INTERACTIONS OF p_σ AND p_π ORBITALS IN TRANSITION ELEMENT FLUORIDES

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We have measured the nuclear magnetic resonance of fluorine in single crystals of $KNiF_3$ and K_2NaCrF_6. Both crystals have high symmetry so that the resonance shifts observed can be interpreted directly in terms of the fraction of unpaired spins in the fluoride ion's $2s$, $2p_\sigma$, and $2p_\pi$ orbitals. The results show relatively large amounts of both p_σ and p_π interactions with the d electrons in these essentially ionic fluorides.

The structure of $KNiF_3$ is cubic perovskite in which the Ni^{++} ions, with site symmetry O_h, are surrounded by a regular octahedron of F^- ions.[1,2] In order to put the Cr^{+++} ion into the center of a regular octahedron of fluorides, we grew a single crystal of K_2NaCrF_6. The structure of this compound has been determined by x-ray diffraction[2]: it is face-centered cubic, $a_0 = 8.266$ A, space group O_h^5 - $Fm3m$ with 4 formula units in the unit cell and a Cr-F distance of 1.933 ± 0.011 A. In both crystals the O_h site symmetry makes it possible to identify the one-electron d orbitals with the fluoride ion axes. In $KNiF_3$ the fluorines have site symmetry D_{4h} while in K_2NaCrF_6 they have C_{4v}, so that there are mutually perpendicular directions along which the fluoride ion p orbitals are directed, and in both cases the two sets of p_π orbitals are identical.

The fluorine resonances were measured with a Varian Associates V-4311 induction spectrometer operating at 60.000 Mc/sec. The resonances were displaced from the normal resonance field of ω/γ_N because of dipole fields and hyperfine interactions[3] arising from the unpaired electrons. In Fig. 1(a) we present measurements recently made[4] on a single crystal of $KMnF_3$ oriented so that H_0 can rotate in the (110) plane. The dipole sum, presented as a dashed line, accounts for most of the anisotropic interaction, in contrast to similar measurements on $KNiF_3$ in Fig. 1(b) and K_2NaCrF_6 in Fig. 1(c). In $KNiF_3$ the dipole sum contributes only a small fraction of the observed anisotropy of the shifts while in K_2NaCrF_6 it is out of phase with the observed shifts. The reason for this, and in fact the basic reason for studying the Ni^{++} and Cr^{+++} compounds, is that measurements of the fluorine hyperfine interaction only determine[4] the difference in occupancy of the fluorine p_σ and p_π orbitals. In Mn^{++}, with

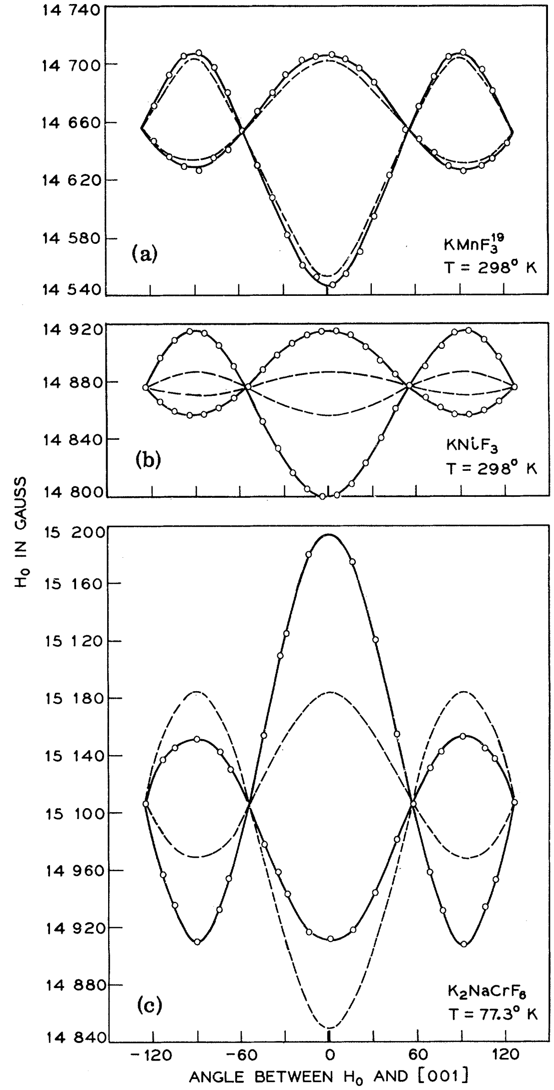

FIG. 1. (a) Resonance field for F^{19} in $KMnF_3$ as a function of angle between H_0 and [001] as H_0 is rotated in (110) plane. The dipole sum, indicated by dashed line, was performed on an IBM 704, and is seen to account for most of the observed anisotropy. For all three compounds the measurements were made at 60.000 Mc/sec; consequently the undisplaced fluorine resonance field should be 14 979.4 gauss. (b) Measurements made under identical conditions on $KNiF_3$. Notice that since the p_π interaction is forbidden the p_σ interaction accounts for most of the observed anisotropy. (c) Similar measurements made at 77.3°K for K_2NaCrF_6. Notice that the measurements are out of phase with the dipole sum as expected for p_π interactions.

a $3d^5$ configuration in a ${}^6S_{5/2}$ ground state, all five of the one-electron functions are half filled, and these unpaired spins are available to form both σ and π bonds with the ligands. However, Ni^{++} in a $3d^8$ configuration is split by an octahedral crystal field so that the triplet (embodying d_{xy}, d_{xz}, and d_{yz}) lies lower and is completely filled while the doublet (d_{z^2} and $d_{x^2-y^2}$) is a half-filled subshell. Since the triplet mixes with ligand functions to form π bonds and the electrons in the doublet mix to form σ bonds, it is clear that the magnetic electrons in Ni^{++} only mix into the σ bonds. In a complementary fashion Cr^{+++} with a $3d^3$ configuration can only form magnetic π bonds.

The hyperfine interactions of the individual bonds derived from these measurements are expressed by the Hamiltonian[3,5]

$$H = \vec{I} \cdot A \cdot \vec{S}, \qquad (1)$$

in which $\vec{I}$ is the fluorine nuclear spin and $\vec{S}$ the metal ion electron spin. The components of the hyperfine interaction tensor A derived from the experiments are listed in Table I along with f_S and $f_\sigma - f_\pi$, the fraction of unpaired $2s$ and $2p_\sigma - 2p_\pi$ spins in fluoride ion orbitals. The large values of $f_\sigma - f_\pi$ in $KNiF_3$ and K_2NaCrF_6 are noteworthy. The negative value of the latter is caused by $A_\sigma = 0$ to a first approximation so that the large effects of the p_π interactions are not obscured by p_σ interactions of opposite sign. The interactions in $KMnF_3$ and qualitatively similar values reported[3] for MnF_2 in which $f_\sigma - f_\pi = (0.3 \pm 0.3)\%$ are presumably explained by large σ interactions being almost cancelled by the unexpectedly large π interactions. It had been suggested[6] that the s-electron hyperfine interactions could be explained by overlap effects between F^- and Mn^{++} orbitals. Keffer, Oguchi, O'Sullivan, and Yamashita[7] have computed that the p electrons could participate in electron transfer, which is equivalent, in their atomic orbital approach, to covalent bonding in the molecular orbital approach previously used[3,4,8,9] to discuss these results. However, their rough calculation of the p-electron interaction was too small. One possible change, which would improve the agreement with experiment, would be a smaller value for the energy denominator for transfer than the 10-15 ev they estimated. In this event the cubic field splitting between the triplet and doublet levels of 2 ev would be more important and tend to increase the relative amount of p_π bonding. It is clear that the extra degree of freedom accorded the p electrons in a calculation of this sort is required to explain the experimental results.

Table I. The values of A_S and $A_\sigma - A_\pi$ are given in units of 10^{-4} cm^{-1}. Limits of error in $KNiF_3$ and K_2NaCrF_6 are relatively large because of uncertainties in the susceptibilities.

	$KMnF_3$	$KNiF_3$	K_2NaCrF_6
A_S	16.26 ± 0.5	39.1 ± 4	-1.1 ± 0.5
f_S	$(0.52 \pm 0.02)\%$	$(0.50 \pm 0.05)\%$	$-(0.021 \pm 0.01)\%$
$A_\sigma - A_\pi$	0.17 ± 0.1	10.9 ± 1.4	-7.2 ± 1.2
$f_\sigma - f_\pi$	$(0.18 \pm 0.1)\%$	$(4.95 \pm 0.6)\%$	$-(4.90 \pm 0.8)\%$

On the other hand, calculations by Marshall[10] of the overlap effect using expanded Mn^{++} orbitals agreed reasonably well with the relatively small p-electron hyperfine interactions reported for MnF_2. It is clear that this agreement was fortuitous since it depended upon the cancellation of larger p_σ and p_π interactions. Furthermore, the overlap effects alone could not explain the large σ-electron interactions observed in $KNiF_3$ since f_S is the same in these two compounds, and the Ni^{++} ion radial function once adjusted to give the proper s-electron overlap will not give a large enough p-electron interaction.

The small negative isotropic shift in K_2NaCrF_6 can be explained[11,12] by excited states and its magnitude used to determine their contribution to the eigenstate of the system. The effects of these large p_σ and p_π interactions upon crystal field splittings, spin-orbit interactions, term values, and cation interactions are being studied.

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FERMI SURFACES OF GOLD AND SILVER FROM ULTRASONIC ATTENUATION*

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Recent experiments have confirmed that the Fermi surface in copper contacts the Brillouin zone boundary in the [111] direction as suggested by Pippard.[1-5] Using the low-temperature magnetic dependence of ultrasonic attenuation, we have found that the Fermi surfaces in gold and silver contact the zone boundary in a similar way. In gold the size of the contact area and the shape of the "neck" joining this to the main body of the surface have been obtained in a very direct way.

An oscillatory variation of ultrasonic attenuation in a magnetic field occurs because of geometrical coincidences between certain electron orbits and the periodic electric fields accompanying the sound wave. Liquid helium temperatures are needed to have the mean free path longer than the wavelength, λ. The effect, when $\vec{H}\perp\vec{q}$ (where $\vec{q}$ is the propagation vector of the wave), gives the dimensions and ultimately the shape of the Fermi surface because the period observed in $(H\lambda)^{-1}$ is determined by the Fermi momentum perpendicular to $\vec{H}$ and $\vec{q}$ at those parts of the surface where this momentum is extremal. If p is such a momentum, and P is the corresponding period in $(H\lambda)^{-1}$, then $p=e/(2cP)$.[6,7]

Magnetic field oscillations were observed in single crystals of zone-refined gold and silver at frequencies up to 154 Mc/sec at a temperature of 4.2°K. Longitudinal waves were propagated along both [001] and [011], and the direction of $\vec{H}$ varied while keeping $\vec{H}\perp\vec{q}$. Stronger oscillations were observed in gold than in silver, as many as 19 maxima and minima being found in certain orientations.

If the Fermi surface contacts a zone boundary, there will be a minimal cross section at the boundary; thus, if touching occurs in [111], there should be a long-period oscillation due to electrons circulating around this "neck" when $\vec{H}$ is along [111] and $\vec{q}$ is along [011]. Such a period has been observed in copper.[3] A pronounced period, which is shown in Fig. 1(a), is found also in gold and is the strongest evidence for the surface making contact. The momentum calculated from this period is 0.22, in units of 10^{-19} g cm sec^{-1}. (In the remainder of the paper all momenta will be expressed in these units.) This

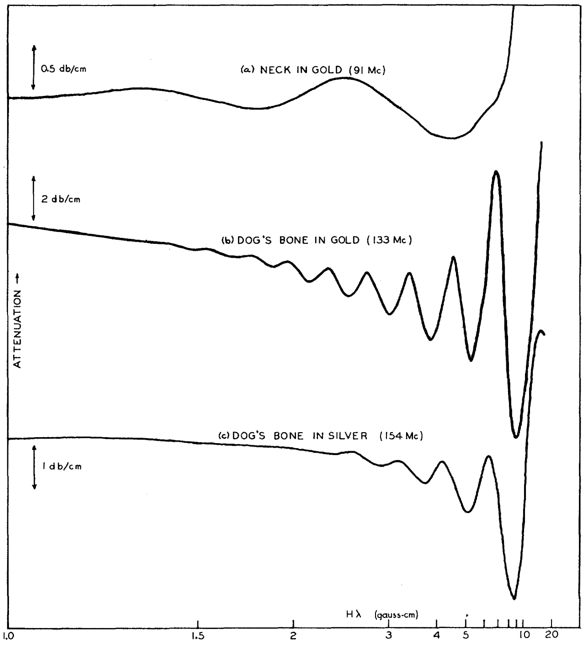

FIG. 1. Relative attenuation as a function of $H\lambda$ plotted on a reciprocal scale. (a) Attenuation in gold with $\vec{q}$ along [011] and $\vec{H}$ along [111]. (b) Attenuation in gold with $\vec{q}$ along [001] and $\vec{H}$ along [110]. (c) Attenuation in silver with $\vec{q}$ along [001] and $\vec{H}$ along [110]. (Note that attenuation scales are different for each curve.)