publication.

[20]P. Löwdin, J. Chem. Phys. 19, 1396 (1951).

[21]R. L. Bell and K. T. Rodgers, Phys. Rev. 152, 746 (1966).

P[31] Spin Echoes in Metallic Phosphorus-Doped Silicon*

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Observations of solid echoes in the P[31] spin system in metallic Si : P are reported. Homogenous linewidths and spin-lattice relaxation times are given.

The experimental data reported herein is an extension of that reported previously by Sundfors and Holcomb.[1] It consists of spin-echo data for the P[31] nuclear spin resonance, taken from 1.3 to 2.0 °K in two of the samples listed in Ref. 1, at phosphorus donor concentrations of 1.4×10^{20} and 9×10^{19} cm^{-3}. (These were samples P-1 and P-2 listed in Table I of Ref. 1.)

The experiments were performed using a phase-coherent pulsed NMR spectrometer designed by Clark.[2] The cryogenic system used was that described by Sundfors.[3] The experiments were conducted using a field of 50 G at 8.5 MHz. The echoes were produced by the usual 90°-τ-180° pulse sequence. T_2 was measured by changing the pulse spacing τ. T_1 was measured by observing the recovery of the echo amplitude, after the second of two such echo-producing pulse sequences, as a function of the time between sequences. The samples were immersed directly in the helium bath which was pumped below the λ point. The results of experimental tests to determine if there was Ohmic heating in the samples due to the rf pulses showed that such heating was negligible.

The experimental data for relaxation times are given in Table I, together with other relevant numbers for comparison. Figure 1 shows a spin-echo signal from sample P-2 at 1.3 °K.

The calculated value of T_2 given in the fifth column of Table I was obtained under the assumption that it is determined entirely by magnetic dipolar interaction with Si^{29} nuclear spins and with other P[31] nuclear spins. The exponential echo-decay plots which were obtained suggest a Lorentzian shape for the homogeneous line. Consequently, we write the expression for the observed P[31] spin-echo decay time $(T_2)_P$ as

$$1/(T_2)_P = 1/(T_2)_{P\text{-}P} + 1/(T_2)_{Si\text{-}P} , \qquad (1)$$

where[5]

$$1/(T_2)_{P\text{-}P} = 3.8 \, \gamma_P^2 \, \hbar N_D \qquad (2)$$

and[6]

$$1/(T_2)_{Si\text{-}P} \cong \gamma_P^2 \, (2.5 \gamma_{Si} \, \hbar N_{Si})^2 / 3.8 \gamma_{Si} \, \hbar N_{Si} . \qquad (3)$$

Given the uncertainty concerning the exact applicability of Eqs. (2) and (3), the numbers in column 5 of the table, calculated on the basis of those equations, are in reasonable agreement with the experimental values of T_2 in column 4. They certainly indicate that there are no significant sources of broadening for the P[31] resonance which are unaccounted for. (As shown in Ref. 1, there is a huge inhomogeneous broadening from the distribution in Knight shifts, giving the short value for T_2^*. The fact that the calculated values of T_2 are shorter than the experimental may, among other things, represent an effect of that Knight-shift distribution in weakening mutual spin-flip processes between
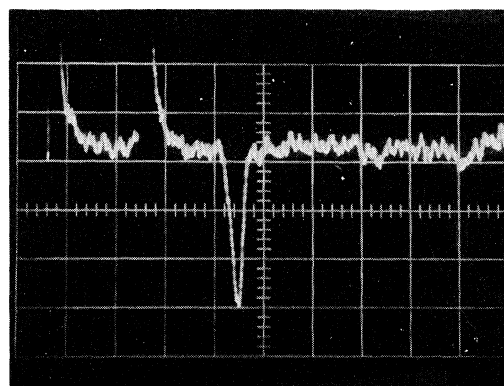

FIG. 1. Spin echo from P[31] system at 1.3 °K, for sample with $N_D = 9 \times 10^{19}$ cm^{-3}. Oscilloscope is sweeping at 0.2 msec/cm.

TABLE I. Experimental and calculated relaxation times for P^{31} in Si : P. T_2^* is the free-induction decay time, T_2 the spin-echo decay time, and T_1 the spin-lattice relaxation time.

Sample	N_D (cm^{-3})	T_2^* (μsec)	T_2(expt) (msec)	T_2(calc) (msec)	T_1(msec) 1.3 °K	2.0 °K	$T_1 T$ Expt	Korringa[a]
P-1	1.4×10^{20}	20 ± 4	7.0 ± 0.7	3.8	130 ± 15		0.17 ± 0.02^{b}	0.22 ± 0.04
P-2	0.9×10^{20}	20 ± 4	5.0 ± 0.6	4.1	140 ± 12	76 ± 10	0.18 ± 0.02	0.26 ± 0.05
P-3	0.45×10^{20}		Signal unobservable					
P-4	0.18×10^{20}							

[a]From the Korringa relation (Ref. 4) and Knight-shift data of Ref. 1.
[b]On basis of 1.3 °K point only.

neighboring P^{31} spins.)

The values of T_1 for P^{31} represent more accurate values than the rough numbers reported in Sec. III A of Ref. 1. They are consistent with the Ker-

ringa relation, and show that Knight shift and relaxation are both determined by the hyperfine interaction of the P^{31} nuclei with the mobile conduction electrons.

[1]R. K. Sundfors and D. F. Holcomb, Phys. Rev. 136, A810 (1964).

[2]W. G. Clark, Rev. Sci. Instr. 35, 316 (1964).

[3]R. K. Sundfors, Ph. D. thesis (Cornell University, 1963) (unpublished).

[4]J. Korringa, Physica 16, 601 (1950).

[5]This equation, appropriate to the case of broadening by interactions among a dilute system of randomly located spins, was derived by P. W. Anderson. See A. Abraham, The Principles of Nuclear Magnetism (Oxford U. P., London, 1961), pp. 125–128.

[6]This equation is derived by C. P. Slichter [Principles of Magnetic Resonance (Harper and Row, New York, 1963), p. 154, Eq. (31)]. We have replaced H_g of that equation by the expression $2.5\gamma_{Si}\,\hbar\,N_{Si}$. This local-field expression is derived from Eq. (1), reduced by a factor of $\frac{2}{3}$ because the mutual spin-flip contribution to the linewidth is missing for the case of unlike moments.

Infrared and Raman Studies of Long-Wavelength Optical Phonons in Hexagonal MoS₂

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Infrared and Raman measurements of lattice vibrations in hexagonal MoS$_2$ have been made over the combined range 20–4000 cm^{-1}. Two infrared-active modes at 384 and 470 cm^{-1} and three Raman-active modes at 287, 383, and 409 cm^{-1} have been observed. Classical dielectric oscillators are fitted to the reflectivity data, which are also analyzed by means of the Kramers-Kronig relations. The degeneracy of the E_{1u} and E_{2g}^1 modes is interpreted as indicating that the layer-layer interaction is weak. All 15 optical modes are assigned to irreducible representations and their frequencies tabulated or predicted.

I. INTRODUCTION

Lattice vibrations in MoS$_2$ (molybdenite) have been studied by measuring the infrared reflectivity and Raman scattering from natural crystals. The semiconductor MoS$_2$ occupies a central position in the large class of layered compounds formed by transition metals and sulfur, selenium, or tellurium.[1] These compounds show a broad variation of properties, ranging from electrical insulators such as HfS$_2$ to metals such as NbSe$_2$, which is a

superconductor below 7 °K. Moreover, the compounds are highly anisotropic, cleave easily along a preferred plane, and appear in a number of stacking polytypes. These properties provide an interesting basis for studies of lattice dynamics. The present paper is the second in a projected series on this class of compounds.

In Sec. II the crystal structure is presented, and the normal-mode displacements are assigned to the irreducible representations given by the authors in an earlier paper.[2] Natural MoS$_2$ has six
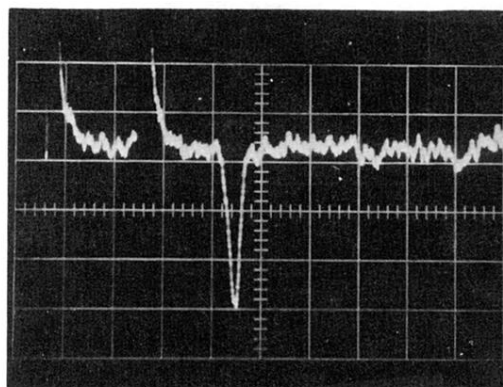
FIG. 1. Spin echo from P^{31} system at 1.3 °K, for sample with $N_D = 9 \times 10^{19}$ cm^{-3}. Oscilloscope is sweeping at 0.2 msec/cm.