

In the infrared absorption of ammonium sulfate⁵ there are two characteristic features below its Curie point. The 3.3μ band due to the NH_4^+ shows a change similar to that in the transition region of ammonium chloride. At the same time, the absorption spectrum due to the SO_4 tetrahedra shows a similar rearrangement. One could therefore assume that an ordinary ammonium transition acts as a trigger to induce a moment in the SO_4^{--} groups. The mechanism would be thus strongly reminiscent of the one causing ferroelectricity in KH_2PO_4 as described by Slater.⁶ This point of view suggests a formal similarity among the ferroelectric sulfates thus far encountered regardless of crystal structure or water of crystallization. The role of ammonium is played by guanidinium in GASH, by methylamine or urea in some alums, and by glycine in the material here reported.

We want to thank A. N. Holden for his critical reading of this paper.

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² B. T. Matthias and J. P. Remeika, *Phys. Rev.* **103**, 262 (1956).

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⁵ R. Pohlman, *Z. Physik* **79**, 394 (1932).

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Nuclear Resonance Saturation Effects and Multiple-Quantum Transitions

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THE theory presented by Bloch¹ indicates that different lines of a spectrum observed by using high-resolution nuclear magnetic resonance techniques may have different relaxation times. Differences in line widths within a spectrum have been observed²⁻⁴; however, in many cases magnetic field inhomogeneities prevent quantitative measurements. Saturation techniques may be employed to demonstrate differences in relaxation times even though magnetic field inhomogeneities may obscure the natural widths.

A simple case treated by Bloch¹ is a nuclear spin system consisting of two identical nuclei with spin $\frac{1}{2}$ and Larmor frequencies which differ because of a chemical shift. The molecule 2-bromo-5-chlorothiophene is of this type and its spectrum under conditions of low radio-frequency fields has been previously investigated.³ Interesting modifications of this spectrum have been observed with radio-frequency fields of large amplitudes by using a Varian Model 4300 Spectrometer with a 30-Mc radio-frequency unit.

Spectra obtained at three different levels of radio-frequency power are shown in Fig. 1. Spectrum (a) was made with a radio-frequency field low enough to avoid

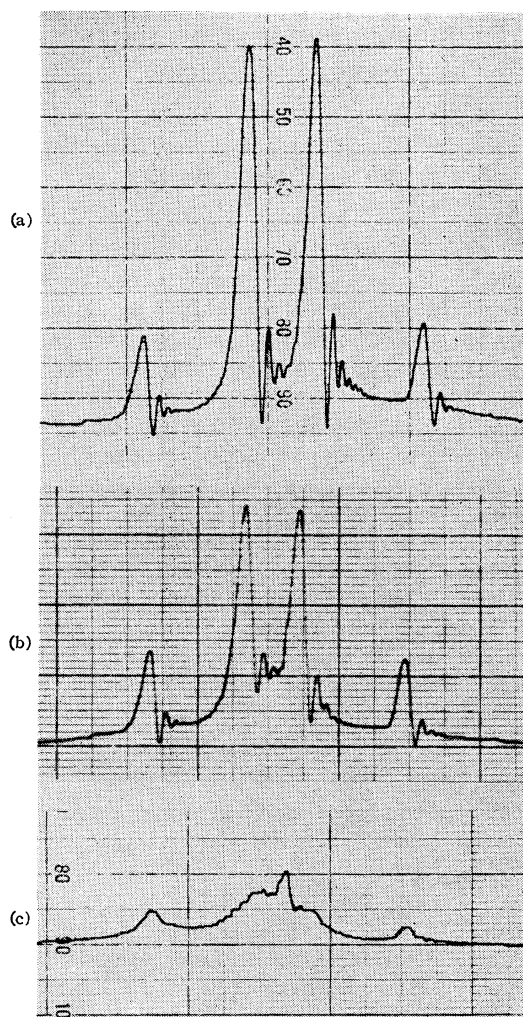


FIG. 1. Nuclear magnetic resonance spectra of 2-bromo-5-chlorothiophene. (a) Spectrum taken using low radio-frequency power. (b) Radio-frequency field increased by approximately 3.4 with a corresponding decrease in radio-frequency amplifier gain. (c) Radio-frequency field increased by another factor of 3.4 with a corresponding decrease in radio-frequency amplifier gain. The spacing between the two extreme peaks is approximately 10 cps at 30 Mc/sec and the sweep rate is approximately 5 cps/min.

saturation of any of the lines. In spectrum (b) the radio-frequency field has been increased by a factor of approximately 3.4 while the gain of the receiver has been decreased by the same factor. The size of the outside pair of lines is nearly the same in both spectra, indicating that they are not saturated, while the height of the central pair of lines has decreased by approximately 35%. Spectrum (c) was obtained upon increasing the radio-frequency field by another factor of approximately 3.4 with a corresponding decrease in receiver gain. Here the outside pair of lines have also been partially saturated.

Bloch¹ has shown that for well-resolved lines the nuclear resonance signal for a transition between levels

(a) and (b) is proportional to

$$\frac{\gamma^2 H_1 (T_2)_{ab} (b|m^+|a)^2 [1 + i\Delta\omega (T_2)_{ab}]}{1 + [\Delta\omega (T_2)_{ab}]^2 + T_{ab} (T_2)_{ab} \gamma^2 H_1^2 (b|m^+|a)^2 / 4}, \quad (1)$$

where the terms are defined in reference 1. Since the two outer lines as well as the two central lines have, to within experimental error, identical saturation characteristics, the molecular surrounding responsible for relaxation must be nearly the same at the two protons. With this assumption, each quantity T_{ab} and $(T_2)_{ab}$ is the same for all transitions. By using the values for the matrix elements $(b|m^+|a)^2$ as determined at low radio-frequency fields, the experimental data have been found to be consistent with Eq. (1).

Another interesting feature in spectrum (c) is the appearance of a line at the center of the spectrum occurring only at large radio-frequency fields. This line is attributed to a double-quantum transition and is understood qualitatively by an analysis similar to that used to describe multiple-quantum transitions as observed in molecular beam experiments.^{5,6} A quantitative explanation must however include the effects of relaxation.

Multiple-quantum transitions have also been observed in the spectrum of *p*-chlorobenzoyl chloride. A more complete report of this effect will be published later.

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⁴ See also Varian Tech. Information Bull. **1**, No. 4.

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Electron Irradiation of Copper below 10°K

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THE problem of determining the nature, number, and physical effects of crystal imperfections introduced by high-energy radiation has not yet been completely solved for even those systems which have been studied the most extensively.¹⁻³ Although it has been realized for some time that bombardment with high-energy electrons at ambient temperatures near absolute zero probably provides the simplest type of damage situation to study, experiments of this kind have not heretofore been reported. We have, therefore, undertaken a study of the changes produced in pure metals under these conditions. This letter reports the change in electrical resistivity in a thin, high-purity copper foil bombarded below 10°K by 1.35-Mev electrons. Pre-

liminary data on the subsequent annealing of the resistivity change are also reported.

In order to execute *in situ* measurements of resistivity, temperature, and lattice parameter, and perform isothermal annealing, the specimen foil is supported in a stream of helium. The cylindrical cryostat is fitted with a side arm providing entrance and collimating windows, specimen locating pins, and the specimen holder. The specimen (0.0032 cm foil) is supported from its ends in a cylindrical Be-Cu pill box with 8×10^{-3} -in. Be windows normal to the vertical electron beam. The specimen temperature is regulated by adjusting the He flow rate through the pill box and also during annealing by an external heater on the Cu pill box. Thermometry is provided by carbon thermometers in the entrance and exit He streams, a thermocouple in the He stream adjacent to the specimen and one attached to the pill box, and the resistance of the specimen.

Copper obtained from American Smelting and Refining (99.999% pure) was zone-refined, cold-rolled to 0.0032 cm, and annealed to form the specimen foil. The specimen was photoengraved from this foil with attached potential and current leads. The resistance was determined from both beam-on and beam-off potential measurements on both the irradiated and unirradiated sections of the foil. A residual bulk resistivity of 1.5×10^{-9} ohm cm for the specimen was obtained by measurements of the residual resistance at 4.2°K and the room temperature resistance. The resistivity at 0°K was taken to be 1.55×10^{-6} ohm cm.

The electron accelerator is of the resonant-transformer type producing a chopped-sine-wave voltage pulse 34° wide. The electron energy was determined from the Be(γ, n) (1.655 Mev) reaction and an electrostatic voltmeter. The current was measured with a Faraday cage and checked by a calorimetric beam heating experiment.

TABLE I. Run V: Resistivity change with electron flux.

Elapsed time (in min)	Resistivity change ^a (10^{-10} ohm cm)	Resistivity change per unit time (10^{-12} ohm cm/min)
71	1.79	2.52
116	2.92	2.52
208.7	5.27	2.53
277.6 ^b	6.99	2.52

^a Corrected for thin-film scattering by using values from E. H. Sondheimer [Advances in Phys. **1**, 1 (1952)] assuming diffuse reflection at surfaces.

^b Integrated flux of 8.39×10^{18} electrons/cm².

Table I shows the results of the longest irradiation which has been made to date. The fact that this run, which was made at an ambient temperature 15°K, gives essentially the same value for the resistivity change per (electron/cm²) as earlier runs taken with lower beam currents and ambient temperatures <8°K demonstrates that the temperature of the sample is not raised high enough by the beam to cause annealing. From this experiment and the linearity of resistivity change with

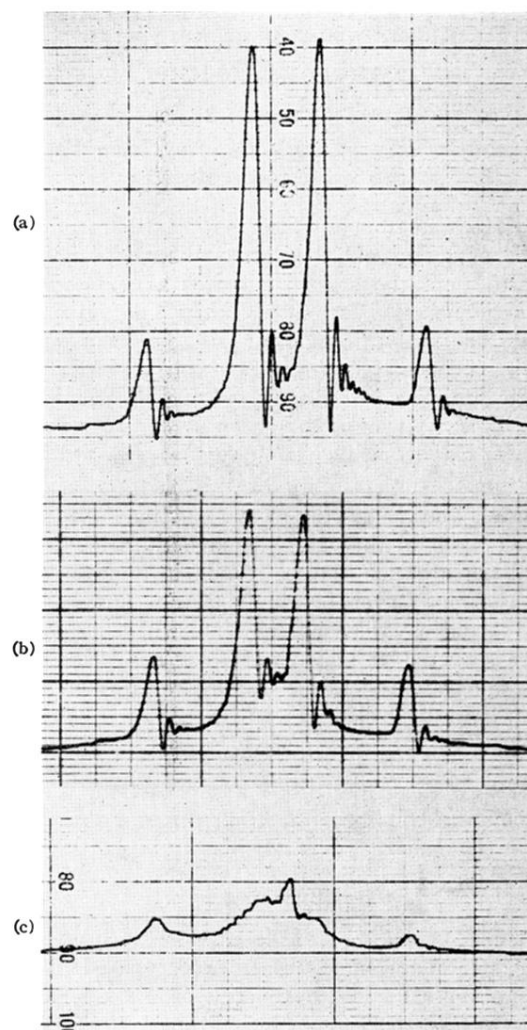


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