

pected chemical shift effects become manifest in the approach to infinite strain. The utility of the large strain technique described here extends to the study of other transport properties as well: With the availability of purer material, one may study the strain and temperature dependence of the lattice mobility at or near the large strain limit.²⁵ Finally, it will be of interest to compare the deformation potentials now being determined for Ge by cyclotron resonance studies of strained material²⁶ with those obtained here in the effective-mass approximation.

²⁵ P. J. Price and Yi-Han Kao, IBM J. Research Develop. **5**, 63 (1961).

²⁶ J. C. Hensel (private communication).

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Theory of Double Magnetic Resonance in Solids

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Expressions accounting for the changes in the shape of absorption lines for solids under conditions of double magnetic resonance were obtained. The shift of the absorption line maximum for one of the resonance frequencies with increase of saturation of the other resonance frequency was calculated. The expressions obtained are in agreement with experiment.

THE behavior of aluminum samples under conditions of double magnetic resonance was investigated in a recently published work carried out by Holcomb, Pederson, and Sliker.¹ The authors succeeded in observing a number of interesting properties displayed in the saturation of the sample by one of the radio-frequency fields.

The present note is concerned with the theoretical treatment of double resonance under conditions of magnetic-resonance saturation with respect to one frequency.

The frequencies and amplitudes of the rf fields will be denoted by ν_1 , ν_2 and H_1 , H_2 , respectively. One of the rf fields will be assumed weak compared with the other: $H_2 \ll H_1$.

Let us begin by considering the most simple case, $H_1 \ll H_{100}$. (Here $H_{100} = \mu/d^3$, where μ is the magnetic moment of an individual particle and d is the separation between neighboring magnetic particles.) Due to the smallness of H_2 its value may be taken, to a first approximation, as zero. The problem will then be restricted to that of saturation for ordinary magnetic resonance. This was discussed by the author in a previous paper,² which contained the following expres-

sions for the stationary values of the full spin projection on the direction of the constant magnetic field $I_z(t)$ and for the average energy of the spin-spin interaction $H_{ss}^0(t)$:

$$I_{z\text{st}} = I_{z0} \frac{1 + \gamma^2 H_1^2 \times \frac{1}{2} g(\nu_1) T_1 h^2 (\Delta\nu_1)^2 / 2H_0^2}{1 + \gamma^2 H_1^2 \times \frac{1}{2} g(\nu_1) T_1 [1 + h^2 (\Delta\nu_1)^2 / 2H_0^2]}, \quad (1)$$

$$\frac{h\Delta\nu_1(H_{ss}^0)_{\text{st}}}{H_0^2}$$

$$= I_{z0} \frac{\gamma^2 H_1^2 \times \frac{1}{2} g(\nu_1) T_1 h^2 (\Delta\nu_1)^2 / 2H_0^2}{1 + \gamma^2 H_1^2 \times \frac{1}{2} g(\nu_1) T_1 [1 + h^2 (\Delta\nu_1)^2 / 2H_0^2]}. \quad (2)$$

Here $\Delta\nu_1 = \nu_1 - \nu_0$, $\nu_0 = \gamma H_0 / 2\pi$, T_1 is the spin-lattice relaxation time $I_z(t)$, $g(\nu)$ is a function normalized to unity and describing the absorption line shape in the absence of saturation,

$$H_0^2 = \text{Spur}(H_{ss}^0)^2 / \text{Spur} I_z^2,$$

I_z is the operator of full spin projection on the direction of the constant magnetic field, and H_{ss}^0 is the operator of the secular part of the spin-spin interaction.

In accordance with reference 2, the energy of the H_2 field absorbed by the spin system per unit time is

$$P(\nu_2, H_2) = h\nu_2 \gamma^2 H_2^2 \times \frac{1}{2} g(\nu_2) \times (I_{z\text{st}} - h\Delta\nu_2(H_{ss}^0)_{\text{st}}/H_0^2). \quad (3)$$

Here $\Delta\nu_2 = \nu_2 - \nu_0$.

¹ D. F. Holcomb, B. Pedersen, and T. Sliker, Phys. Rev. **123**, 1951 (1961).

² B. N. Provotorov, J. Exptl. Theoret. Phys. (U.S.S.R.) **41**, 1582 (1961) [translation: Soviet Phys.—JETP **5**, 1126 (1962)].

In the case of heavy saturation,

$$T_1\gamma^2 H_1^2 g(\nu_1) h^2 (\Delta\nu_1)^2 / \bar{H}_0^2 \gg 1, \quad I_{z\text{ st}} = h\Delta\nu_1 (H_{ss}^0)_{\text{st}} / H_0^2,$$

and the absorption line observed will be given by the relation

$$P(\nu_2, H_2) = h\nu_2 \gamma^2 H_2^2 I_{z\text{ st}} \times \frac{1}{2} g(\nu_2) (1 - \Delta\nu_2 / \Delta\nu_1). \quad (4)$$

As seen from Eq. (4), for a Gaussian absorption line $g(\nu_2)$, the position of the line maximum will be accounted for by the expression

$$\Delta\nu_2 / \Delta\nu_1 = \frac{1}{2} - \left(\frac{1}{4} + \langle (\Delta\nu)^2 \rangle / (\Delta\nu_1)^2 \right)^{1/2}.$$

Here $\langle (\Delta\nu)^2 \rangle$ is the second moment of the absorption line in the absence of saturation. This result shows agreement with experimental data both in displacement and in the order of magnitude.

For the case of $H_1 \sim H_{\text{loc}}$ the distribution function of the spin system is³

$$\rho = c \exp \left(- \frac{h\Delta\nu_1 I_z + (\mu H_1 / 2I)(I^1 + I^{-1}) + H_{ss}^0}{kT^*} \right).$$

³ A. G. Redfield, Phys. Rev. **98**, 1797 (1955).

For a stationary case the T^* value will be

$$\frac{1}{T^*} = \frac{1}{T_0} \left(1 + \frac{\nu_0 \Delta\nu_1}{(\Delta\nu_1)^2 + \gamma^2 H_1^2 / 4\pi^2 + H_0^2 / h^2} \right).$$

It may be seen that in passing to a system of coordinates rotating together with H_1 , the rf field H_2 will induce transitions between Hamiltonian levels $h\Delta\nu_1 I_z + (H_1 / 2I)(I^1 + I^{-1}) + H_{ss}^0 = H$, the energies of which differ by $h(\nu_2 - \nu_1)$. Thus, by analogy with equations for ordinary resonance (see Van Vleck⁴), we may write for the absorbed energy of field H_2 :

$$P(\nu_2, H_2) = h\nu_2 \gamma^2 H_2^2 I_{z\text{ st}} (1 - \Delta\nu_2 / \Delta\nu_1) G(\nu_1 - \nu_2),$$

$$G(\nu_1 - \nu_2) = \int_{-\infty}^{+\infty} dt e^{2\pi i(\nu_1 - \nu_2)t} \text{Spur } I^1 e^{iHt} I^{-1} e^{iHt} / \text{Spur } I^1 I^{-1}. \quad (5)$$

The position of the $G(\nu)$ line maximum is determined by the first moment of this line. Direct calculation gives $\int_{-\infty}^{+\infty} \nu G(\nu) d\nu = \Delta\nu_1$. The second and fourth moments of the $G(\nu)$ line are characteristic of its shape and may be calculated by the Van Vleck method.⁴

⁴ J. Van Vleck, Phys. Rev. **74**, 1168 (1948).

Electron Spin Resonance of a Center in Calcium Fluorophosphate

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A spin-resonance center whose concentration is sensitive to x irradiation has been observed in synthetic calcium fluorophosphate crystals. It shows an electron spin of 1/2 and hyperfine interaction with two equivalent F^{19} nuclei. Arguments are presented which lead to its identification as an O^- ion occupying an F^- site.

I. INTRODUCTION

CALCIUM halophosphate, $3[\text{Ca}_3(\text{PO}_4)_2] \cdot \text{CaX}_2$, where X represents Cl or F or a mixture of the two, occurs widely in nature as the mineral apatite. Synthetic microcrystals containing small additions of manganese and antimony¹ are the most common fluorescent lamp phosphors. Recently large single crystals have been successfully grown from the melt by the Kryopoulos technique.² Irradiation with far ultraviolet and x ray has been found to create optical absorption bands in the near ultraviolet, visible, and infrared spectral regions.³ The availability of these crystals and the possibility of producing color centers

have prompted us to investigate defects in the apatite structure using electron spin resonance. In the present paper we discuss a resonant center in calcium fluorophosphate which we believe to be O^- occupying a F^- site. Subsequently, we plan to report on centers involving impurities, such as manganese, which play a role in luminescent processes.

II. RESULTS

Synthetic single crystals of calcium fluorophosphate were examined in a spin-resonance spectrometer which has been described previously.⁴ A spectrum observed in most crystals is shown in Fig. 1. For the applied magnetic field H parallel to the hexagonal (c) axis the spec-

¹ H. G. Jenkins, A. H. McKeag, and P. W. Ranby, J. Electrochem. Soc. **96**, 1 (1949).

² P. D. Johnson, J. Electrochem. Soc. **108**, 159 (1961).

³ P. D. Johnson, J. Appl. Phys. **32**, 127 (1961).

⁴ G. W. Ludwig and H. H. Woodbury, Phys. Rev. **113**, 1014 (1959); H. H. Woodbury and G. W. Ludwig, *ibid.* **117**, 102 (1960).