separation of the energy levels is greater than the Zeeman energy, the

longitudinal relaxation of the electronic spins is impeded and this should result in an augmentation of the relaxation time T_1 . This effect has been confirmed by a number of experiments. For example, the paramagnetic resonance of small particles of lithium in irradiated crystals of LiF has been studied by C. Taupin [6]. Following an anneal of the LiF crystals, she observed a spectrum composed of very narrow resonance lines which increased in intensity as the temperature decreased. K. Saiki, *et al.* [7], have also used E.P.R. techniques to study lithium particles with diameters between 100 and 3 000 Å which were prepared by evaporation in a rare gas. For the particles whose diameter was greater than 1 000 Å, they found a broadening of the resonance line due to surface scattering effects (reverse scattering). For particles whose diameter was less than 1 000 Å, they observed a diminution in the resonance line width as the particle size decreased.

In our laboratory, we have studied small particles of lithium which were dispersed in a matrix of CO_2 [8]. In particular our results have established that for very small particles, the relaxation time T_1 as measured by the saturation method is not equal to the spin-spin relaxation time T_2 which may be deduced from measurements of the line widths. Additionally, the spin lattice relaxation time T_1 has been observed to decrease with decreasing temperature and with decreasing particle size.

(*) This work supported by the Swiss National Fund for Scientific Research under grant 2.377-0.75.

In the present work, we have prepared samples in which the CO_2 matrix has been replaced by xenon in order to obtain results which are more independent of the matrix properties. The spectra associated with small particles of Li dispersed in CO_2 and Xe matrices will be compared here and the details of the results obtained using xenon matrices will be presented.

2. Experimental technique. — The small-particle samples utilized in the present work were fabricated using the procedure described as follows: The lithium metal was evaporated in an evacuated chamber and condensed on a substrate which was maintained at low temperature. The matrix material (i.e. CO_2 or Xe) was condensed on the substrate simultaneously with the metal evaporation to form a sample consisting of small lithium particles suspended in the solid matrix. Following the evaporation procedure, the sample was scraped from the substrate into a cooled quartz tube which is then sealed under vacuum. For CO_2 matrices at 77 K we initially obtained an atomic dispersion of Li which then diffused during a subsequent anneal to form the small lithium metal particles. In the case of a xenon matrix we obtained the small particles directly even at a temperature of 63 K. The apparatus utilized for the preparation of small lithium particles in CO_2 is quite simple in principal and is shown schematically in figure 1. When the evaporation was complete, the upper tube shown in the figure is removed and the sample was scraped away so that it fell directly into liquid nitrogen. Even when they were not sealed under vacuum these samples were stable for a long period of time (more than one month). This convenience is not present for the case of the samples formed in a Xe matrix which apparently does not afford sufficient protection against oxidation of the small lithium particles. For this reason it was necessary to develop an apparatus considerably more complicated than that shown in figure 1 in order to continuously maintain the sample in high vacuum conditions or in an atmosphere of high-purity helium. The problem was resolved by using a quasi-spherical plexiglass glove box which could be evacuated to a pressure of less than 2×10^{-6} torr by using a high speed diffusion pump with a liquid nitrogen baffle. In order to prevent a deformation of the gloves, the vacuum was initially maintained on both sides of the glove input ports. The vacuum quality was controlled with a mass spectrograph (Micromass), and the residual gas was found to consist of the principal ingredients CO and He along with small quantities of CO_2 and traces of heavier elements. During the formation of the sample, we observed an increase in the pressure (to approximately 10^{-5} torr) which corresponded to the appearance of a xenon peak in the mass spectrum.

System for sample preparation using a CO_2 matrix.

FIG. 1. — Apparatus utilized for preparation of small particles in CO_2 matrix.

The actual sample preparation procedure was carried out as follows: The lithium metal was placed in an iron or tungsten boat which could be heated by a small furnace. In order to prevent a high rate of dissipation of the thermal energy, the furnace-boat assembly was isolated with boron nitride. A thermocouple which was soldered to the crucible was used in order to accurately and reproducibly control the evaporation rate. The xenon gas (purity 4N7) was introduced through a copper tube which has previously been carefully evacuated, and the flow rate of the gas was controlled with a Hasting's flowmeter. Both the xenon matrix and the lithium were condensed on a pyrex surface which was cooled to 63 K by solid nitrogen. The time required to produce a small particle-matrix sample was approximately 15 minutes. Following the evaporation and condensation process described above, high-purity (5N7) helium is introduced into the glove box, and at the same time, liquid argon is prepared on the glove-box lock chamber. The liquid argon is used to cool both the tools used to remove the sample from the pyrex substrate and the quartz tube to which the sample is to be transferred. These sample tubes have been previously degassed by heating for 24 hours under vacuum at a temperature of 300 °C. The tubes are fitted with valves which enable them to be removed from the chamber without exposing their interior to air. The removal of the sample from the substrate and the transfer into the quartz tubes are carried out in the helium atmosphere using special tools and solid neoprene gloves which are

sealed to the walls of the enclosure. Following the sample transfer, the quartz tubes are sealed under a vacuum of 10^{-6} torr and are stored in liquid nitrogen.

A determination of the size of the lithium particles produced as described above presents a difficult problem for the following reasons: First, the small Li particles are characterized by a low-contrast image in the electron microscope; second, the high reactivity of lithium makes the preparation of a suitable microscope grid quite difficult; and finally, the evaporation of the lithium itself in the beam of the electron microscope is enhanced when the particle size is very small (i.e. the vapour pressure of small particles is increased due to a thermodynamics size effect). In spite of these difficulties, a direct measurement with the electron microscope yields acceptable results when the particle size is greater than 100 Å. For smaller particles, however, the direct method only furnishes an order of magnitude result. Accordingly, a second method has been employed in order to measure the sizes of the very small particles.

In the following, we will show that the small lithium particles have a magnetic susceptibility which is accurately described by a Curie law. Accordingly, it may be assumed that the susceptibility is due principally to those small particles which have an odd number of conduction electrons and that each of these particles represents a paramagnetic center. If we make the assumption that the sample is composed of particles with an equal probability of having an even or odd number of conduction electrons, then from a measurement of the magnetic susceptibility and of the total mass of lithium contained in the sample it is possible to determine the number of atoms per Li particle. These results have been found to be in agreement with those obtained by electron microscopy.

The E.P.R. measurements have been made using a Varian E-Line spectrometer which was equipped with an Oxford Instruments variable temperature, flowing helium gas cryostat. Additionally, in order to determine the line width under low magnetic field conditions, a number of measurements have been made using a frequency of 500 MHz.

3. Results with a CO₂ matrix. — Some of the results obtained using a CO₂ matrix have been the subject of a previous publication [8]. Essentially, these results have established that the relaxation time T_1 as measured by the saturation technique, increases as the particle size diminishes. For example, for particles having diameters between 7 and 12 Å, measurements at 500 MHz yield a value of $T_1 = 4 \times 10^{-6}$ s, while for particles with a diameter of 15 Å a value of $T_1 = 2.8 \times 10^{-7}$ s was obtained. Additionally, it was found that the relaxation time increased as the temperature

decreased. The E.P.R. line-width, on the other hand, was found to be practically independent of the temperature. The experimentally determined line width is much larger than that calculated based on the assumption that $T_1 = T_2$. Between 500 MHz and 35 GHz an inhomogeneous broadening of the line was observed. The spectrum obtained at a frequency of 9 GHz for Li particles whose average size was 15 Å is shown in figure 2c. The structure which is apparent in this figure is attributed to an interaction between the CO₂ matrix and the small particles.

FIG. 2. — E.P.R. spectrum of Li in CO₂ matrix; a) Li atoms (Gain $\times 1$); b) Li atoms and small particles (central line) (Gain $\times 20$); c) Small particles (Gain $\times 100$).

The spectrum obtained before the sample had been annealed is shown in figure 2a. Where the hyperfine structure due to the isotopes ⁶Li and ⁷Li is clearly resolved. We have determined a value of $A = 31$ MHz for the hyperfine constant of Li in CO₂. This value is much smaller than the values of $A = 401.77$ MHz and $A = 264$ MHz previously determined for the free atom and for Li in argon respectively [9]. Figure 2b shows the spectrum obtained following an intermediate anneal and the spectra due to Li atoms and to small particles are simultaneously present. The results noted above motivated us to look for improved experimental conditions which led, in turn, to the production and study of small Li particles in a rare gas matrix.

4. Results with a xenon matrix. — Xenon was chosen as the rare gas matrix material since it forms

a solid at liquid nitrogen temperatures. Additionally, the low vapour pressure of Xe enabled us to use the previously established method of sample preparation without major modifications. During the sample preparation process, the substrate temperature must not exceed 63 K, but this temperature is easily achieved by pumping on liquid nitrogen.

The E.P.R. spectrum for a sample in which the small Li particles had a diameter of approximately 32 Å is shown in figure 3. The resonance line is

FIG. 3. — E.P.R. spectrum for a sample of small Li particles of diameter of approximately 32 Å in Xe matrix.

obviously quite narrow and has a g -value equal to 2.0023. The effects associated with the matrix which were evident in the case of CO₂ have apparently been drastically reduced. In our measurements, depending on the size of the particles, we have observed lines whose peak-to-peak widths (in a first-derivative presentation) were between 0.55 and 12.5 gauss. These values compare favorably with those obtained by Saiki, *et al.* The line-width of 12.5 gauss which was observed for Li particles whose average diameter was slightly larger than 1000 Å is a little greater than that observed by other authors, but the values are, in any event, comparable. Results for particles with diameters less than 100 Å were not given in the work of Saiki, *et al.* For this particle-size region, we have found E.P.R. spectra where the line-width was of the order of 0.6 to 1.0 gauss. It should be noted that these experimentally-determined values are clearly smaller than those associated with considerations of the mechanism of *nuclear contact hyperfine broadening* as discussed by Gordon [10].

E.P.R. techniques have been employed in the present work to measure the magnetic susceptibility of Li particles as a function of temperature. For those particles having line widths which were

relatively large (e.g. 5 to 10 gauss) we have found a Pauli-type susceptibility in the temperature region between 2 and 120 K. For smaller particles at low temperature a Curie-type susceptibility was observed and, at higher temperatures a Pauli-type behaviour was found. Results illustrating this effect are shown in figure 4 for lithium particles with a

FIG. 4. — Normalized susceptibility vs reduced inverse temperature δ/kT of small Li particles in Xe matrix.

diameter of about 32 Å. In this figure the ratio χ/χ_p of the measured susceptibility to the Pauli susceptibility is shown as a function of the reduced inverse temperature δ/kT . (Here δ is the inverse of the density of states at the Fermi level.) These experimental results clearly establish the existence of a transition temperature region in which the susceptibility changes from a Pauli- to a Curie-type behaviour and, accordingly, they qualitatively confirm the previous theoretical predictions. The precision of the current measurements and the existence of a particle size distribution in the sample does not, at present, permit a distinction to be made between the different possibilities which have been proposed for the energy-level distribution (i.e. to distinguish between an orthogonal, symplectic, unitary, or random distribution). A phenomenon similar to that noted above has recently been described by Marzke [11] *et al.*, for the case of 22 Å platinum particles dispersed in a gelatine matrix. For even smaller particles (approximately 10 Å) Monot [12] has found a Curie type susceptibility between 8 and 190 K. These cumulative results enable us to conclude that a quantum size effect exists when the condition $\delta > kT$ is satisfied.

Acknowledgments. — We wish to thank the Interdepartmental Institute of Metallurgy of the E.P.F.L. for the electron micrographs.

References

- [1] KUBO, R., *J. Phys. Soc. Japan* **17** (1962) 975.
- [2] DENTON, MÜHLSCHLEGEL, R., SCALAPINO, B., *Phys. Rev. B* **7** (1973) 3589.
- [3] KAWABATA, A., *J. Phys. Soc. Japan* **29** (1970) 902.
- [4] BOREL, D., DOLIVO, J., BOREL, J.-P., QUATTROPANI, A., *Nuovo Cimento* **26** (1975) 272.
- [5] FRÖHLICH, H., *Physik* **4** (1937) 406.
- [6] TAUPIN, C., *J. Phys. & Chem. Solids* **28** (1967) 41.
- [7] SAIKI, K., FUJITA, T., SHIMIZU, Y., SAKOH, S., WADA, N., *J. Phys. Soc. Japan* **32** (1972) 447.
- [8] BOREL, C., BOREL, J.-P., MONOT, R., *Helv. Phys. Acta* **47** (1975) 537.
- [9] PAKE, G. E. and ESTLE, T. L., *The Physical Principles of Electron Paramagnetic Resonance* 2nd ed. (Benjamin, Reading, Mass.) 1973, 241.
- [10] GORDON, D. A., *Phys. Rev. B* **13** (1976) 3738.
- [11] MARZKE, R. F., GLAUSINGER, W. S., BAYARD, M., *Solid State Commun.* **18** (1976) 1025.
- [12] MONOT, R., NARBEL, C., BOREL, J.-P., *Nuovo Cimento B* **19** (1974) 253.