JUN 28 1966

ELECTRON PARAMAGNETIC RESONANCE STUDIES OF ELECTRON-IRRADIATED
LITHIUM SULFATE AT LIQUID NITROGEN TEMPERATURE⁺

MASTER

by

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ABSTRACT

Single crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ with controlled concentrations of Li^7 - and Li^6 -isotopes have been irradiated in beams of 1 Mev electrons at 77°K. Studies of the Li-isotope effect on the electron paramagnetic resonance (EPR) absorption of the irradiated samples at 77°K have revealed that the Li-isotopes do not affect the anisotropy of the angular-dependent EPR spectrum investigated previously by Wigen and Cowan.¹ The results seem to support Ovenall's view² that the Li nucleus is not significantly involved in the nuclear hyperfine interaction responsible for the spectrum.

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⁺Work supported by the U. S. Atomic Energy Commission
Contract No. AT(11-1)-1054.

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ABZIEHUNG

Einkristalle von $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ und $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ mit kontrollierten Konzentrationen von Li^7 - und Li^6 -isotopen sind mit 1 Mev Elektronen bei 77°K bestrahlt worden. Untersuchungen über den Einfluss von Li-Isotopen auf die Absorption der elektronen-paramagnetischen Resonanz (EPR) von bei 77°K bestrahlten Proben zeigen, dass die Li-Isotope nicht die Anisotropie der winkelabhängigen EPR Spektren beeinflussen, die früher von Wigen and Cowan¹ untersucht worden sind. Die Ergebnisse scheinen die Ansicht von Ovenall² zu erhärten, dass der Li-Kern nicht wesentlich zu der Kern-hyperfein-wechselwirkung, die für das Spektrum verantwortlich ist, beiträgt.

Recently, Wigen and Cowan¹ have studied the electron paramagnetic resonance (EPR) absorption of single crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$, which were irradiated in beams of 1 Mev electrons at 77°K. Two distinct EPR spectra have been observed: one is anisotropic with regard to the orientation of the samples in the magnetic field, H, while the other is isotropic and centered at approximately the free electron g-value. The anisotropic spectrum has been described in terms of the following spin Hamiltonian pertaining to a "hole" with spin $S=1/2$ interacting with a proton of spin $I=1/2$:

$$\mathcal{H} = \beta \vec{S} \cdot \vec{g} \cdot \vec{H} + \vec{S} \cdot \vec{A} \cdot \vec{I}. \quad (1)$$

The g-tensor has been found to be axially symmetric, while the hyperfine tensor A has been found to deviate from axial symmetry. In order to account for the observed deviation of A from axial symmetry, Wigen and Cowan have postulated the contribution to A of an additional hyperfine interaction of the "hole" with a Li nucleus of spin 3/2. Subsequently, however, the hole model and the postulate in particular have been disputed theoretically by Ovenall.²

The purpose of the present work is to determine experimentally a possible contribution of the disputed hyperfine interaction with the Li nucleus to the tensor A in Eq. (1).

Single crystals of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{D}_2\text{O}$ with controlled relative concentrations of the Li-isotopes (Li^7 and Li^6) have been grown from liquid solutions of the salt. Subsequently, these samples have been

irradiated in beams of 1 Mev electrons at 77°K , and kept at the same temperature. EPR spectra of the irradiated samples have been investigated at 77°K without warming by means of a Varian Associates Model 4500-10A EPR spectrometer operated in the X-band of microwave frequencies with 400 cps magnetic field modulation. The first derivative of the EPR absorption has been recorded.

Figure 1 illustrates a typical EPR spectrum from a sample of Li_2^6SO_4 containing a mixture of H_2O and D_2O . The magnetic field is perpendicular to the two-fold b-axis of the monoclinic lattice of the sample, and makes an angle of 30° with the a-axis. The two lines labelled as h_1 and h_2 are characteristic to the monohydrated samples, while the three lines labelled as d_1 , d_2 , and d_3 , to the monodeuterated samples. The isotropic line observed by Wigen and Cowan has also been observed in the present work, but its intensity is very weak. In Fig. 1 it is masked by the h_2 line. The observed angular dependence of the doublet (h_1 , and h_2) and the triplet (d_1 , d_2 , and d_3) is illustrated in Fig. 2.

The doublet, the triplet and the isotropic line seem to correspond to the proton hyperfine structure, the deuteron hyperfine structure and the isotropic line of the spectra investigated by Wigen and Cowan (simply W-C spectra in the following). However, there are some discrepancies between the present spectra and the W-C spectra. First, the g-tensor of the doublet and the triplet of the present spectra is not identical to the corresponding g-tensor of the W-C spectra. Secondly, the separation between the two lines of the doublet is approximately 2 times larger than that of the proton structure of the

W-C spectra. Otherwise, the present spectra appear to be very similar to the W-C spectra. Table I compares some data pertaining to the two spectra.

The anisotropy of the doublet and the triplet and their positions relative to the isotropic line have been found to be the same for all combinations of the H-isotopes and the Li-isotopes. The only noticeable effect of the Li-isotopes on the doublet and the triplet is that the width of the doublet lines and the triplet lines of the Li^6 -doped samples is narrower than the width of the corresponding lines of the Li^7 -doped samples. This result indicates that the hyperfine interaction with the Li nucleus does not significantly affect the position and anisotropy of the doublet and the triplet. Consequently, the result of the present work verifies Ovenall's view² that the hyperfine interaction with the Li nucleus is not responsible for the deviation of the A tensor from axial symmetry.

References

1. Wigen, P. E., and Cowen, J. A., J. Phys. Chem. Solids 17, 26 (1960).
2. Ovenall, D. W., J. Phys. Chem. Solids 21, 309 (1960).

Captions

- Fig. 1: EPR spectrum of $\text{Li}_2^{6}\text{SO}_4$ containing a mixture of H_2O and D_2O , electron irradiated at 77°K . The magnetic field is perpendicular to the b-axis and makes an angle of 30° with the a-axis. (+) indicates the free electron g-value.
- Fig. 2: The observed anisotropy of the EPR spectrum. The ordinate, ΔH , indicates the position of the lines relative to the isotropic line located approximately at $g=2.0023$ and the angle is in degrees.
- (a) Rotation about the b-axis
 - (b) Rotation about an axis perpendicular to the a-b plane.
- In this case, there are six lines due to the triplet. Because of their complexity, they are not shown.

Table 1

Comparison of g-Tensor

	W-C ⁺	A-K [*]
Polar angle measured from b-axis	69.3°	74.5°
Azimuthal angle measured from a-axis	-46.8°	-40°
$g_{\perp}$	2.002±.001	2.006±.001
$g_{\parallel}$	2.040±.001	2.066±.001

⁺Ref. 1.

^{*}Present experiment.

FIG 1