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Electron-Transfer States of Pairs of Unlike Transition-Metal Ions in Perovskite Fluorides

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Experimental evidence is presented for the observation of electron-transfer bands between unlike transition-metal ions. Two examples are considered. First, the spectra of crystals of composition $KMn_xNi_{1-x}F_3$ and $KZn_{1-x-y}Mn_xNi_yF_3$ show an intense ultraviolet band (greater than 50 000 cm^{-1}) associated with electron transfer from nickel to manganese. Polarization data from $BaMn_{1/2}Ni_{1/2}F_4$ crystal spectra support this conclusion. Second, an electron-transfer band has been observed for the pair Cu – F – Mn in $KZnF_3$ crystals. The band is centered near 41 500 cm^{-1}, it is very broad with a long vibrational progression and it has an absorption intensity which increases on cooling of the crystal. These features can all be explained by the assignment $Mn^{2+}(3d^5)$, $Cu^{2+}(3d^9) \rightarrow Mn^{1+}(3d^54s)$, $Cu^{3+}(3d^8)$. It is concluded that this state determines the antiferromagnetic coupling in the ground state of the pair. A consideration of the possible electron-transfer states available to the pair when the manganese is in its excited $^4A_{1g}$ state provides an explanation for the observed ferromagnetic coupling of this state with Cu^{2+}.

I. INTRODUCTION

The theoretical interpretation of the antiferromagnetism exhibited by transition-metal ion crystals is extremely complicated, as can be seen from a recent discussion of the problem by Gondaira and Tanabe.[1] The main difficulty in the quantitative treatment of many electron ions lies in the large number of virtual states which enter into the calculation of the over-all exchange energy of the antiferromagnetic ground state. As these states are, in principle, accessible by direct absorption from the ground state, measurements of absorption spectra of these materials should be very valuable in sorting out the relative importance of the multitude of possible states. In practice, this is not easy because the spectral region concerned lies in the vacuum ultraviolet and, apart from an early study by Parkinson and Williams,[2] this region of the spectrum has not been examined at all. However, some of the difficulties can be eliminated if we turn our attention to the absorption spectra of unlike pairs of ions instead of concentrating on the pure materials.

The choice of crystal system is also another important factor because of the need to minimize the number and type of superexchange paths. The perovskite fluorides are particularly useful in this regard because of the simple nature of the exchange interaction through fluorine in a linear arrangement. The disadvantage is the lack of anisotropy in the absorption process because the crystal system is usually cubic. Earlier work has demonstrated that the exchange interaction between Mn^{2+} and Ni^{2+} leads to an enhancement of the absorption intensity of certain electronic transitions which are localized on either ion,[3] together with the appearance of new bands which correspond to the simultaneous electronic excitation of both ions.[4] It was speculated that the mechanisms of both types of absorption process involve primarily those virtual states for which there is electron transfer from nickel to manganese. The present paper presents experimental confirmation of this in the form of an intense ultraviolet absorption edge which can be assigned to this type of electron transition. In addition, a study has been made of the absorption spectrum of pairs of Mn^{2+} and Cu^{2+} in $KZnF_3$. A very broad band centered at 41 500 cm^{-1} has been found which can be assigned to the electron transfer from Cu^{2+} to Mn^{2+}. An assignment of this band is given and the nature of the states which determine the exchange energy is discussed.

II. RESULTS AND DISCUSSION

A. Nickel-to-Manganese Electron Transfer

It has been shown earlier[4] that there are two intense bands in the ultraviolet spectra of crystals of composition $KMn_xNi_{1-x}F_3$, for $0<x<1$, at approximately 40 000 and 45 000 cm^{-1}, which correspond to the simultaneous excitation of Mn^{2+} and Ni^{2+}. Further examination of the spectra of these crystals shows that there must be an intense far-ultraviolet absorption process which involves the nickel and manganese together, because there is a marked dependence of the background absorption on the value of x. The evidence for this is shown in Fig. 1, from which it can be seen that the absorption coefficients of the solid solutions are greater, in the wave-number region shown, than either of the pure components. As the other intensity enhancements involve exchange interactions, it is reasonable to expect a similar explanation for this absorption process. To show this, the absorption spectrum of a sample containing both Ni^{2+} and Mn^{2+} in $KZnF_3$ was compared with the spectra of samples of the individual components.

The result, shown in Fig. 2, indicates that the absorption tail is connected with pair interactions because statistically, at these concentrations, isolated pairs are the most probable type of aggregate.[5] As the process involves a pair of manganese and nickel ions, it is reasonable to assume that it represents an electron transfer from one ion to the other because there are no single-ion excited states which can account for the absorption. It is also reasonable to assign the direction of transfer as nickel to manganese so that the absorption of light corresponds to the following transition:

$$Mn^{2+} - F - Ni^{2+} \rightarrow Mn^{1+} - F - Ni^{3+} .$$

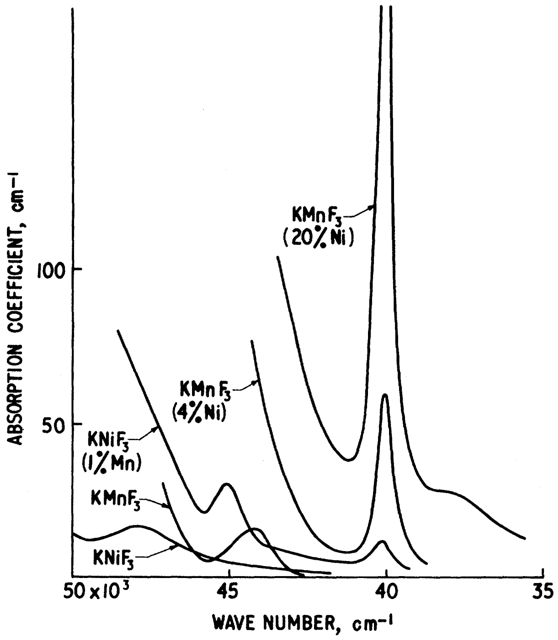

FIG. 1. Room-temperature absorption spectra of $KMn_xNi_{1-x}F_3$ crystals.

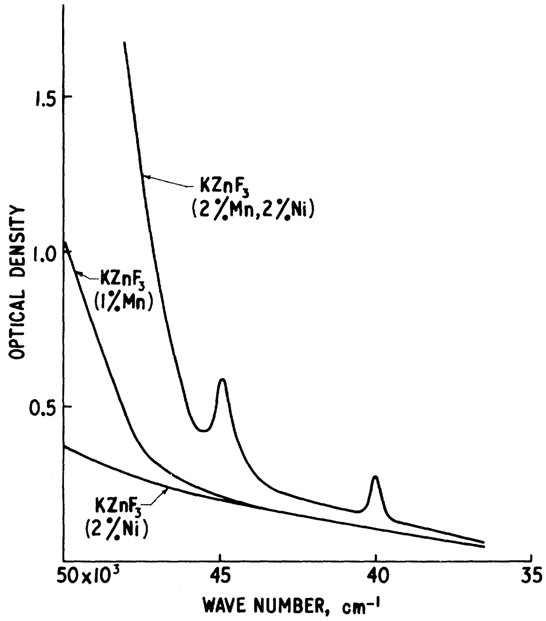

FIG. 2. Room-temperature absorption spectra of $KZn_{0.96}Mn_{0.02}Ni_{0.02}F_3$ (2 mm thick), $KZn_{0.99}Mn_{0.01}F_3$ (4 mm thick), $KZn_{0.98}Ni_{0.02}F_3$ (2 mm thick).

This type of transition should be strongly polarized in the direction of charge transfer, although this cannot be confirmed for the cubic perovskite fluorides because they are optically isotropic. Recently, however, another crystal system has become available, one which is anisotropic.[6] This contains crystals of the general formula $BaMF_4$(M = Mn, Fe, Co, Ni, Zn). They are orthorhombic with the space group C_{2v}^{12}. The structure is shown in Fig. 3, and it can be seen that there are chains of connected octahedra running parallel to the a axis. Each octahedron is connected to octahedra above

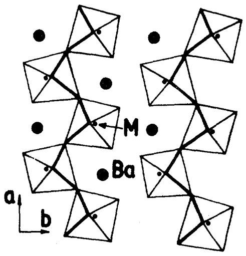

Fig. 3. Structure of $BaMF_4$, projection on *ab* face. The superexchange path is shown by the thick lines.

and below the plane of the paper, so that there are, in effect, two-dimensional sheets of connected octahedra lying in the *ac* plane.

$BaMF_4$ crystals, therefore, contain two principal superexchange paths, one connecting metal ions in a nearly linear path along the *c* axis, the other more angular path is along the chains shown in Fig. 3. Crystals of nominal composition $BaMn_{1/2}Ni_{1/2}F_4$ were therefore examined and their spectra measured with light incident normal to the *ac* face and the result is given in Fig. 4. The same type of absorption tail observed with $KMn_xNi_{1-x}F_3$ crystals is present in the spectrum of this crystal, and it is very strongly polarized parallel to the *c* axis. This is the direction of the more linear of the two superexchange paths and this supports the interpretation of the absorption process which gives rise to this tail, as one which corresponds to the transfer of an electron from nickel to manganese. The less intense *a*-polarized absorption is then attributed to a similar electron-transfer process involving metal ions in the other superexchange path. Qualitatively, this transition would be less intense because the overlap between metal and fluorine orbitals would be less than for the other more linear path.

Although the results presented so far establish the presence of an absorption process involving electron transfer between a pair of metal ions, they are incomplete because only the tail of the absorption band can be observed. However, the interpretation of the absorption edge suggests that the energy of the process might be decreased and brought into an accessible region by looking at another unlike pair, viz., Mn – F – Cu. Crystals of $KZnF_3$ containing Mn^{2+} and Cu^{2+} were therefore grown and their absorption spectra measured. The results are considered in Sec. II B

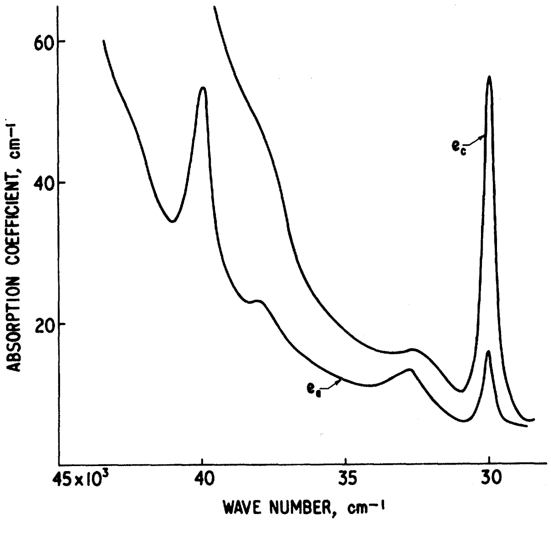

FIG. 4. Low-temperature (77 °K) absorption spectrum of $BaMn_{1/2}Ni_{1/2}F_4$, light incident normal to the *ac* face. e_c and e_a denote light vector parallel to the *c* and *a* axes, respectively.

B. Copper-to-Manganese Electron Transfer

Crystals of $KZnF_3$ containing 1.5 mole% each of Mn^{2+} and copper were grown and the absorption spectra were measured in the range 5000 – 50 000 cm^{-1}. These crystals are expected to contain approximately 86% of the total manganese and copper as isolated single ions and 10% as isolated pure and mixed pairs.[5] The remaining 4% would be accounted for mainly by triples. Examination of the spectra of these crystals shows absorption due to Cu^{2+} in the near infrared region, but the absorption by isolated Mn^{2+} is too weak to measure.[7] Instead, the absorption by manganese is detected by observing the absorption due to Mn – F – Mn and Mn – F – Cu pairs in the region of the $^6A_{1g}\to{}^4A_{1g}$, $^4E_g^a$ absorption. The intensity of the absorption by Mn – F – Cu pairs is very high compared to that by Mn – F – Mn by about two orders of magnitude. We plan to consider these absorption bands in another publication.[8] However, we note for the purpose of the present discussion, that the ground state shows antiferromagnetic coupling[9] while the excited state has ferromagnetic coupling[9] between the manganese and copper.

The presence of Mn – F – Cu pairs is also shown by the absorption due to the transition $^6A_{1g}\to{}^4E_g^b$ and at higher energy there is a very broad absorption band. Both are shown in Fig. 5. The intensity of the broad absorption band shows a one-to-one correspondence with the intensities of the transitions $^6A_{1g}\to{}^4A_{1g}$, $^4E_g^a$ and $^4E_g^b$ of the Mn – F – Cu pairs, and there is no doubt that it involves the same pair of ions. We assign the transition to an electron transfer from Cu^{2+} to Mn^{2+} and we show that the features associated with this band can be accounted for by the following assignment:

$$Mn^{2+}\ (3d^5),\ Cu^{2+}\ (3d^9) \to Mn^{1+}\ (3d^5 4s),\ Cu^{3+}\ (3d^8).$$

A transferred electron can give rise to a large number of possible states of the manganese ion. From tables of energy levels[10] it can be found that the ground state of Mn^{1+} is $3d^5 4s(^7s)$. The positions of a number of the excited states with configurations $3d^5 4s$, $3d^6$, and $3d^5 4p$ are shown in Fig. 6. As these are free-ion energies, the effect of the crystal field has to be considered for a discussion of the present case. There are two main effects. First, the energy separation between

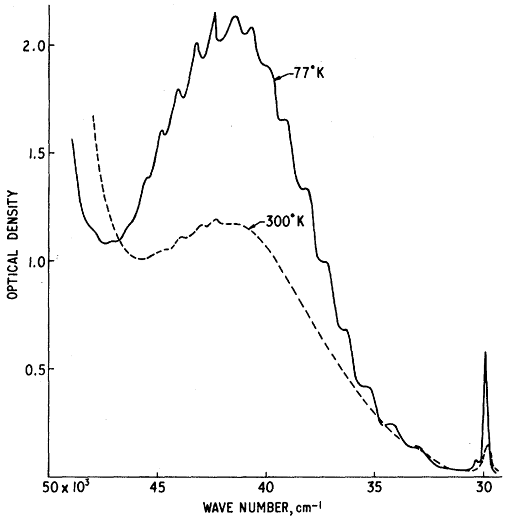

FIG. 5. Room-temperature and 77 °K spectra of $KZn_{0.96}Mn_{0.02}Cu_{0.02}F_3$ (nominal). Crystal thickness 3.05 mm.

terms will be diminished, probably by about 90% for the fluoride environment. Second, the separation between the energies of the e_g and t_{2g} electrons splits the $D, F, G, \ldots$ terms, alters the energies of the P terms, but it has no effect on the S terms. This is the usual crystal-field effect and the matrices for d^5 and d^6 could be used to construct a complete energy-level diagram for Mn^{1+}. However, this is unnecessary for the present discussion because only the lowest state is observed in the spectrum (Fig. 5) and it must be $^7A_{1g}$, from the ^7S term. The first excited state should be $^5A_{1g}$ (from ^5S) with $^5T_{2g}$ and ^5E_g (from ^5D) lying above it.

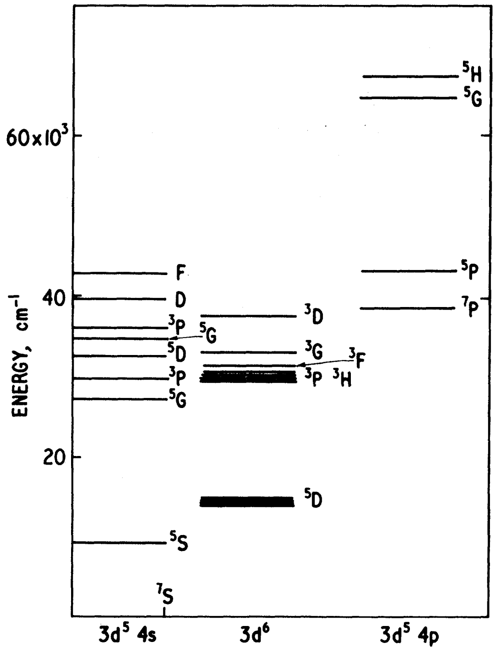

FIG. 6. Free-ion energy-level diagram for Mn^{1+} (configurations $3d^54s$, $3d^6$, and $3d^54p$). The ground state is $^7S(3d^54s)$.

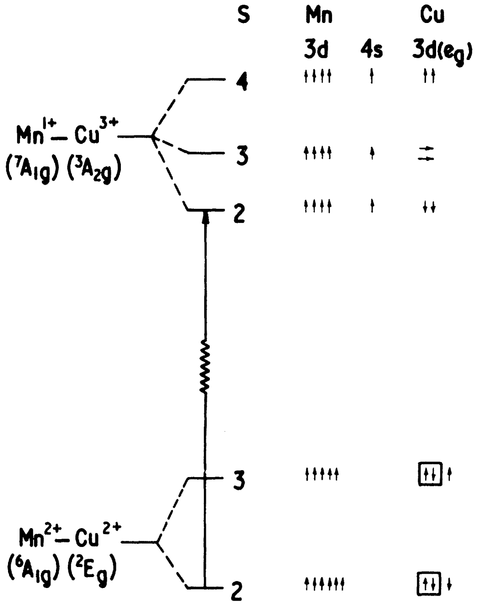

FIG. 7. Schematic energy-level diagram for the pair states and spin configurations of $Mn^{2+} - Cu^{2+}$ and $Mn^{1+} - Cu^{3+}$. The allowed transition connects the two $S = 2$ states.

The configuration of Mn^{1+} in the final state of the electron transfer of lowest energy is therefore $3d^54s$, with six electrons having parallel spin. Consider now the configuration of the copper ion.

The transfer of an electron from Cu^{2+} leaves it with the configuration $3d^8$, which has a ground state $^3A_{2g}$ in an octahedral field. Therefore, the final state of the electron transfer of lowest energy is one in which the Cu^{3+} has the configuration $3d^8$ with two electrons in e_g orbitals having parallel spin.

Consider now the possible spin configurations of the ground and excited states of the pair, shown diagrammatically in Fig. 7. The ground state can have either $S = 2$ or $S = 3$ spin configuration, and we show elsewhere[8] that the $S = 2$ state lies lower in energy, while the excited state can have the spin configurations $S = 2$, 3, or 4. The only allowed transition couples the two $S = 2$ states because the electron cannot change spin during the electron transfer. This transition is shown by the vertical arrow in Fig. 7. This selection rule explains the temperature dependence of the absorption band intensity, which increases on cooling of the crystal, as a result of the increased population of the $S = 2$ level of the ground state.

The other feature of the band to consider is its large width with a pronounced vibrational progression. This indicates that there is a considerable change in the nuclear geometry of the pair as a result of the electron transfer. Certainly the ionic size of Mn^{1+} will be larger than that of Mn^{2+}, while Cu^{3+} will be smaller than Cu^{2+}. The fluorine nuclei which are around the manganese ion will therefore relax outwards to increase the manganese-fluorine internuclear distance. The nuclear geometry around the copper is complicated by the Jahn-Teller distortion of the ground state of Cu^{2+}, which we have neglected until now.

It is highly probable that the Jahn-Teller distortion is of the four short and two long bond type, which has tetragonal symmetry. The two spin-paired e_g electrons are then in the d_{z^2} orbitals which is directed along the tetragonal axis. When the copper-manganese pairs are considered this tetragonal axis can be either collinear with the manganese or normal to the Mn – F – Cu direction. The restrictions on the nature of the electron-transfer transition of lowest energy, described above, are satisfied by the first of these nuclear configurations. It is the one in which the d_{z^2} copper orbital is directed towards the manganese ion. The energy-level diagram of Fig. 7 then applies to this nuclear configuration, the one of lowest energy. The other two, equivalent, distortions will have spin parallel and spin antiparallel energies lying above this level and the electron-transfer states arising from them will have higher energy than the one in Fig. 5. (The lowest of these will be higher by an amount approximately equal to the energy of the excited ^1E_g state of Cu^{3+}.)

These arguments point to the conclusion that the ground state of the manganese-copper pair involved in the observed electron-transfer band has a tetragonal distortion in which the two long Cu – F bonds are collinear with the manganese. However, in the excited state both metal ions have nondegenerate orbital configurations and consequently the nuclei would be expected to adjust their positions in a way which removes the ground-state tetragonal distortion. This can be achieved by the operation of the Jahn-Teller active mode "in reverse," so that a long progression of a single mode would be expected to feature in the vibrational structure. This appears to be the case and it provides an explanation for the observed vibrational structure of the band in Fig. 5.

The foregoing analysis accounts for the qualitative features of the observed electron-transfer band in terms of a definite assignment of the states involved. It is a consequence of the analysis that the lowest-energy electron-transfer state must give an antiferromagnetic contribution to the exchange energy of the ground state. The next higher transition, in which the manganese goes to $^5A_{1g}$ $(3d^54s)$, must give a ferromagnetic contribution. The other two higher transitions, to $^5T_{2g}$ and ^5E_g from ^5D of the d^6 configuration, also give rise to ferromagnetic contributions to the ground state. As the ground state shows antiferromagnetic coupling then this must arise primarily from admixtures of the lowest-energy electron-transfer state. It is obvious that these results indicate the need for a theoretical evaluation of the various contributions to the exchange energy of the ground state for this particularly simple case. The number of electron-transfer states is small and their energies can be fixed, via Fig. 6, relative to the energy of the lowest state, so that the calculations should be tractable. They would serve as a very useful check on the ability of available wave functions to deal with calculations of the exchange energy. Although we have not specifically stated the mechanism of electron transfer, it is assumed that it involves a two-step transfer, from fluorine to manganese followed by transfer from copper to fluorine. Theoretical calculations would also be able to assess the relative probabilities of this process and the direct copper-to-manganese transfer.

Whereas, so far as the ground state is concerned, the lowest-energy electron-transfer state gives rise to an antiferromagnetic contribution to the exchange energy, the situation is different when we consider the electron-transfer states available to the pair when the manganese is in the $^4A_{1g}$ state. The strong field functions describing the $^4A_{1g}$ state have the same orbital configuration as the ground state except that the spin of either an e_g or a t_{2g} electron has been "flipped" antiparallel to the spins of the other electrons. Considerations of the strong field functions describing $3d^5$ and $3d^6$ states [11] show that the lowest-energy-allowed transfer places the Mn^{1+} in the ^5E_g state. Both of these states provide ferromagnetic contributions to the exchange energy of the pair. There are also three triplet states of d^6 which couple ferromagnetically. The only state which gives an antiferromagnetic contribution is $^5A_{1g}$ from the $3d^54s$ configuration. This qualitative reasoning therefore provides an explanation of the observed ferromagnetic coupling[8] when the manganese is in the $^4A_{1g}$ state. Here again, quantitative calculations using available wave functions would be extremely valuable to check the theoretical method.

III. EXPERIMENTAL

The absorption spectra were measured with Cary 14 and 14 RI spectrophotometers. For the low-temperature spectra the crystals were immersed in liquid nitrogen in an optical silica cryostat.

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PHYSICAL REVIEW B VOLUME 1, NUMBER 11 1 JUNE 1970

Theory of NMR Line Shapes in Dipolar-Broadened Spin Systems and Applications to SrF_2, CsF, and NaCl

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Detailed line-shape measurements of fluorine resonance in SrF_2 have been made and the results compared with theories of dipolar broadening and with Barnaal and Lowe's data from CaF_2. It was recognized that the theoretical results of Evans and Powles (EP) and of Lee, Tse, Goldburg, and Lowe (LTGL) were derived from the same basic expansion for the free-induction-decay function. This made it appropriate to combine their results in order to obtain an improvement in the theory. The combined result was compared with experimental data of LTGL from NaCl and with Hutchins and Day's results from CsF. In most cases, the combined result gave as good or better agreement than either the approximation of EP or that of LTGL.

I. INTRODUCTION

We have studied NMR line shapes observed in several single crystals of alkali halides and other ionic compounds. These crystals provide excellent tests of theories of dipolar broadening which have recently been developed. Our work has included a detailed analysis of line shapes in strontium fluoride which led us to consider, in detail, the theoretical development and its generalizations described in this paper. Before describing our results we will review the development of the theory.

In 1948, Bloembergen, Purcell, and Pound[1] proposed the Gaussian model for a system of spin-$\frac{1}{2}$ particles on a rigid lattice. A given spin experiences local magnetic fields due to neighboring spins. It was found by an approximate calculation that the distribution of this local field at a representative spin is essentially Gaussian in shape. Later that year, Van Vleck[2] published exact calculations of the second and fourth moments of such a spin system. Comparison of moments for a Gaussian shape with these exact results showed that the Gaussian was only a rough approximation.

The continuous-wave (cw) experimental analysis of calcium fluoride by Pake and Purcell,[3] in 1948, indicated that Van Vleck's results were correct. Bruce,[4] in 1957, using the same calcium fluoride crystal of Pake and Purcell,[3] repeated the cw ex-