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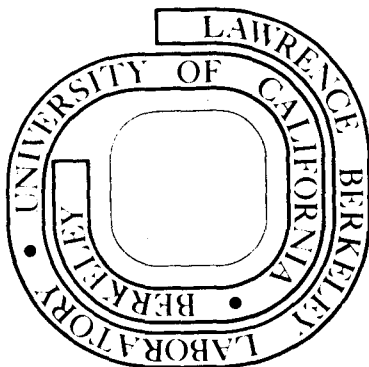H. H. Rinneberg, G. P. Schwartz, and D. A. Shirley

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MEASUREMENT OF SPIN DEVIATIONS, PRESSURE INDUCED HYPERFINE FIELD

SHIFTS, AND SUBLATTICE MAGNETIZATIONS USING PERTURBED ANGULAR

CORRELATIONS[*]

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ABSTRACT

A PAC study of ^{111}Cd-substituted antiferromagnetic transition

metal salts is reported. Supertransferred hyperfine fields at ^{111}Cd

nuclei were used for the first time to observe three effects:

zero-point spin deviations, temperature variation of sublattice

magnetization, and pressure shift of the hyperfine field.

Comparison of $KNiF_3$ and $RbMnF_3$ with their corresponding quadratic-

layer fluorides K_2NiF_4 and Rb_2MnF_4 yields an estimate for the

magnitude of the zero-point spin deviation in doped antiferromagnets.

The temperature dependences of the sublattice magnetizations in

$RbMnF_3$/Cd and MnF_2/Cd have been determined by measuring the internal

fields as functions of temperature. The shift in hyperfine

field observed for α-MnS/Cd under external pressure further supports

our model for the origin of the supertransferred hyperfine fields.

1. Introduction

Time-differential perturbed angular correlation (TDPAC) has been applied increasingly to study solid-state properties. In most cases quadrupole interactions have been measured to infer the electric field gradient produced by the lattice at the site of the radioactive nucleus[1]. Recently the well-known γ-γ cascade of ^{111m}Cd has been used to determine magnetic hyperfine fields at the impurity in Cd-doped antiferromagnetic insulators[2]. The observed internal fields have been discussed considering overlap and charge-transfer efforts of the neighboring anions[3].

The purpose of this paper is to demonstrate how the PAC technique can be used to probe properties of the magnetic lattice itself. The zero point spin deviations in the impure two-dimensional Heisenberg-like antiferromagnets K_2NiF_4/Cd and Rb_2MnF_4/Cd have been measured. The temperature dependences of the hyperfine fields in $RbMnF_3$/Cd and MnF_2/Cd yield the temperature dependence of the sublattice magnetization next to the impurity. Finally we report the pressure dependence of the internal field in MnS/Cd. Section 2 contains the experimental details while Sections 3 and 4 treat the results and discussion of these experiments.

2. Experimental

The preparation of Cd-doped MnF_2[4], $RbMnF_3$[2], $KNiF_3$[2], K_2NiF_4[3], Rb_2MnF_4[3], and α-MnS[3] has been reported previously. $^{111m}CdF_2$ was thermally diffused into the corresponding fluoride

under anhydrous conditions. Radioactive α-MnS/Cd was prepared by coprecipitation of MnS and ^{111m}CdS. Subsequently the precipitate was heated in a stream of H_2S at 1000°C. The concentration of the Cd dopant generally did not exceed 0.1 at.% in any of the compounds.

A conventional fast-slow eight-detector set up was used to measure the angular correlation. The spectra taken at liquid helium or liquid nitrogen temperatures were obtained by immersing an aluminum sample holder directly into the refrigerant. For intermediate temperatures a regulator of the type described by Welber et. al.[5] was used. The temperature was measured using a Au(Fe)/Fe thermocouple which has been calibrated against a doped germanium thermometer. A stability of ±0.2°K in regulation was achieved over several hours for temperatures between 15° and 100°K.

The pressure cell employed in this work is similar to that described by Bader[6]. Commercially available steel No. A286 was used for the construction of the cell body. In the center portion four windows were partially machined through the wall in order to reduce absorption and scattering of γ-rays to a tolerable level. The pressure was calibrated by measuring the change in the quadrupole frequency of ^{111}InCd with respect to atmospheric pressure and comparing the shift with the published data of Raghaven et. al.[7].

3. Results

The experimentally observed perturbation factors $G_{22}(t)$ for

Cd doped α-MnS are shown in Fig. 1. The PAC spectra for the

perovskites[2] ($KNiF_3$, $RbMnF_3$), quadratic layered fluorides[3]

(K_2NiF_4, Rb_2MnF_4), and difluorides[4] (MnF_2) have been published

previously. Using standard techniques, theoretical fits for the

perturbation factors were obtained consistent with single-phase,

randomly-oriented polycrystalline probes. Damping in α-MnS under

pressure was accounted for in the least-squares fitting routine

by assuming a Gaussian distribution of hyperfine fields.

Table 1 summarizes the data relevant to the spin reduction in

two-dimensional antiferromagnets while Tables 2A, B and Table 3

list the measured parameters for the temperature-dependence of the

sublattice magnetization and for the pressure-induced hyperfine-

field shift.

4. Discussion

A. Zero-Point Spin Deviation

In the past few years considerable experimental evidence has

been gained for the existence of zero-point spin deviations

in pure Heisenberg antiferromagnets. Whereas the effect has been

predicted theoretically[8] to be small for the three-dimensional

antiferromagnet (Δ_3 = 7.8%) a much larger reduction is to be found

for a two-dimensional magnetic lattice[8] ($\Delta_2 \approx 20\%$). Because of

the small reduction in the case of a three-dimensional antiferromagnet,

experimental verification turned out to be very difficult. However,

excellent agreement between experiment and theory was obtained for the layered fluorides K_2NiF_4[9,10,11] and K_2MnF_4[9,12] or their Rb analogues which are two-dimensional antiferromagnets to a good approximation.

In the following paragraph we estimate the zero-point spin deviation for the impure two-dimensional Heisenberg antiferromagnets K_2NiF_4/Cd and Rb_2MnF_4/Cd by comparing the hyperfine fields with those found in the corresponding perovskites $KNiF_3/Cd$ and $RbMnF_3/Cd$. The hyperfine field at the impurity can be written as

$$H_n = Z_n \cdot \frac{\langle S_z \rangle}{S} \cdot H_0,$$ where $\langle S_z \rangle$ is the expectation value for the z-component of the electronic spin at the Z_n magnetic ions next to the impurity. The factor H_0 corresponds to the hyperfine field produced by one magnetic neighbor with a spin expectation value $\langle S_z \rangle = S$. This field is caused by spin transfer from the (half occupied) d_σ orbital of the transition metal ion into the s orbitals of cadmium. It depends on the charge transfer from the $2p_\sigma$ orbital of the intervening F^- ion into the d_σ function and cadmium 5s orbital. In addition the overlap of the F^- $2p_\sigma$ orbital with the d_σ function and the cadmium ns orbitals (n = 1,..4) contributes to the transfer of spin density and therefore to H_0. Comparing the hyperfine fields observed for $KNiF_3$ Cd and K_2NiF_4/Cd, we assume H_0 to be the same for both hosts because of the almost identical $Ni^{2+} - F^- - Cd^{2+}$ paths along which spin density is transferred. As can be seen from Fig. 2, Cd^{2+} (which enters substitutionally for Ni^{2+}) is surrounded by an octahedron of F^- ions in both lattices.

For K_2NiF_4 only the four anions in the (001) plane are connected to neighboring Ni^{2+} ions with a $Ni^{2+} - F^-$ bond distance (2.003Å) almost identical to that found in $KNiF_3$ (2.007Å). Therefore the overlap integrals between the F^- $2p_\sigma$ orbital and the d_σ function or cadmium ns orbitals are expected to be nearly the same in both lattices. The change in H_0 caused by the small difference in the lattice parameters can be estimated to be less than 1% by comparing the experimentally observed fields in Rb_2NiF_4 (d = 2.043Å, H_{exp} = 51.3 kOe) and K_2NiF_4 (d = 2.003Å, H_{exp} = 54.9 kOe). From ^{19}F NMR measurements the anisotropic part A_σ of the ^{19}F hyperfine coupling was found - within experimental errors - to be the same for both the perovskite[13] $KNiF_3$ (A_σ = $8.8 \cdot 10^{-4} cm^{-1}$) and the layered fluoride[14] K_2NiF_4 (A_σ = $9.15 \pm 0.5 \cdot 10^{-4} cm^{-1}$). This further supports our assumption that H_0 is the same in both fluorides, because A_σ directly measures the charge transfer from the F^- $2p_\sigma$ orbital into the Ni^{2+} d_σ orbital. The expectation values $\langle S_z \rangle$ for the two- and three-dimensional anti-ferromagnets are written as $\langle S_z \rangle = S - \Delta_2$ and $\langle S_z \rangle = S - \Delta_3$ respectively. The number of nearest magnetic neighbors contributing to the hyperfine field is $Z_2 = 4$ and $Z_3 = 6$ for the layered fluoride and perovskite. From the ratio of the hyperfine fields in both host lattices we obtain:

$$\Delta_2 = S \left\{ 1 - \frac{3}{2} \frac{H_2}{H_3} \left(1 - \frac{\Delta_3}{S} \right) \right\} .$$

For K_2NiF_4 (S = 1) and Rb_2MnF_4 (S = 5/2) the experimentally observed

hyperfine fields listed in Table 1 have to be corrected upward in

magnitude for dipolar contributions to the internal fields of + 1.3 kOe and

+2.5 kOe, respectively. For the zero-point spin deviation Δ_3 of

the impure three-dimensional antiferromagnets we use the theoretical

value Δ_3 = 0.078 expected for the pure magnetic lattice. In this

way we obtain

$$\Delta_2 \ (K_2NiF_4/Cd) = 0.26 \pm 0.03,$$

$$\Delta_2 \ (Rb_2MnF_4/Cd) = 0.25 \pm 0.10.$$

The error limits are derived from random errors in the hyperfine

fields (Table 1). Spin-wave formalism yields a theoretical

value Δ_2 = 0.197 for the pure two-dimensional antiferromagnet

uncorrected for anisotropy[8]. Lines[9] has calculated the effect

of finite anisotropy to give Δ_2 (K_2KiF_4) = 0.18 and Δ_2 (Rb_2MnF_4) =

0.167. These latter values are in excellent agreement with recent

experimental NMR[10,11] and ENDOR[12] studies of the pure two-

dimensional antiferromagnets, yielding 0.20 (K_2NiF_4) and 0.17

(Rb_2MnF_4). As can be seen, the above estimates of Δ_2 for the Cd-

doped magnetic system are somewhat high: however, because

of the approximations made in our analysis no conclusion can be

drawn about the difference in the zero-point spin deviation between

pure and Cd-doped antiferromagnets. This method shows promise for

deriving values of Δ_2.

B.   Temperature Dependence of the Sublattice Mangetization

The temperature dependences of the hyperfine fields at the Cd

impurity in $RbMnF_3$/Cd and MnF_2/Cd are shown in Fig. 3. For

comparison we include the molecular field approximation (MFA)

Brillouin function for S = 5/2 and the temperature dependence of

the sublattice magnetization in pure MnF_2 as measured by ^{19}F NMR[15].

$RbMnF_3$ has the simple perovskite structure shown in Fig. 2.

The hyperfine field at the impurity is proportional to the magnetic

moment of the six nearest magnetic neighbors belonging to the same

sublattice. Therefore by measuring the hyperfine field as a function

of temperature, the temperature dependence of the sublattice magneti-

zation can be inferred. However, because the magnetic ions next

to the diamagnetic impurity are partially demagnetized, the observed

temperature dependence should differ slightly from that of the bulk

magnetization with the former decreasing more rapidly with increasing

temperature. Unfortunately, to our knowledge there are no precise

measurements available for the bulk magnetization in $RbMnF_3$ as a

function of temperature.

In MnF_2/Cd two nearest manganese ions of one sublattice and eight

next-nearest magnetic neighbors belonging to the other sublattice

contribute to the hyperfine field, with the latter probably dominat-

ing[2]. Furthermore, in order to obtain the hyperfine field the

experimental values (Table II A) have to be corrected for a dipolar

contribution (5.8 kOe at 4.2°K). Although the relative sign of the

dipolar and hyperfine fields is not known unambiguously, the dipolar

contribution is at most a 20% correction and is expected to have a

temperature dependence very similar to that of the observed internal field. For pure MnF_2 the interlattice exchange integral (next-nearest neighbors) is large and antiferromagnetic while the intra-lattice exchange (nearest neighbors) is small and ferromagnetic. Hence the replacement of a manganese ion by a diamagnetic impurity is expected to demagnetize the next-nearest neighbors much more than the nearest magnetic ions. Therefore as a first approximation we take the temperature dependence of the internal field in MnF_2/Cd to be representative for the temperature dependence of the next-nearest magnetic neighbors. Although the error of the experimentally determined fields in MnF_2/Cd is rather large due to the presence of a quadrupole interaction, the ratio H(T)/H(0) is seen in Fig. 3 to lie systematically below the ratio for the host magnetization. Recently[16] ^{19}F NMR was used to study the mixed system MnF_2/Zn at small diamagnetic impurity concentrations. The high frequency resolution of ^{19}F NMR allows the temperature dependences of the magnetizations at the nearest and next-nearest neighbors of a Zn impurity to be inferred separately from the experimental data. For the latter the magnetization decreased faster with increasing temperature than the bulk magnetization, yielding a reduction of 1.5% at approximately 30°K, the highest temperature measured. This is consistent with the reduction of ~2% shown at the same temperature in Fig. 3. To measure the demagnetization in Cd-doped antigerromagnets quantitatively, more precise PAC data are needed, preferentially for cubic

antiferromagnets for which the temperature variation of the bulk

magnetization is known. Again, however, the present results

establish that PAC is capable of this type of measurement, through

the supertransfer effect.

C. Pressure-Induced Shift of the Supertransferred Hyperfine Field

in α-MnS/Cd

In antiferromagnetic α-MnS doped with cadmium the supertransferred

hyperfine field at the Cd impurity arises through overlap and covalency

effects which transfer unparied spin density from the neighboring

magnetic ions through the intervening anions into the s shells of

Cd, as in the above cases. These processes are similar to both

correlation and delocalization superexchange leading to the exchange

interaction between the d_σ and d_π orbitals of neighboring manganes

ions. The absolute value of the antiferromagnetic exchange integral

increases with decreasing Mn^{2+} - Mn^{2+} internuclear distance, as

seen by the rise in Néel temperature with external pressure[17].

Similarly the saturation hyperfine field at the cadmium impurity

is expected to increase under applied pressure.

To estimate the pressure dependence we write the hyperfine

field at the impurity as the product of overlap and charge-transfer

components in the Mn - S and S - Cd bonds separately:

$$H_{hf} \sim (\gamma_\sigma + \langle d_\sigma | 3p_\sigma \rangle)^2 \cdot F^2_{S-Cd}$$

F_{S-Cd} contains the overlap intergrals of the outermost sulphur $3p_\sigma$ orbital with the s shells of Cd and the amplitudes of the s wavefunctions at the Cd nucleus. γ_σ^2 measures the charge transfer from the sulphur $3p_\sigma$ into the manganese d_σ orbital. With externally applied pressure the Mn – S and S – Cd internuclear distances become smaller and hence the corresponding overlap integrals and charge transfer parameters will increase, leading to a rise in the hyperfine field. The divalent cadmium impurity which replaces a manganese ion has a larger ionic radius (Cd^{2+}: 0.97Å compared to Mn^{2+}: 0.80Å). Hence there will be a local compression of the lattice around the impurity even at zero applied pressure, and the local compressibilities of the Mn – S and Cd – S bonds will be smaller than the corresponding pure sulphides. Since the local compressibilities are unknown, we assume that, within the range (20 kbar) of the external pressures applied, the Cd – S bond is incompressible but that the Mn – S distance changes according to the compressibility of pure MnS. We furtherfore adopt the overlap model; i.e. we assume $\gamma_\sigma \sim S_\sigma \equiv \langle d_\sigma | p_\sigma \rangle$. In this way we obtain

$$\frac{\Delta H_{hf}}{H_{hf}} = 2\left(\frac{\partial \ln S_\sigma}{\partial p}\right)_T \Delta p \; .$$

Unfortunately there are no reliable 3p wavefunctions available for a S^{2-} ion in an ionic lattice. However, Johnson et. al.[18] have calculated the variation of S_σ overlaps with internuclear spacing R for a number of oxides and fluorides including MnO, yielding

$\dfrac{\partial \ln S_\sigma}{\partial \ln R}$ values between -2.50 and -2.60. As the ratio of the relative

changes in the S_σ overlap integral and the bond length R is almost

independent of the anion, we use the theoretical value for MnO

$(\dfrac{\partial \ln S_\sigma}{\partial \ln R} = -2.59)$ in our analysis here. Therefore

$$\frac{\Delta H_{hf}}{H_{hf}} = 2 \left(\frac{\partial \ln S_\sigma}{\partial \ln R}\right)_T \left(\frac{\partial \ln R}{\partial p}\right)_T \Delta p .$$

The compressibility of MnS at room temperature was measured by

Clendenen and Drickamer[19] to be $\left(\dfrac{\partial \ln R}{\partial p}\right)_T = -4.167 \cdot 10^{-4}$ (kbar)$^{-1}$.

For an applied pressure of $p = 20$ kbar we expect $\left(\dfrac{\Delta H_{hf}}{H_{hf}}\right)_{calc} = +4.3\%$,

is excellent agreement with the experimental value

$\dfrac{\Delta H_{hf}}{H_{hf}}_{exp} = +3.8\% \pm 0.8\%$. Within our approximations, the magnitude

of the pressure-induced shift further support our model for the

origin of the measured hyperfine fields.

V.   Summary

The measurements presented in this paper further establish the

applicability of PAC methods to the study of solid-state phenomena

in insulators For the first time, supertransferred hyperfine field

at ^{111}Cd dopant nuclei were used to measure several effects. We

have presented an estimate for the zero-point spin deviation in

doped two-dimensional antiferromagnets which is in fair agreement

with NMR, susceptibility, and ENDOR results. We have also shown

that temperature-dependent sublattice magnetizations and pressure-

induced supertransferred hyperfine fields shifts can be measured

using the technique of perturbed angular correlations. A wide

variety of additional solid-state properties still remain to be explored.

Acknowledgements

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Table 1

Supertransferred hyperfine fields in two- and three-dimensional antiferromagnets at 4.2°K.

HOST	T_N	H_{exp} (4.2°K)	$\nu_Q = 3e^2qQ/20h$
	(°K)	(KOe)	(MHz)
$KNiF_3$	253	104.8±1.0	0.0
$RbMnF_3$	82.9	113.8±1.0	0.0
K_2NiF_4	97	54.9±1.5	3.7±0.2
Rb_2MnF_4	38.5	67.9±1.5	4.7±0.2

Table 2 A.

Temperature dependence of the internal field at the Cd impurity in
MnF$_2$. The quadrupole interaction is ν_Q = 16.5 MHz, η = 0.06 and
T$_N$ = 66.9°K.

T (°K±0.2)	H$_{exp}$ (KOe±1.2)
4.2	34.0
14.5	33.3
21.0	32.3
27.4	31.5
32.1	29.6
37.0	28.3
40.3	27.1
45.2	25.2
50.3	23.0
56.9	18.8
61.5	14.6

Table 2 B.

Temperature dependence of the Cd hyperfine field in $RbMnF_3 \left(T_N = 82.9°K \right)$.

T	H_{exp}
(°K±0.2)	(KOe±1.0)
4.2	113.8
17.0	111.8
30.0	104.6
40.0	97.5
50.0	87.3
60.0	75.0
66.0	65.8
72.0	51.0
77.0	39.8

Table 3

Pressure dependence of the internal field at the Cd impurity in

α-MnS at 4.2°K.

Pressure	H_{exp} (KOe)
1 bar	244.4±2.0
20±4 kbar	253.6±2.0

Figure Captions

Fig. 1. Time spectrum of ^{111}Cd-doped MnS at 1 bar and 20 kbar.
The solid line is a least-squares fit to a pure magnetic
interaction in polycrystalline material. The time
calibration is 0.888 ns/chennel.

Fig. 2. Crystallographic and magnetic structures of $KNiF_3$ and
K_2NiF_4.

Fig. 3. Reduced temperature/hyerfine field plot for Cd-doped MnF_2
and $RbMnF_3$.
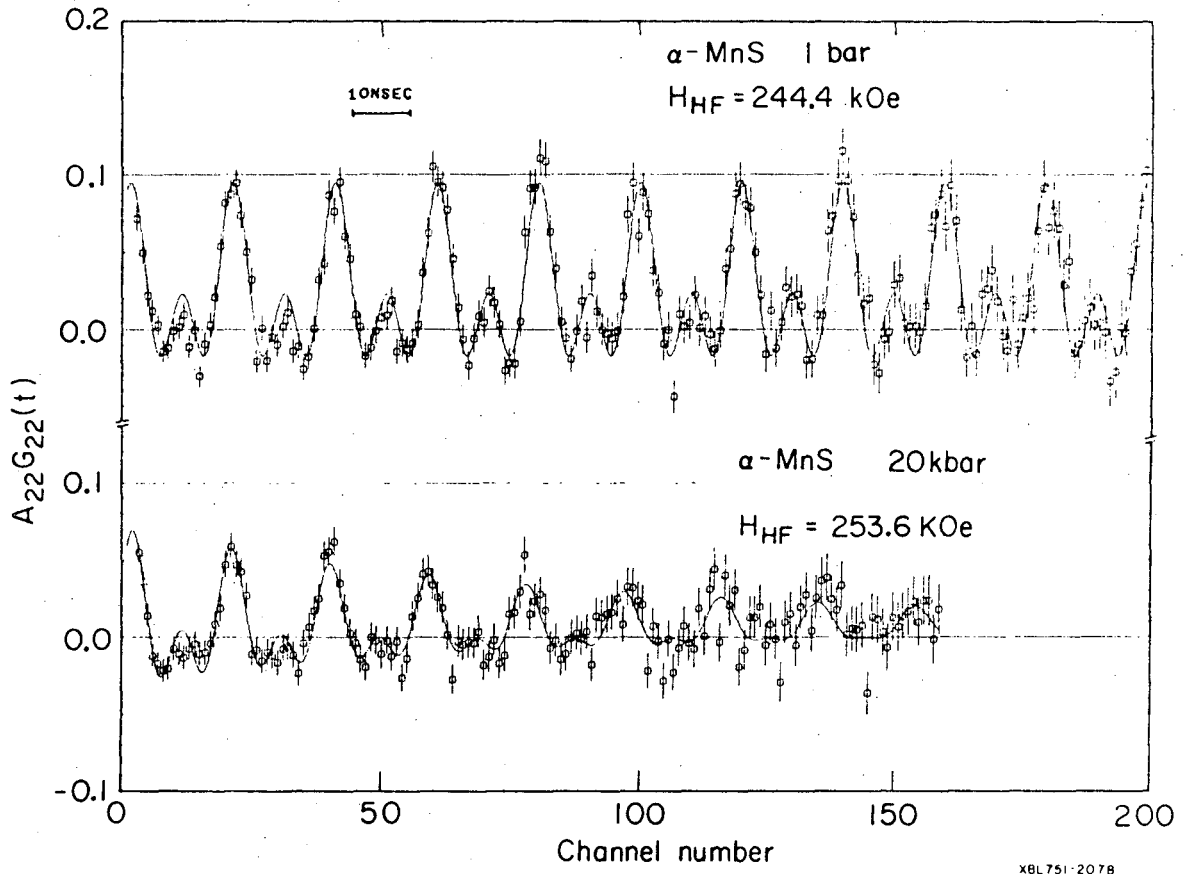
Fig. 1
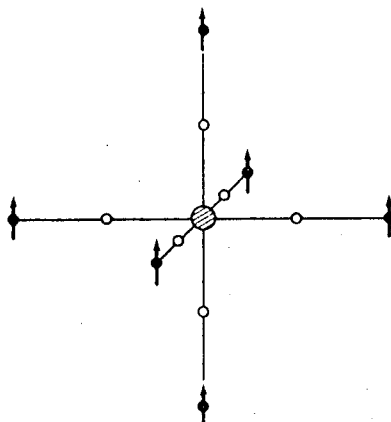
K Ni F$_3$/Cd

○ Fluorine
● Ni
◉ Cd

K$_2$Ni F$_4$/Cd

XBL 758-3701

Fig. 2

Fig. 3

XBL751-2075