

A single crystal of tellurium, a piezoelectric element with the same symmetry, 32, as quartz, also yields boundary harmonics of the same order of magnitude as GaAs. A characteristic variation of $\vartheta(2\nu)$ is obtained for rotation about the normal, which coincides with the trigonal axis. When the incident field $E_1(\nu)$ is perpendicular to the axis, one polarization of the reflected harmonic beam has zeros at $\psi=0$ and π , the other polarization at $\psi=\frac{1}{2}\pi$ and $\frac{3}{2}\pi$.

A program is planned to determine the dispersion of the nonlinear index of refraction of many III-V and II-VI compounds with $\bar{4}3m$ symmetry. This new method will give additional information about the structure of the optical absorption bands in these materials. Many other features of the BP theory will also be subjected to experimental verification.

The assistance of Dr. J. A. Armstrong in

building the experimental arrangement is gratefully acknowledged. The crystal of tellurium was kindly given to us by Professor Aigrain and Dr. Rigaux of the University of Paris, Paris, France.

*This research was supported jointly by the U. S. Office of Naval Research, the U. S. Army Signal Corps, and the U. S. Air Force.

¹N. Bloembergen and P. S. Pershan, Phys. Rev. 128, 606 (1962), hereafter referred to as BP.

²B. Lax, J. G. Mavroides, and D. F. Edwards, Phys. Rev. Letters 8, 166 (1962).

³J. A. Armstrong and J. Ducuing, Bull. Am. Phys. Soc. 8, 233 (1963).

⁴All angles occurring in this equation are constant in the present experiment. Note that θ_T and θ_S are complex in an absorbing medium.

⁵R. Kronig and J. I. Boukema, Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B 66, 8 (1963).

Cl nmr IN ANTIFERROMAGNETIC $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

W. J. O'Sullivan, W. W. Simmons, and W. A. Robinson
Space Technology Laboratories, Incorporated, Redondo Beach, California
(Received 22 April 1963)

While $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ qualifies as the most frequently studied antiferromagnet, only the proton nmr¹⁻³ has been observed below T_N (4.32°K). In contrast with the protons which are coupled to the magnetic system through long-range dipolar interactions, the Cl^- valence electron distributions are modified by the formation of a partial covalent bond with neighboring Cu^{++} ions. Hence, the chlorine nmr will be importantly influenced by short-range magnetic interactions dominated by the effective hyperfine coupling with nearest-neighbor copper ions.

In this Letter we wish to report the preliminary results of observations of the Cl^{35} and Cl^{37} zero external field nmr in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ within the temperature range 1.3°K-4.24°K. Initial theoretical analysis of the observed nmr frequencies predicts an internal magnetic field of 28.00 ± 0.50 kG at a chlorine nuclear site in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at 0°K. The temperature dependence of the departure of the internal field from the estimated saturation value displays a T^4 dependence within the temperature range $1.4^\circ\text{K} \leq T \leq 3.8^\circ\text{K}$, in agreement with the zero-field proton nmr measurements of Poulis et al.³

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ has an orthorhombic unit cell,

space group D_{2h}^7 . The b axis is a common principal axis for both the Cl site and the electric field gradient (EFG) and effective hyperfine interaction tensors. There are two distinguishable chlorine sites per unit cell, related by symmetry operations in such a way that their EFG are equivalent in the general sense (principal axis systems identical but rotated relative to each other). Below 4.32°K, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ orders antiferromagnetically with the sublattice magnetization vectors lying in ac planes, either along the a axis² or canted slightly from the a axis.⁴

The resonances were studied in a single-crystal sample (≈ 0.1 cm³) using externally quenched superregenerative detectors and sine-wave magnetic field modulation. The frequency range 2.5 Mc/sec-40 Mc/sec was covered. Attempts to detect the Cl nmr with marginal oscillator or pulse techniques proved unsuccessful. While it was not possible to determine an accurate value for the linewidth from the rather complicated recorder tracings of the resonances (the total pattern width ≈ 140 kc/sec), the estimated linewidth is ≈ 40 kc/sec for all the observed transitions with no detectable temperature variation through the range $1.3^\circ\text{K} < T < 5.1^\circ\text{K}$ and at $T = 77^\circ\text{K}$. It was

not possible to achieve observable sideband separation, even at the maximum quenching frequency, 120 kc/sec. Previously reported Cl nmr linewidths in paramagnetic-antiferromagnetic materials are much narrower.⁵ For example, the Cl³⁵ nmr linewidths in CoCl₂·2H₂O⁶ (nearly isomorphic to CuCl₂·2H₂O) and CoCl₂·6H₂O⁷ at 77°K are 7 kc/sec and 5 kc/sec, respectively.

The observed Cl nmr frequencies are plotted as functions of temperature in Fig. 1. A total of three Cl³⁵ and three Cl³⁷ lines were detected and followed as the temperature was varied. The Cl³⁷ nmr's were observed over temperature ranges just wide enough to make their identification definite. The temperature ranges through which the Cl³⁵ nmr's [(A), (B), (C) in Fig. 1] were detected are (A) 1.35°K-4.24°K; (B) 1.35°K-4.15°K; (C) 1.35°K-3.82°K. Sharply reduced signal/noise with increasing temperature limited observation of (C) to temperatures ≤3.82°K and (B) to ≤4.15°K.

Assignment of the observed nmr to specific transitions between Cl nuclear spin levels is non-trivial. The asymmetry parameter, η , has not

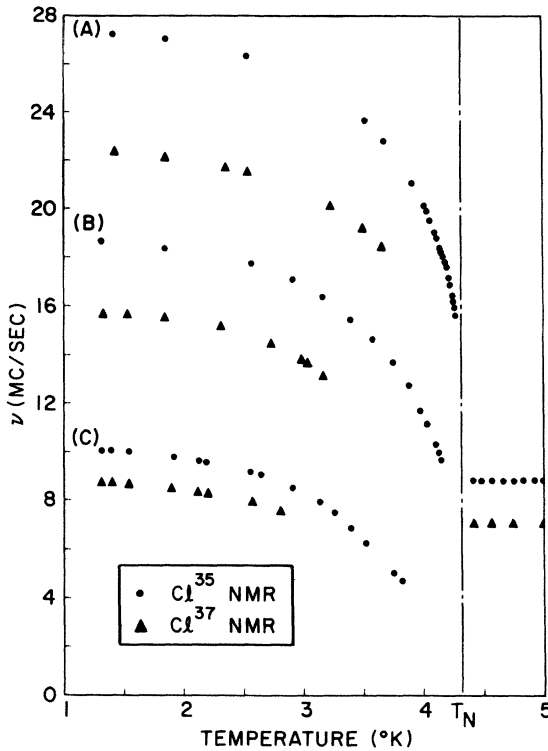


FIG. 1. Observed Cl nmr frequencies as a function of temperature in antiferromagnetic CuCl₂·2H₂O. The Cl³⁵ and Cl³⁷ pure quadrupolar frequencies at 4.4°K are, respectively, 8.98 Mc/sec and 7.00 Mc/sec.

been measured, nor have we determined the rotation angle between the EFG principal axes lying in the *ac* plane and the *a* axis. In addition, the magnetic and quadrupolar contributions to the Cl nuclear spin Hamiltonian are roughly equivalent in magnitude throughout the temperature range covered. Hence, the total Hamiltonian,

$$H = [e^2 q_{z,z} \text{Cl} \text{Cl} / 4I(2I-1)] [3I_z^2 - I(I+1) + \frac{1}{2}\eta(I_+^2 + I_-^2)] - (\frac{1}{2}\gamma_N \text{Cl} \hbar) H_{\text{eff}}(T) \times [2I_z \cos\theta + (I_+ e^{-i\varphi} + I_- e^{i\varphi}) \sin\theta], \quad (1)$$

must be diagonalized. In (1) we have replaced the combined magnetic dipolar and hyperfine terms at a Cl site by a temperature-dependent effective field, $H_{\text{eff}}(T)$. The angles θ, φ relate the direction of $H_{\text{eff}}(T)$ to the Cl nuclear EFG principal-axis system. In the spirit of a first approximation, we assume that only the magnitude of $H_{\text{eff}}(T)$ changes with temperature, i. e., θ, φ remain constant. Further, since $H_{\text{eff}}(T)$ lies in the *ac* plane, $\cos 2\varphi$, the only factor in the resultant eigenvalue equation⁸ with φ dependence, has either the value +1 or -1. The eigenvalue equation for the $I=3/2$ system was solved, using a combination of graphical and hand calculator techniques, for $\varphi=0^\circ$ and 90° and a net of η and θ values as a function of the parameter

$$\xi(T) = \frac{\gamma_N \text{Cl} H_{\text{eff}}(T)}{3e^2 q_{z,z} \text{Cl} \text{Cl} / 2I(2I-1)}. \quad (2)$$

In the limit as $\xi \rightarrow 0$, the eigenvalue spectrum coalesces into two doubly degenerate levels separated by the pure quadrupolar resonance frequency. For $T > 4.32^\circ\text{K}$ in CuCl₂·2H₂O,

$$(E_{\pm 1/2'} - E_{\pm 3/2'}) / \hbar = 3e^2 q_{z,z} \text{Cl} \text{Cl} (1 + \frac{1}{3}\eta^2)^{1/2} / 2\hbar I(2I-1) = 8.98 \text{ Mc/sec (Cl}^{35}\text{)},$$

and

$$= 7.00 \text{ Mc/sec (Cl}^{37}\text{)}. \quad (3)$$

The factors $q_{z,z} \text{Cl} \text{Cl} (1 + \frac{1}{3}\eta^2)^{1/2}$ are identical to within the sensitivity of our measurements (± 50 kc/sec) at 4.4°K and 77°K, and were considered temperature independent below the Néel point. The theoretical transition frequencies for fixed η and θ , $\cos 2\varphi = +1$ or -1 , were compared to the three observed Cl³⁵ nmr frequencies over their

respective temperature ranges, and then required to predict the Cl^{37} nmr frequencies as functions of temperature using the relation $\xi(T)_{\text{Cl}^{37}} = 1.068 \times \xi(T)_{\text{Cl}^{35}}$. The best fit between experiment and theory was determined for the combination of parameters $\eta = 0.2$, $\theta = 30^\circ$, $\cos 2\theta = -1$ (V_Z, Z and V_Y, Y in the ac plane), where η was varied in increments of 0.1 within the limits (0, 1), and θ in increments of 2° from 20° to 45° . The maximum deviation between any one observed transition frequency and its theoretically predicted value for the selected set of parameters was ± 250 kc/sec for $1.35^\circ\text{K} \leq T \leq 3.5^\circ\text{K}$, increasing to ≈ 500 kc/sec for $T > 4^\circ\text{K}$. The assignment of the observed frequencies to transitions between particular eigenstates of (1) may be made without ambiguity. We identify each level by two labels, the primed labels characterizing the state in the limit $\xi \rightarrow 0$ and the unprimed in the limit $\xi \rightarrow \infty$. If we assume $q_{z,z} \text{Cl} \text{Cl} < 0$, the transitions and the states they connect are (A) $(+3/2', +3/2) \rightarrow (+1/2', -1/2)$; (B) $(-3/2', +1/2) \rightarrow (-1/2', -3/2)$; (C) $(-3/2', +1/2) \rightarrow (+1/2', -1/2)$. The transition $(+1/2', -1/2) \rightarrow (-1/2', -3/2)$ has not been detected, as yet. That the signal/noise for (C) deteriorated much more rapidly with increasing T than either (A) or (B) is probably related to the fact that transition (C) approaches a β transition, while (A) and (B) each approach α transitions as $\xi \rightarrow 0$.

The value of $H_{\text{eff}}(0)$ at a Cl site in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in the limit as $T \rightarrow 0^\circ\text{K}$ was determined from the extrapolated experimental curves to be 28 ± 0.50 kG [$\xi_{\text{Cl}^{35}}(0) \cong 1.300$], where the quoted error corresponds to the maximum frequency deviation between the experimental frequencies extrapolated to 0°K and theory. The temperature dependence of $H_{\text{eff}}(T)$ at a Cl site is identical to that of the field at the proton positions, within the accuracy limits of our measurements and associated analysis. Figure 2 consists of a plot of $\log[\nu_H(0) - \nu_H(T)]$ for Cl^{35} as a function of $4 \log T$, with $\nu_H(T) = (\gamma/2\pi)H_{\text{eff}}(T)$. The points in Fig. 2 were taken from a curve of ν_H as a function of T and indicate the adherence of the internal field to the relation $H_{\text{eff}}(0) - H_{\text{eff}}(T) = CT^4$.

It was observed that the experiment-theory fit is very sensitive to small variations in θ . One

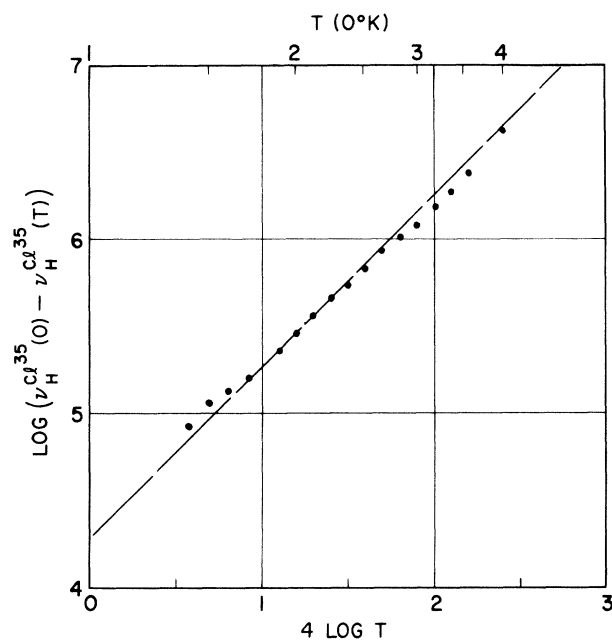


FIG. 2. $\text{Log}[\nu_H^{\text{Cl}^{35}}(0) - \nu_H^{\text{Cl}^{35}}(T)]$ as a function of $4 \log T$. The straight line has a slope of 45° .

can decide, even for θ changes of less than a degree, whether the fit has been improved or worsened when the comparison is made over the total temperature variation. Therefore, if the EFG principal axis system orientation can be determined to within 2° in the ac plane, it should be possible to distinguish between the Moriya⁴ and Leiden group² sublattice structures.

¹N. J. Poulis and G. E. G. Hardeman, *Physica* **18**, 201 (1952).

²N. J. Poulis and G. E. G. Hardeman, *Physica* **18**, 315 (1952).

³N. J. Poulis, G. E. G. Hardeman, W. Van Der Lugt, and W. P. A. Hass, *Physica* **24**, 280 (1958).

⁴Tôru Moriya, *Phys. Rev.* **120**, 91 (1960).

⁵R. G. Barnes and S. L. Segel, *Phys. Rev. Letters* **3**, 464 (1959).

⁶A. Narath, B. Morosin, and A. T. Fromhold, *Bull. Am. Phys. Soc.* **8**, 359 (1963).

⁷W. W. Simmons, W. A. Robinson, and W. J. O'Sullivan, *Bull. Am. Phys. Soc.* **6**, 363 (1961).

⁸C. Dean, *Phys. Rev.* **96**, 1053 (1954).