ion. This means that if $a$ is positive and decreasing as the atomic number of the alkali increases, $a_F$ must be decreasing. This would indicate that the overlap integrals are decreasing. An increase of distance between the two $F^-$ ions in the $F_2^-$ molecular ion would cause this. Das, Jette, and Knox[17] find, by semiphenomenological methods, that the distance between the atoms $A$ and $C$ decreases while that between $A$ and $E$ increases when a $F_2^-$ molecular ion is formed. The notation is as follows: The two atoms $A$ refer to the two fluorine ions in the $V_k$ center, the two atoms $C$ are the nearest alkali atoms ($C$ and $D$ in notation of Das et al.), and the four atoms $E$ are the next-nearest alkali atoms ($E, F, G$, and $H$ in the notation of Das et al.). It would seem that if the ionic radii of $C$ (the nearest alkali atoms) are increasing (as is true for alkalis with larger atomic number), the two fluorine ions would be forced further apart. If the sign of $a$ is chosen to be negative, similar argument would indicate that the fluorine ions would be pulled together as the radii of the nearest atoms ($C$'s) increased. Although an elaborate analysis would be required before a positive statement about which sign should be assigned to $a$ can be made, this last information along with that from the $g$ values makes the positive sign seem more likely. Thus the sign of $a$ will be assumed to be positive for the rest of this paper unless specified otherwise.

From Table I it is seen that $b$ changes by only 6.3% while $a$ changes by 47% in the alkali fluorides studied in detail. This is in agreement with the expression for $b$ derived by Das, Jette, and Knox[16] who show the $b$ is not particularly sensitive to $R$, the spacing between the two ions in the $F_2^-$ molecular ion, while $a$ is quite sensitive to $R$.

The value of $a+b$ seems to be increasing as the alkali radii are increased, but from a plot of $a+b$ versus interionic spacing it would appear that the value of $a+b$ for CsF would not be greatly different from RbF.

## Summary

This study has shown that the $V_k$ center is stable in all the alkali fluorides at liquid-nitrogen temperature and unstable at room temperature; the theoretical picture of the $V_k$ center as derived by Woodruff and Känzig[4] gives a good description of the $V_k$ center in the samples studied in detail; the linewidths depend upon the magnetic moment of the alkali; the sign of $a$ appears to be positive, the amount of $p$ state is increasing; and many of the effects can be explained if the distance between the two ions in the $F_2^-$ molecular ion is increasing as the radius of the alkali ion is increased.

### ACKNOWLEDGMENTS

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# Excitation of Coupled Nuclear Antiferromagnetic Resonance Modes[*]

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The presence of a strong hyperfine coupling in the antiferromagnets $KMnF_3$ and $CsMnF_3$ leads to a strong intermixing of the nuclear magnetic resonance and antiferromagnetic resonance (AFR) modes at low temperatures. In the experiments described here, $Mn^{55}$ resonance absorption is detected by monitoring the field for AFR while driving at appropriate nuclear frequencies. Such resonance absorption is observed for a range of frequencies many times larger than the nuclear linewidth. A spin-pinning model is proposed which provides nucleation centers for this "off-resonance" saturation.

## 1. INTRODUCTION

IN a previous paper[1] it was shown that the presence of a large hyperfine coupling in antiferromagnetic $KMnF_3$ leads to a substantial mixing of the nuclear and electronic resonance modes. The results reported there are in agreement with the theoretical calculations of deGennes et al.[2] who demonstrated that these effects can be thought of as arising from the coupling of the nuclei through the Suhl-Nakamura indirect interaction.[3] As a consequence, it is found that the field for antiferromagnetic resonance (AFR) and the nuclear magnetic resonance (NMR) frequency are depressed at lower temperatures.

[1] G. L. Witt and A. M. Portis, Phys. Rev. 135, A1616 (1964).

[2] P. G. deGennes, P. A. Pincus, F. Hartmann-Boutron, and J. M. Winter, Phys. Rev. 129, 1105 (1963).
[3] H. Suhl, Phys. Rev. 109, 606 (1958); T. Nakamura, Progr. Theoret. Phys. (Kyoto) 20, 542 (1958).

In KMnF$_3$ the NMR frequency[1] drops from a high-temperature value of 687 to 565 Mc/sec at 4.2°K. NMR absorption can be observed by driving at a given frequency between these two values while monitoring the corresponding shift of the field for AFR (at fixed microwave frequency). It remains to be explained how substantial NMR saturation can occur over such a broad range of driving frequencies. Exciting in the wings of the resonance line would require saturating powers orders of magnitude larger than those observed experimentally. It is proposed that such nuclear absorption spreads out from nucleating centers.[4] A model is adopted and used to calculate the power for NMR saturation and comparison made with experiment.

The magnetic properties of KMnF$_3$ have been described in a series of papers.[5] Below a transition temperature at 81.5°K ($T_N = 88.3°K$) the material exhibits a weak ferromagnetism resulting from a slight canting of the sublattice magnetization vectors. The crystal structure is of the perovskite type.

CsMnF$_3$ is[6] hexagonal in structure with a reported Neèl temperature of 53.5°K. A large anisotropy field ($-7500$ Oe) along the $c$ axis forces the spins into the transverse plane; in this plane a weak sixfold anisotropy field of about 1.1 Oe is found. The magnitude of the latter field allows the AFR to be observed at microwave frequencies for applied static fields in the transverse plane. The resulting normal modes are similar to those for KMnF$_3$. The low-temperature behavior of the field for AFR and the indirect observation of Mn$^{55}$ resonance absorption follow the theory of deGennes and his co-workers.

## 2. NUCLEAR-ANTIFERROMAGNETIC DOUBLE RESONANCE

### Experimental Results

The hyperfine interaction can be written in the form

$$\mathcal{H} = -\alpha \mathbf{M} \cdot \mathbf{m}, \tag{1}$$

where $\mathbf{M}$ and $\mathbf{m}$ denote the electronic and nuclear magnetizations on either sublattice. The electrons experience an effective field given by $\alpha \mathbf{m}$. For KMnF$_3$ and CsMnF$_3$ the values for this field are $9.48/T$ and $9.15/T$ Oe, respectively, $T$ denoting the absolute temperature. It is this term that gives rise to a shift of the field for AFR[7] with changing lattice temperature or with NMR absorption.

The nuclear hyperfine field is $\alpha \mathbf{M}$. At liquid-helium temperatures the sublattice magnetization can be taken as the saturation value and the resulting fields are

[4] A. M. Portis, G. L. Witt, and A. J. Heeger, J. Appl. Phys. 34, 1052 (1963).

[5] See Ref. 1 for a resume.

[6] A. Nakamura, V. Minkiewicz, and A. M. Portis, J. Appl. Phys. 35, 842 (1964).

[7] A. J. Heeger, A. M. Portis, Dale T. Teaney, and Gerald Witt, Phys. Rev. Letters 7, 307 (1961).
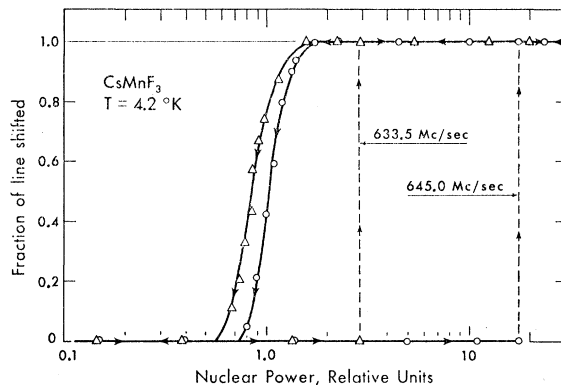
FIG. 1. The detailed nature of the shift of the field for AFR at two nuclear driving frequencies. When increasing from zero power the line appears suddenly at the high-temperature position. By carefully reducing the power level a region is found in which lines at both field positions can be observed.

651 kOe for KMnF$_3$ and 633 kOe for CsMnF$_3$. In the absence of mode intermixing, the expected NMR frequencies would be 687 and 668 Mc/sec. However, the depressed resonance frequencies at 4.2°K are found to be 565 and 624 Mc/sec. In previous experiments[1,6] it has been shown that NMR absorption at that temperature can be detected by AFR field shifts by driving between the "pulled" and "unpulled" frequencies.

Figures 1 and 2 show the detailed nature of the field shift at various driving powers. At lowest powers only the unshifted line is observed. Above a threshold level the entire line moves to a higher value which depends upon the applied frequency. If the power is then decreased, a second line develops at the unshifted position. The amplitude of this line increases at the expense of the shifted portion as the power is further reduced. Finally only the unshifted line remains. This behavior is found in either crystal.
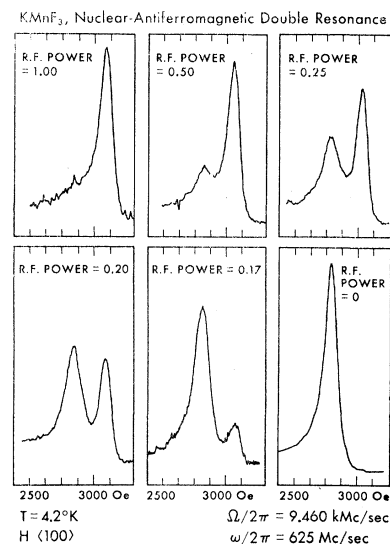
FIG. 2. Tracings of the AFR absorption line for nuclear power levels in the region of partial shift. Both field positions are independent of the power. The high-field portion shifts upward for higher driving frequencies.

The threshold level for increasing power is poorly defined as there appears to be an instability associated with the initial field shift. The data in Fig. 1 represent an average over several measurements. The region of partial shift, as in Fig. 2, gives reproducible results. If the power is decreased to a value on the low-power side of the hysteresis curve and then increased again, the same path is retraced. Once the shifted portion of the line is allowed to go to zero, the high-power side of the curve must be followed to reobtain the shift.

The threshold power is such a strong function of nuclear frequency that it was necessary to shift the AFR at low frequencies and then to increase the frequency, carefully maintaining a high-power level, in order to observe the shift near the upper frequency limit. Figure 3 displays the power required for 50% shift when decreasing from full shift.

Obtaining the high values of rf fields necessary for these measurements required up to 5 W of applied power. To reduce the possibility of rf heating of the sample, the microwave cavity containing the sample and the rf coil was filled with liquid helium. An indication of the amount of direct heating resulting from this arrangement is the small observed power dependence, at fixed frequency, of either the unshifted or the shifted portion of the AFR line. With the power varied over the entire range available, either line changed no more than an amount corresponding to an increase of $+0.3°K$.

### Theory for Nucleation of Saturation Absorption

As yet unexplained is the means by which nuclear saturation can be attained at frequencies far removed from the resonance frequency. As will be discussed below, the NMR linewidth is less than 1 Mc/sec at 4.2°K—many times narrower than the spread of frequencies used in the experiments.

A theory has been proposed[4] which suggests that the partial saturation grows out from nucleating centers. Such centers may exist near volume imperfections or at twin planes. Here the electron spins will be "pinned" and prevented from responding to driving fields at nuclear frequencies. This, in turn, serves to reduce the nuclear frequency depression and nuclei in such regions will resonate at nearly $\gamma \alpha M$. Farther away, the resonance frequency in the bulk will approach the value $\omega(T)$ at the lattice temperature.

The distribution of nuclear frequencies is written in terms of a pinning function $f(z)$ which is taken to have a value of unity at the nucleating center and to fall to zero in the bulk. Here $z$ denotes the distance from the imperfection.

It is assumed that

$$\omega^2(z) = \omega_0{}^2 - [\omega_0{}^2 - \omega^2(T)](m/m_0)[1 - f(z)]. \quad (2)$$

Here $\omega_0 = \gamma \alpha M$, $m_0$ is the equilibrium value of the nuclear magnetization, and $m$ is the local value. The

function $\omega(z)$ is sketched in Fig. 4. When driving at a frequency between $\omega_0$ and $\omega(T)$ the nuclei at $z$ can absorb energy from the applied field. As the power is increased, the magnetization on the low-frequency side of the curve will be reduced, bringing the resonance frequency there up to $\omega$. A shoulder is thereby produced as in curve a in Fig. 4.

The experimental results imply that a certain amount of power is necessary to form the plateau. For power beyond this point the energy is then spread throughout the sample, represented by curve b, and the electronic resonance line shifts to a value consistent with the higher nuclear spin temperature. The curve labeled c is obtained by reducing the power level to a point such that only a fraction of the nuclei in the crystal are saturated.

To calculate the power required to bring about the partial saturation, the resonance frequency is taken to be constant over the region from $z_1$ to $z_2$. The power absorbed by this region is given by

$$P = \gamma^2 H_1{}^2 H_0 T_2 \int_{z_1}^{z_2} m \, dz. \quad (3)$$

Competing with this process is the relaxation of energy to the lattice written as

$$dW/dt = (H_0/T_1) \int_{z_1}^{z_2} (m_0 - m) dZ. \quad (4)$$

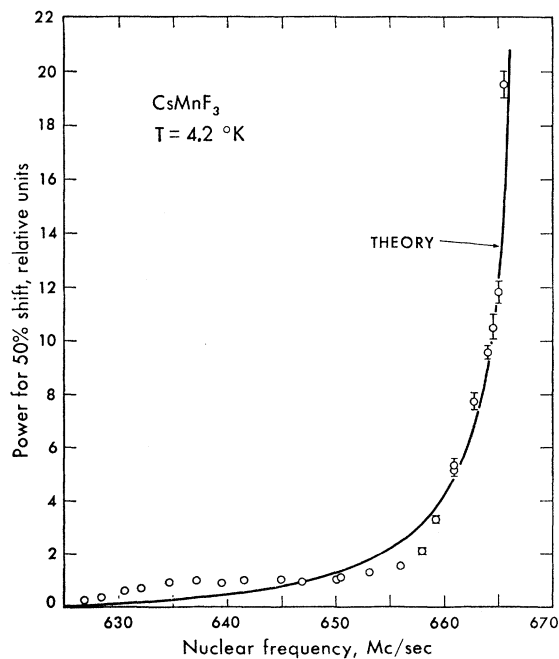Balancing these two effects and making use of the



FIG. 3. The frequency dependence of the power required to shift the AFR line. The solid curve denotes the theory outlined in the text.
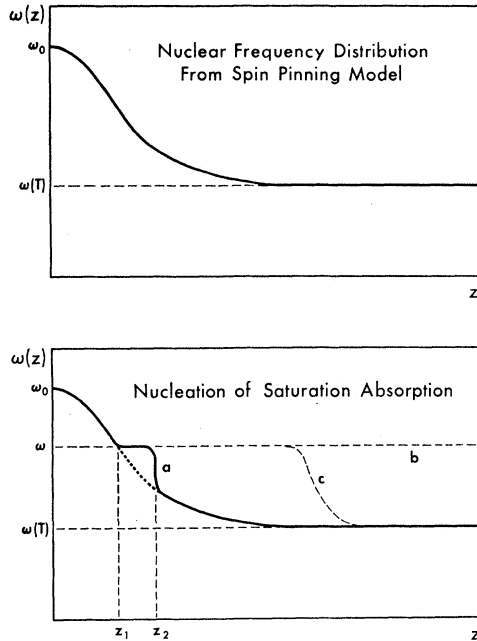
FIG. 4. The distribution of the NMR frequencies as given by the spin-pinning model. The lower diagram represents the system in various states as suggested by the data.

constancy of $\omega$ over the region, the result is

$$\frac{\omega_0^2-\omega^2(T)}{\omega_0^2-\omega^2}\frac{z_2-z_1}{1+\gamma^2H_1^2T_1T_2}=\int_{z_1}^{z_2}\frac{dz}{1-f(z)}. \quad (5)$$

The power necessary to bring the resonance frequency of the entire spin system up to the driving frequency $\omega$ is

$$\gamma^2H_1^2T_1T_2=[\omega^2-\omega^2(T)]/[\omega_0^2-\omega^2]. \quad (6)$$

This is plotted as the solid curve in Fig. 3.

## Discussion

The experimental results in Fig. 3 agree generally with the theoretical expression above. There is an unexplained flat region in the data at lower frequencies before the rapid rise sets in near $\omega_0$. In order to obtain quantitative information from Eq. (6) it is necessary to know $T_1$ and $T_2$ for the $Mn^{55}$ nuclei in the two materials used.

For the transverse relaxation time $T_2$ the Suhl-Nakamura theory[3] will be used. According to this theory an indirect coupling exists between the nuclei in ordered magnetic materials through the electronic spin-wave system. They find for the second moment due to this interaction

$$\langle(\Delta\omega)^2\rangle=\frac{\pi I(I+1)\omega_0^2}{6S^2\Omega_E^{3/2}\Omega_e^{1/2}}, \quad (7)$$

where $\Omega_E$ is the exchange frequency and $\Omega_e$ is the electronic resonance frequency (9.5 kMc/sec in this case). Using the appropriate numbers gives $T_2(CsMnF_3)=0.26\,\mu sec$ and $T_2(KMnF_3)=0.48\,\mu sec$. The latter value is in agreement with the direct observation of $Mn^{55}$ NMR in the substance.[6]

The nuclear spin lattice relaxation time was measured using the double resonance technique. That is, the recovery of the field for AFR was measured following the application of a saturation pulse. This in turn yields the nuclear spin temperature as a function of the time and $T_1$ can be determined. Details of these measurements will be published later. At $4.2°K$, $T_1(CsMnF_3)=14.5$ msec and $T_1(KMnF_3)=18.5$ msec. Selecting a frequency of 645 Mc/sec for comparison, the theory predicts $H_1(CsMnF_3)=2.3$ Oe and $H_1(KMnF_3)=2.2$ Oe. As there is an enhancement of the rf field at the relatively slow NMR frequencies, this factor must be included.

For $KMnF_3$ the static field was applied along an $\langle001\rangle$ direction and $H_1$ along a $\langle100\rangle$ direction. The enhancement factor for this case is

$$\eta=[H_N(H_0+H_A)/\sqrt{2}](\Gamma/\Omega)^2,$$

where $H_N=\alpha M$, $H_0$ is the applied magnetic field, $H_A$ is the anisotropy field responsible for the canting, $\Omega$ is the AFR frequency, and $\Gamma$ is the electronic gyromagnetic ratio. The factor $\sqrt{2}$ results from $H_1$ being $\pi/4$ out of the canting plane. Then $\eta=124$.
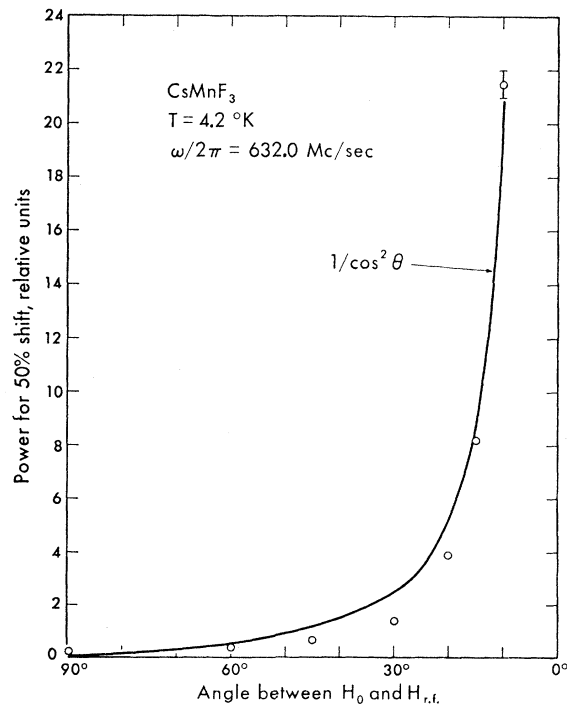


FIG. 5. The orientation effects of the power required for NMR saturation at one frequency. Both $H_0$ and $H_{rf}$ are applied in the transverse plane and the angle between them varied.

z ⟨00.1⟩          z ⟨00.1⟩
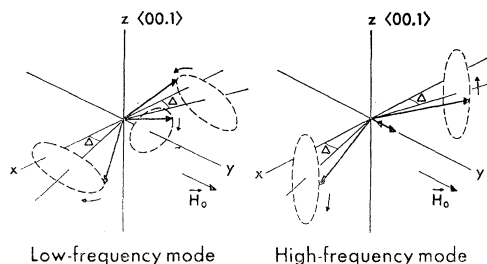
Low-frequency mode          High-frequency mode

FIG. 6. The antiferromagnetic resonance modes in CsMnF$_3$ with the applied dc magnetic field in the transverse plane. The low-frequency mode is identified as one being excited in the experiments.

With $H_0$ and $H_1$ in the transverse plane (see Fig. 5) and mutually perpendicular, the enhancement factor for CsMnF$_3$ is about 170. The experimental arrangement positioned $H_1$ $\pi/4$ out of the plane and so $\eta=120$ in this case. Using these two values the predicted rf fields necessary to saturate the resonance at the selected frequency is 0.019 Oe for CsMnF$_3$ and 0.018 Oe for KMnF$_3$.

$H_1$ was produced by introducing a one-loop coil into the microwave cavity through a small hole in a side wall. The sample was then mounted inside this coil. As the absolute output of the rf power oscillator used to drive the coil could not be measured directly, it was necessary to perform an auxiliary experiment to determine the actual driving field $H_1$.

This was done by replacing the sample by a small sphere of yttrium iron garnet (YIG).[7] With $H_0$ perpendicular to the plane of the coil, the ferromagnetic line showed satellites at $\pm\omega_M/\gamma$, where $\omega_M$ is the frequency of the rf oscillator. Comparison of the intensities of the main line and the satellites gave the value of $H_1$ in the coil. Using this technique the relative output meter of the oscillator was calibrated over the range of frequencies used.

At $\omega/2\pi=645$ Mc/sec and an output meter reading of 110 $\mu$A, $H_1=1.18$ Oe. The power level necessary to shift 50% of the AFR line (chosen as an experimentally convenient value) at this frequency was found to be 0.075 $\mu$A or a field of 0.031 Oe. This is for CsMnF$_3$.

The agreement with the value of 0.019 Oe derived from (6) is reasonable. There are several possible sources of the disagreement. It is possible that the enhancement factor is off by some few percent. Also the power dependence of the NMR frequency could cause a shift of the resonance line at high-power levels, reducing the effectiveness of the driving field. Finally, the Suhl-Nakamura line width given by (7) must be accepted with some caution. Preliminary results of the direct observation of Mn$^{55}$ NMR in[6] KMnF$_3$ indicate

a value of $T_2$ close to the predicted value; however, the temperature dependence is in disagreement with (7). The results of the power for the shift in KMnF$_3$ are not as accurate due to the broader AFR line (90 Oe compared to 20 Oe for CsMnF$_3$). However, the power required to shift the line at 645 Mc/sec appeared to be the same to within a factor of 2.

The spin-pinning mechanism fails to predict the threshold of power necessary to shift the AFR line. One of the main sources of the hysteresis behavior of Fig. 4 is the reduced enhancement found for nuclei near the pinning centers. The electrons on such atoms are restrained from following at nuclear frequencies and therefore only the applied field $H_1$ would be effective for driving the nuclei. Once the system is in the state represented by curve b in Fig. 4, the large enhancement found in the bulk comes into play. Then the rf power level can be reduced considerably and still maintain the saturation. It is for this reason that the value of $H_1$ required for 50% line shift was used to compare with the theory.

## 3. IDENTIFICATION OF THE NUCLEAR RESONANCE MODES

In Fig. 6 are shown the two antiferromagnetic resonance modes for CsMnF$_3$ when the static magnetic field is in the transverse plane.[8] The net moment is induced by the applied field. The low-frequency mode $\Omega_1$ is the one excited in the experiments—$\Omega_2$ lies in the far infrared due to the large axial anisotropy field.

The theory of the coupled AFR-NMR modes indicates that there is a nuclear mode $\omega$ corresponding to each electronic one. It can be seen that $\omega_1$ should also be excited by an oscillating field at right angles to $H_0$. The enhancement factor calculated previously applies to this case. There should be no enhancement for the other nuclear mode $\omega_2$.

To confirm the fact that $\omega_1$ is the mode being driven, the CsMnF$_3$ crystal was mounted so that $H_0$ and $H_1$ were in the $x$-$y$ plane with $H_0$ free to rotate in that plane. When the two fields were at right angles the smallest amount of nuclear power was required to shift the line. This is shown in Fig. 5. The data show that it is only the perpendicular component of $H_1$ that is effective in exciting the nuclear resonance. (The difference between the curve and the data is probably due to a slight misalignment of the crystal.) This identifies the modes as $\Omega_1$ and $\omega_1$. It was not possible to make the same check on KMnF$_3$ as the AFR broadens rapidly as $H_0$ is rotated away from a cubic axis.

[8] Kenneth Lee, A. M. Portis, and G. L. Witt, Phys. Rev. 132, 144 (1963).