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ABSTRACT

Nuclear alignment of iodine in a single crystal of copper p-iodo-benzenesulfonate at a temperature of about 0.03°K has been detected by measurement of the anisotropic angular distribution of gamma radiation from aligned I^{131} . No evidence was found for a nuclear spin-lattice relaxation time longer than a few seconds. The spin of the 637-kev level in Xe^{131} was established as $5/2$, and the E2/M1 mixing ratio of the 364-kev transition was found to be $\delta = -6.7 \pm 0.5$. The quadrupole coupling constant eQq/h was found to be -950 ± 190 Mc.

NUCLEAR ORIENTATION OF IODINE BY ELECTRIC HFS ALIGNMENT*

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I. INTRODUCTION

The electric-field gradient $q = (\partial^2 v / \partial z^2)_0$ at a nucleus arises from electrons that have nonspherically symmetrical charge distributions, i.e., from those outside closed shells and subshells. It may sometimes be as large as 10^{16} esu/cm². If the nucleus has a spin I of 1 or more it will have an electric quadrupole moment Q associated with its spheroidal shape. The interaction between the nuclear quadrupole moment and the electric-field gradient gives rise to hyperfine structure where the $2I + 1$ nuclear magnetic substates are split so that their energies are given by

$$E(M) = \frac{3 e Q q}{4 I (2 I - 1)} \left[M^2 - \frac{1}{3} I (I + 1) \right].$$

Pound has pointed out that this coupling could be used to produce nuclear alignment provided a crystal could be found in which the axis of symmetry of the crystalline field has the same direction for similar nuclei throughout the crystal.¹ By cooling the crystal to low temperatures such that $\Delta E \sim kT$,

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the nuclei will become aligned with respect to a crystal axis. Quadrupole coupling then offers a method for aligning nuclei of diamagnetic atoms, where magnetic hyperfine structure is not available. Dabbs et al. have employed this method to align nuclei in uranyl salts about 1°K ,² and the extension to demagnetization temperatures seemed desirable.

In 1954 Daniels attempted to align I^{131} nuclei by this method.³ Quadrupole-resonance measurements show that for I^{127} covalently bonded to carbon atoms in benzene rings, eQq/h is typically of the order of -2000 Mc . The negative sign indicates that the lowest state has $M = \pm I$, corresponding to alignment of the nuclear spin along the bond rather than in the plane perpendicular to it. For I^{131} , which has a smaller quadrupole moment by a factor of about two, the coupling should be of the order of -1000 Mc . The over-all splitting will be about 0.022°K and the nuclei must be cooled to temperatures in this region to obtain sufficient alignment to produce a measurable γ -ray anisotropy. The salt used was zinc p-toluenesulfonate, which has a monoclinic structure with all the C-CH_3 bonds making a small angle (about 12 deg) with the a axis. To reach the required temperatures this salt was grown in a mixed crystal with cobalt p-toluenesulfonate from a solution containing I^{131} in p-iodobenzenesulfonate ions and cooled by adiabatic demagnetization. The cobalt ions were cooled to about 0.1°K . No anisotropy of the gamma rays greater than 1% was observed,³ and this was attributed to insufficient cooling of the crystal. However the possibility could not be definitely excluded that the iodine nuclei did not reach the temperature of the cobalt ions owing to a long spin-lattice relaxation time.

We have performed a similar experiment using copper p-iodobenzenesulfonate as the magnetic coolant. Lower temperatures would be expected after adiabatic demagnetization of this salt because the Cu^{++} ion has a smaller magnetic hfs splitting than the Co^{++} ion, and hence can remove more entropy from the iodine nuclear spins. Ideally, iodine (except for a trace of radioactive I^{131}) should be excluded in order to attain still lower temperatures, since there is a large contribution to the entropy from the quadrupole splitting at low temperatures. However, copper p-toluenesulfonate, which seems an obvious choice, has a completely different crystal structure.⁴

II. EXPERIMENTAL

A. Preparation of the Crystal

Copper p-iodobenzenesulfonate was prepared by addition of p-iodobenzenesulfonic acid, made by the sulfonation of iodobenzene, to an excess of cupric carbonate. The mixture was stirred until it reached a pH of 7 and then centrifuged. After several recrystallizations, a crystal of dimensions of about 3 by 3 by 0.3 cm was grown from solution. It had a crystal habit similar to that of the p-toluenesulfonates of several other transition-series metals which crystallize in plates perpendicular to the a axis, but with triclinic symmetry.⁵ It might be expected that the orientation of the carbon-iodine bond in this triclinic structure would be essentially the same relative to the external morphology as in the monoclinic structure, and this is indeed borne out both by the unit-cell dimensions and by the

nuclear-alignment results, which set an upper limit of ~ 15 deg in the angle between this bond and the a axis. This small uncertainty is included in the limits of error.

As a preliminary experiment, the crystal was mounted in a liquid helium cryostat and adiabatically demagnetized from 1.11°K and a field of 18 kgauss. The magnetic temperature is $T^* = \lambda/\chi$, where χ is the magnetic susceptibility. This temperature was measured by reversing a current in the primary of a mutual-inductance coil surrounding the crystal and observing the deflection of a ballistic galvanometer in the secondary circuit. The coil had been calibrated in the liquid-helium range. The magnetic temperature fell to 0.033°K immediately after demagnetization. In later experiments the susceptibility was measured with a 20 c/s mutual-inductance bridge, and from χ' (the in-phase component of the susceptibility) T^* was found to be 0.032°K under the same conditions, in good agreement with the dc measurement. The out-of-phase component χ'' was small and almost constant.

A few microcuries of I^{131} were bonded to the para carbon atom of benzenesulfonic acid by diazotisation of sulfanilic acid followed by iodination. Care was taken to exclude iodine not in the required chemical state by oxidation with hydrogen peroxide, extraction with carbon tetrachloride, and boiling. It was found necessary to repeat this process twice to eliminate all the unwanted activity. The entire purification was monitored with stable iodine, which served also as a carrier. The active p-iodobenzenesulfonic acid was added to the saturated copper p-iodobenzenesulfonate solution containing the seed crystal. When the crystal was sufficiently radioactive, it was removed from the solution, rinsed thoroughly in an inactive solution, cut to a convenient shape, and mounted in the demagnetization cryostat.

B. Measurement of the γ -ray Anisotropy

The crystal was cooled to temperatures between about 0.03°K and 1.11°K by adiabatic demagnetization from fields up to 18 kgauss. A pair of 3-in. by 3-in. NaI(Tl) scintillation counters was placed near the cryostat to detect radiation emitted along and perpendicular to the a axis. The counter outputs were amplified, fed into 100-channel pulse-height analyzers, and recorded automatically. The magnetic temperature was observed simultaneously by using the ac bridge. Counting was continued for 5 min after demagnetization, during which time the magnetic temperature of the crystal changed by about 1%. The crystal was then warmed to the temperature of the liquid-helium bath and a 5-min normalization count was taken. This procedure was adopted in order to avoid errors due to temperature inhomogeneities that develop as the time after demagnetization increases.

The pulse-height spectrum showed good resolution in the 364- and 637-kev gamma-ray peaks, which were 12 and 9 times background, respectively. The counts were integrated over each of the peaks, and low temperature values were normalized to the "warm" counting rate in order to eliminate differences in geometry between the two counters. Corrections were made for finite source and counter size, background, scattering, block time and peak shift in the analyzers, and the decay of the source. These corrections were quite small, amounting to not more than 10% of the observed anisotropy. The γ -ray anisotropy ϵ , which was evaluated for each γ -ray, is defined by

$$\epsilon = \frac{I(\pi/2) - I(\theta)}{I(\pi/2)},$$

where $I(\theta)$ is the normalized intensity of radiation emitted at an angle θ with the axis of alignment.

III. RESULTS

Figure 1 shows the anisotropy ϵ for the 364-keV gamma ray as a function of time after demagnetization. Also shown is the variation of $1/T^*$, the reciprocal of the magnetic temperature, with time.

Figure 2 is a graph of ϵ for both gamma rays plotted against $1/T^*$.

We shall assume that the difference between the magnetic temperature T^* and the absolute temperature T is small down to 0.03°K . This may be justified from the experimental observations that ϵ varies linearly with $1/T^*$, and $1/T^*$ decreases linearly with time after demagnetization, which would agree with what would be expected for $T = T^*$. It would in fact be expected that T^* should be close to T for this crystal, since the lowest temperatures reached are limited by the hfs of the iodine and copper, which only affect the susceptibility in the terms of $1/T^3$ and higher powers of $1/T$, and not by magnetic interactions between the copper ions which contribute a term in $1/T^2$.

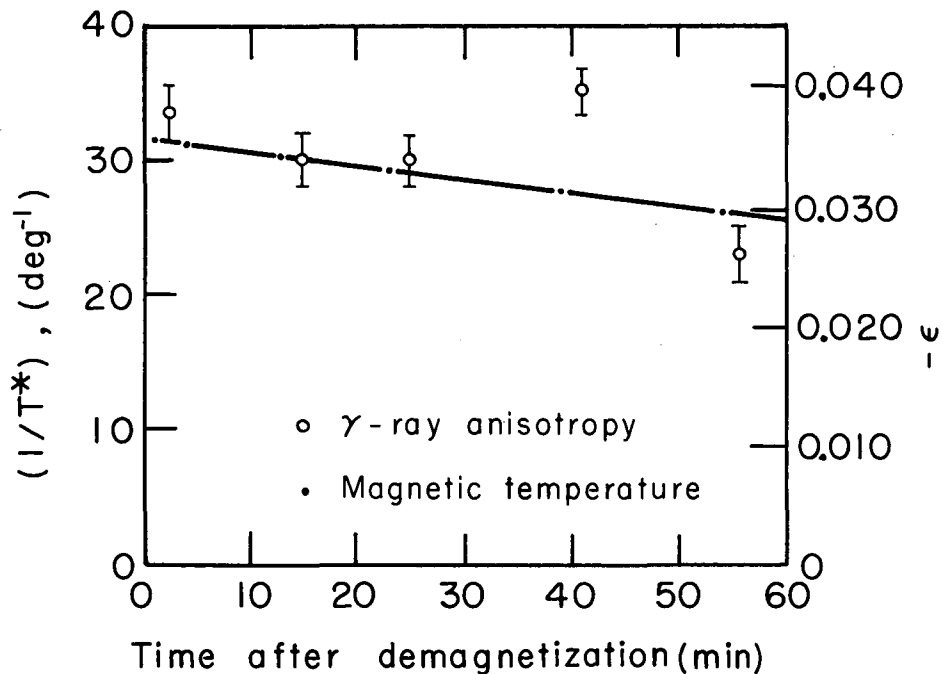
The intensities measured at $\theta = 0$ deg and $\theta = 90$ deg can then be fitted to expressions of the form

$$I(\theta) = 1 + \left(\frac{0.0007 \pm 0.0001}{T} \right) P_2(\cos \theta)$$

for the 364-keV gamma ray and for the

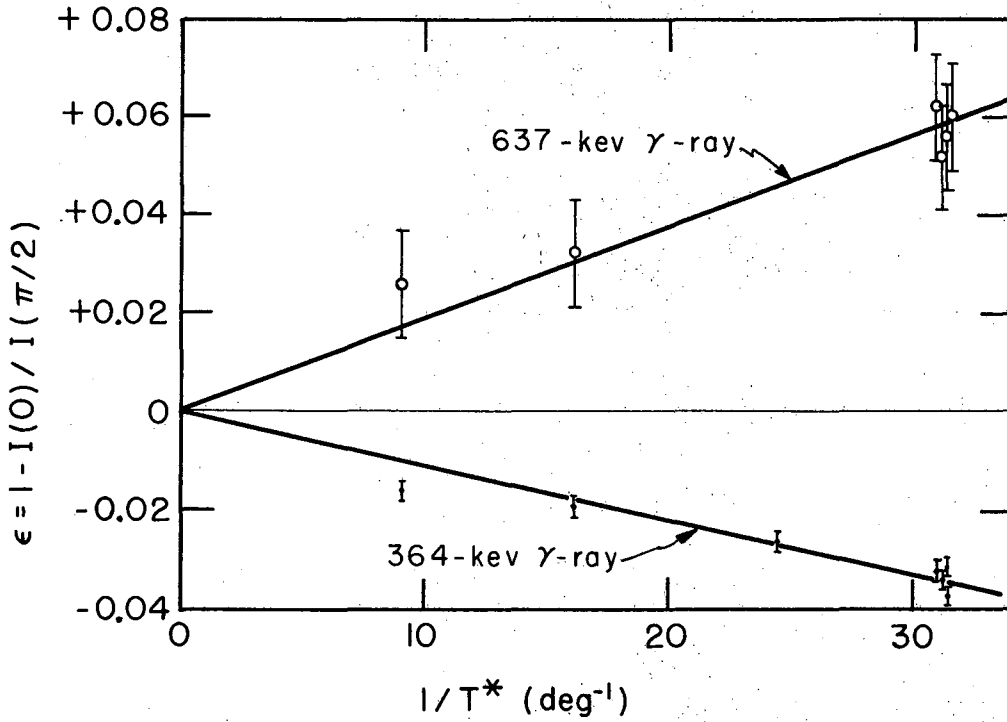
$$I(\theta) = 1 - \left(\frac{0.0013 \pm 0.0003}{T} \right) P_2(\cos \theta)$$

for the 637-keV gamma ray.



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Fig. 1. Magnetic temperature and anisotropy of the 364-kev gamma ray of Xe^{131} vs time after demagnetization of copper p-iodobenzene-sulfonate. The linear time dependence suggests that the cooling process is stopped by removal of entropy from the iodine nuclear spin system well above temperatures where the copper ions show appreciable collective behavior. No relaxation effects are evident.



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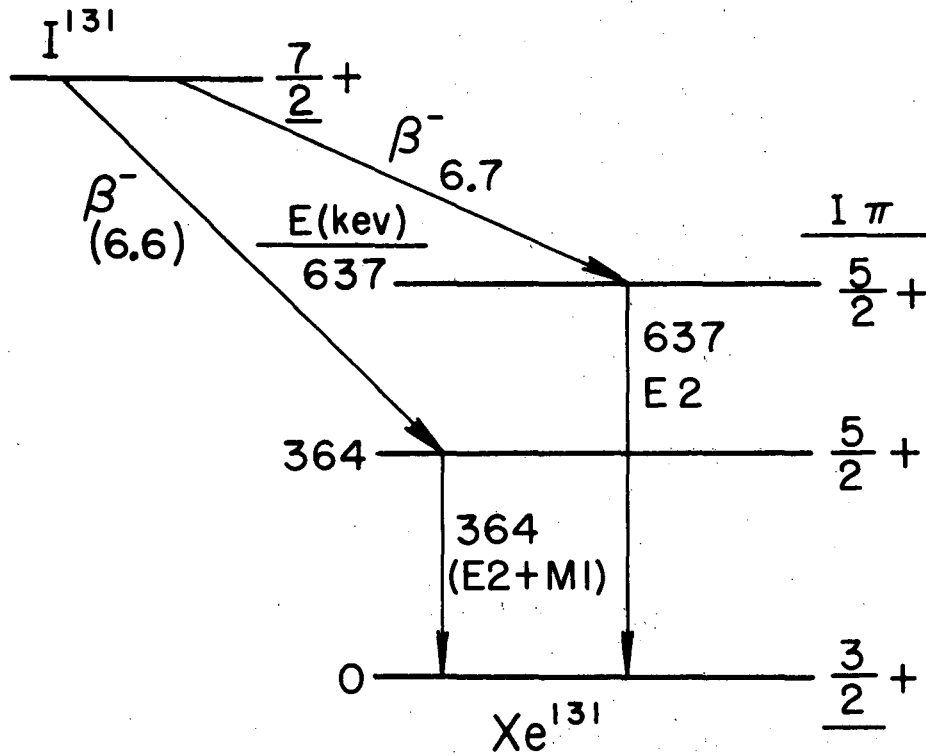
Fig. 2. Anisotropies of the 364- and 637-keV gamma rays of Xe^{131} vs reciprocal magnetic temperature. For quadrupole alignment the anisotropy would be expected to have a $(1/T)$ dependence on temperature for low degrees of alignment.

IV. DISCUSSION

The observation of the anisotropic angular distributions of the I^{131} γ rays shows that the relaxation time of the iodine nuclei is short compared with the time of the experiment. The magnitude of ϵ as well as its essential constancy during one hour after demagnetization and the linear decreases of $1/T^*$ with time all indicate that nuclear alignment takes place immediately. The effect of a relaxation time comparable with the time of the measurement would be that both ϵ and $1/T^*$ would initially increase with time and then level off, as entropy was transferred from the iodine (nuclear) spins to the copper (electronic) spins. Daniels has made a calculation for the relaxation time for bromine nuclei in cobalt p-bromobenzenesulfonate. Within the approximations involved this should give an estimate for iodine in copper p-iodobenzenesulfonate, and indicates that at 0.03°K the relaxation time is less than one second. It is interesting to note that the temperature reached by Daniels (0.1°K) was only slightly too high to produce observable anisotropy as the anisotropies there should have been about -1% and $+2\%$ for the 364- and 637-kev gamma rays respectively.

A. Decay Scheme and Quadrupole Coupling of I^{131}

The features of the decay of I^{131} that are relevant to the discussion of this experiment are shown in Fig. 3.⁶ The spins of the ground state of I^{131} and Xe^{131} have been directly measured. Kurie plots of the β spectrum show the β decay to the 364- and 637-kev levels to be allowed. Internal-conversion data suggest that the 637-kev γ ray is pure E2, while the 364-kev γ ray is mainly E2 with possibly a small admixture of M1 radiation. There is



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Fig. 3. Portion of the disintegration scheme of I^{131} which is relevant to the present research.

also an E2 transition from the 364-keV level to an $s_{1/2}$ state at 80 keV. Hence the spin of the 364-keV level is 5/2 and that of the 637-keV level must be either 5/2 or 7/2. These assignments are in good accord with the shell model.

The theoretically expected angular distribution of γ -radiation for low degrees of nuclear orientation may be written⁷

$$I(\theta) = 1 + B_2 U_2 F_2 P_2(\cos \theta),$$

where B_2 describes the degree of orientation and for quadrupole coupling takes the form

$$B_2 = \frac{1}{4} \left[\frac{(I+1)(2I+3)}{5I(2I-1)} \right]^{1/2} \frac{eQq}{kT}$$

$$= \frac{\sqrt{3}}{4\sqrt{7}} \frac{eQq}{kT}$$

for I^{131} . Here U_2 represents the effect of reorientation of the nucleus during the unobserved transitions preceding the γ transition and depends on the angular momenta involved, while F_2 depends on the angular momenta involved in the γ transition.

Considering the 637-keV γ ray first, the decay can take place with the spin sequences

$$(a) \quad 7/2 \xrightarrow[0,1]{\beta} 7/2 \xrightarrow{E2} 3/2$$

or

$$(b) \quad 7/2 \xrightarrow[1]{\beta} 5/2 \xrightarrow{E2} 3/2.$$

Sequence (a) leads to a coupling constant eQq/h of about - 350 Mc, the exact value depending on the relative fractions of Fermi and Gamow-Teller transitions

in the β decay. If we assume the gamma ray to be pure quadrupole, (b) gives $eQq = -950 \pm 190$ Mc. Since E2 transitions have a lifetime that is short compared with the time in which a nucleus can change its orientation, a reduction in anisotropy due to the interaction of the nucleus with time-dependent atomic fields need not be considered. Hence the spin sequence (a) can be ruled out as unlikely, since it leads to too small a coupling constant. The spin of the 637-keV state in Xe^{131} is therefore $5/2$, and the agreement of the coupling constant for scheme (b) with the expected value for this type of bond confirms that the γ ray to the ground state is pure quadrupole radiation.

Now that the coupling (and hence B_2 as a function of temperature) is known, the ratio $\delta(E2/M1)$ of the amplitude of quadrupole-to-dipole radiation in the 364-keV transition may be determined. The result depends only upon the ratio of the observed anisotropies of the two γ rays, since $B_2 U_2$ is the same for both at any temperature, and we have

$$\delta(E2/M1) = -6.7 \pm 0.5,$$

for the 364-keV γ ray, i.e., the transition is $97.8 (\pm 0.3) \%$ E2 admixture with $2.2 (\pm 0.3) \%$ M1.

CONCLUSIONS

1. Electric hfs alignment was found to be a feasible method for aligning nuclei of atoms without magnetic hfs at adiabatic demagnetization temperatures. A lattice suitable for aligning halogen nuclei was found.

2. The spin of the 637-keV level in Xe^{131} is $5/2+$, and the mixing ratio of the 364-keV transition is $\delta(E2/M1) = -6.7 \pm 0.5$.

3. The quadrupole coupling constant of I^{131} in p-iodobenzenesulfonate was found to be -950 ± 190 Mc, in good agreement with quadrupole-resonance results in similar molecules.

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