Covalency Effects in the Magnetic Form Factor of Ir in K_2IrCl_6

J. W. Lynn and G. Shirane
Brookhaven National Laboratory, Upton, New York 11973*

and

M. Blume
Brookhaven National Laboratory, Upton, New York 11973, and State University of New York at Stony Brook,*† *Stony Brook, New York 11794*

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We report magnetic-form-factor measurements for Ir in the cubic antiferromagnet K_2IrCl_6 ($T_N = 3.05$ K). Even though the Ir ions lie on an fcc lattice and are surrounded by octahedra of Cl, the magnetization density deviates strongly from the cubic symmetry that the charge density shows. This unusual asymmetry is dramatically magnified by the large amount of covalent bonding of the single $5d(t_{2g})$ magnetic hole to the Cl_6 complex.

Neutron-scattering measurements of the magnetic form factor $f(\vec{K})$ give direct information about the spatial distribution of the unpaired "magnetic" electrons. Measurements have been reported on a wide variety of materials containing $3d$, $4d$, and $4f$ magnetic ions, and the results can generally be understood on the basis of free-ion wave functions for the magnetic electrons, with allowances for small changes due to the effects of the solid. For elements of the $5d$ series, on the other hand, the magnetic electrons have a relatively large spatial extent, so that interesting deviations from this free-ion-like behavior might be expected. Nevertheless, there have been no detailed form-factor measurements on $5d$ magnetic materials, principally because there are very few materials in which the $5d$ ions order magnetically, and those that do are generally unfavorable for neutron-scattering experiments. The purpose of this note is to report the determination of a $5d$ magnetic form factor, which in this case is for Ir in K_2IrCl_6. Because of the symmetry of the ground-state wave function, the magnetization density differs radically from the cubic symmetry that the charge density possesses, and this noncubic symmetry reveals the covalent bonding to the Cl_6 complex in a dramatic way. This same magnetic symmetry gives rise to an atomic magnetization density which varies not only in magnitude as a function of position, but also in direction as well, and this noncollinear density is also observed in the magnetic form factor.

Potassium chloroiridate has the antifluorite crystal structure ($Fm3m$) in which the Ir ions occupy an fcc lattice ($a = 9.662$ Å), and are each surrounded by an octahedron of Cl ions located a distance $u = 0.24a$ along the cubic axes. This produces an octahedral crystalline electric field at the Ir site which splits the free-ion $5d$ states into e_g and t_{2g} states, with the triplet t_{2g} lying lower.[1] For Ir^{4+} the crystal field is so strong that the Hund's rule coupling is overcome and the low-spin $(t_{2g})^5$ state is the ground state, which can be conveniently regarded as a single t_{2g} magnetic hole. Application of spin-orbit coupling leaves a doublet lying lowest, so the ground state is, to a first approximation, an effective $S = \frac{1}{2}$ with an isotropic g factor of 2.

At 3.05 K, the moments order antiferromagnetically into the $3A$ magnetic structure.[2] For this structure, the magnetic unit cell is twice the chemical unit cell along one of the three cubic axes, and the spins point along this doubled axis. Referred to the chemical unit cell, the magnetic reciprocal-lattice vectors $\vec{\tau} = (h, k, l)$ are found at $h + k = 2n + 1$, $l = (2m + 1)/2$, where n and m are integers and the index l coincides with the doubled axis. Since the lattice constant is large, there are Bragg reflections at small momentum transfer $|\vec{K}|$ [$\kappa = |\vec{K}| = |\vec{\tau}| = 4\pi \sin(\theta)/\lambda$, where 2θ is the scattering angle], which is where the effects of covalent bonding should be most readily discernible. However, because there is a low density of magnetic ions which in addition have a small moment, and only one-third of the crystal contributes to any reflection due to the different domains, the magnetic intensities are some four orders of magnitude smaller than the nuclear reflections. This coupled with the high absorption cross sections of Cl and Ir makes form-factor measurements very difficult.

The cross section for magnetic Bragg scattering of neutrons[3] is proportional to the square of the structure factor

$$\vec{F}(\vec{K}) = \sum_j e^{i\vec{K}\cdot\vec{r}_j}\hat{K}\times[\vec{M}_j(\vec{K})\times\hat{K}], \qquad (1)$$

where $\hat{K}=\vec{K}/|\vec{K}|$, $\vec{M}_j(\vec{K})$ is the vector form factor of the jth ion in the unit cell, and the sum is over all atoms in the unit cell. For the $3A$ structure and assuming a collinear magnetization density, $|\vec{F}(\vec{K})|^2$ simplifies to

$$|\vec{F}(\vec{K})|^2 = (\gamma e^2/2mc^2)^2\mu^2 f^2(\vec{K}) \times |F_M|^2[1-(\hat{K}\cdot\hat{\eta})^2], \qquad (2)$$

where $\hat{\eta}$ is a unit vector in the direction of the sublattice magnetization, μ is the magnetic moment, and $|F_M|^2 = |\sum\hat{\eta}_j \exp(i\vec{\tau}\cdot\vec{r}_j)|^2$ is independent of (h,k,l). Thus from the Bragg intensities we can determine $f(\vec{K})$, which, when Fourier inverted, is the magnetization density. Our results, taken on a single crystal at 1.75 K with a 2.44-Å filtered neutron beam, are shown in Fig. 1. The data should be expected to deviate somewhat from the $\langle j_0\rangle$ radial integral shown, since the magnetization density is expected to differ from spherical symmetry. However, not only do the data differ radically from spherical symmetry, but they do not show cubic symmetry either. Note, for example, that the form factor falls off very quickly for the sequence of reflections $(01\frac{1}{2})$, $(01\frac{3}{2})$, and $(01\frac{5}{2})$, which progress along the direction of the spin axis, whereas the form factor falls off rather slowly for the $(01\frac{1}{2})$, $(03\frac{1}{2})$, $(05\frac{1}{2})$, and $(07\frac{1}{2})$ reflections, which are basically perpendicular to the spin direction. The form factor does, on the other hand, possess approximate cylindrical symmetry about the spin axis, that is, $f(\vec{K}) \approx f(\kappa,\psi)$ where ψ is the angle between $\vec{K}$ and $\hat{\eta}$. Figure 2 shows the Fourier inversion of the data in Fig. 1, and clearly demonstrates the elongation of the density along the spin direction.

The results shown in Figs. 1 and 2 depend, of course, on the validity of the assumed spin configuration and the spin direction. One can quickly show that changing the spin direction only increases the deviations from spherical symmetry. Furthermore, if the spin structure is collinear then there is no variation in the magnetic structure $|F_M|^2$ with (h,k,l). A variety of general canting structures was also tried, but none improved the shape of the form factor. Thus the density must be elongated along the spin direction, which is somewhat surprising at first since the environment that determines the ground state of the Ir ions is obviously cubic.[4] To understand the source of this asymmetry we note that the ground-state wave function can be written[1] in terms of t_{2g} orbitals (for spin up) as

$$|+\rangle = (\tfrac{2}{3})^{1/2}|a\rangle\chi^+ + (\tfrac{1}{3})^{1/2}|c\rangle\chi^- \qquad (3)$$

with

$$|a\rangle = 2^{-1/2}[|xz\rangle + i|yz\rangle] = |2,1\rangle,$$
$$|c\rangle = |xy\rangle = 2^{-1/2}[|2,2\rangle - |2,-2\rangle], \qquad (4)$$

where $|l,m_l\rangle$ are the orbitals for a single d elec-

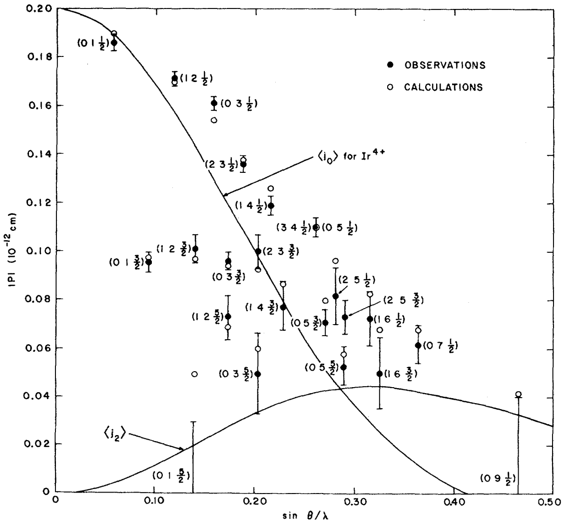

FIG. 1. Measured form factor with $p=(0.27\times10^{-12}\ \mathrm{cm}/\mu_B)\mu f(\vec{K})$ in absolute units. The data not only differ sharply from spherical symmetry, but they also do not show cubic symmetry.

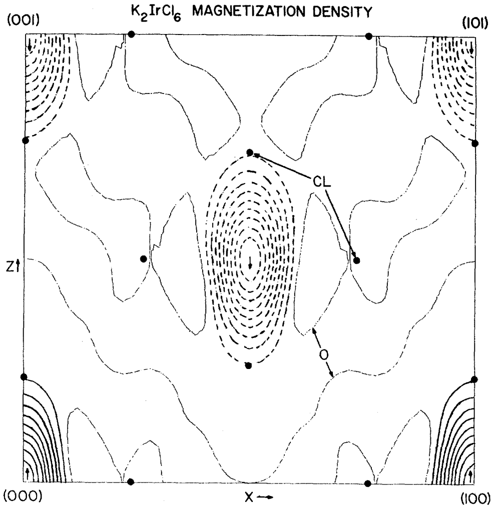

FIG. 2. Fourier inversion of the form-factor data in the $(x0z)$ plane, showing the large elongation of the density in the spin direction (z axis).

tron. Note that the charge density, $\Psi^*\Psi \propto x^2z^2 + y^2z^2 + x^2y^2$, has cubic symmetry, but that the spin density, $\Psi^* S_z \Psi \propto x^2z^2 + y^2z^2 - x^2y^2$, is in fact elongated along the spin direction. This property of the ground-state wave function is a result of the spin-orbit interaction.

To calculate the form factor quantitatively, we need to evaluate[3]

$$\vec{M}(\vec{K}) = \langle + \,|\, 2\vec{S}e^{i\vec{K}\cdot\vec{R}} + \vec{O} \,|\, + \rangle \tag{5}$$

where $\vec{O} = \frac{1}{2}\{\vec{L}f(\vec{K}\cdot\vec{r}) + f(\vec{K}\cdot\vec{r})\vec{L}\}$ is the symmetrized orbital operator introduced by Trammell. Usually the direction of $\vec{M}(\vec{K})$ does not depend on $\vec{K}$, and then the form factor is just a scalar function. In our case, only $\langle S_z\rangle$ and $\langle L_z\rangle$ are nonvanishing, so we expect the largest contribution to come from the collinear [i.e., $M_z(\vec{K})$] part of the magnetization density. However, for $\vec{K} \neq 0$, S_x, S_y, L_x, and L_y, the so-called noncollinear density terms,[5] will also give a contribution to Eq. (5). Thus the form factor is not a scalar, and $\vec{M}(\vec{K})$ must be substituted into Eq. (1) to obtain $|\vec{F}(\vec{K})|^2$. However, the resulting expression can be written in the form of Eq. (2) with a scalar function defined by[6]

$$f(\vec{K}) = \tfrac{1}{3}\{\langle j_0(\kappa)\rangle + 2\langle g_0(\kappa)\rangle - \tfrac{5}{7}[2\langle j_2(\kappa)\rangle + \langle g_2(\kappa)\rangle](3\cos^2\psi - 1)\} - \tfrac{10}{7}[\langle j_2(\kappa)\rangle + \tfrac{3}{2}\langle g_2(\kappa)\rangle]\cos^2\psi, \tag{6}$$

where $j_0(\kappa), j_2(\kappa)$ and $g_0(\kappa), g_2(\kappa)$ are the radial integrals appropriate for the spin and orbital magnetization, respectively.[7] The only contribution from the noncollinear part is the appearance of the last term in Eq. (6). Note that f has cylindrical symmetry about the spin axis. Qualitatively $\langle g_0(\kappa)\rangle$ behaves like $\langle j_0(\kappa)\rangle$, and $\langle g_2(\kappa)\rangle$ like $\langle j_2(\kappa)\rangle$, and the spin radial integrals are shown[7,8] in Fig. 1. Clearly, the form factor has the desired behavior, since for $\psi = 0$ we subtract a function like $\langle j_2(\kappa)\rangle$ from $\langle j_0(\kappa)\rangle$, and for $\psi = 90°$ we add $\langle j_2\rangle$ to $\langle j_0\rangle$, but the observed effect is much larger than can be accounted for via Eq. (6).

The missing ingredient is the covalent bonding to the Cl octahedra. The measured g value of 1.79 ($g = 2$ for a pure d electron) as well as the observed Cl hyperfine spectra suggest there is an appreciable magnetic moment on the Cl ions.[9] Stevens[1] has considered the case with covalent bonding of the Ir^{4+} to the Cl_6 complex, and has estimated that in the paramagnetic state ~ 5% of the moment resides on each Cl. The ground-state wave function is the same as in Eq. (3), but now $|a\rangle$ and $|c\rangle$ are an admixture of d and p states:

$$|a\rangle = N[|a'\rangle + \lambda|a''\rangle], \quad |a''\rangle = (i/2\sqrt{2})[|z_1\rangle - |z_4\rangle + |x_3\rangle - |x_6\rangle + i\{|z_2\rangle - |z_5\rangle + |y_3\rangle - |y_6\rangle\}],$$

$$|c\rangle = N[|c'\rangle + \lambda|c''\rangle], \quad |c''\rangle = \tfrac{1}{2}[|y_1\rangle - |y_4\rangle + |x_2\rangle - |x_5\rangle],$$

where the $|x\rangle$, $|y\rangle$, and $|z\rangle$ refer to p_π orbitals on the Cl, and the 1, 4; 2, 5; 3, 6 refer to Cl sites along $\pm x$; $\pm y$; and $\pm z$. To determine the primary effect of the bonding, we neglect the Ir-Cl overlap terms and just calculate the site-diagonal density terms. The Ir contribution has the same form as before. For the Cl, the important factor is not the type of p_π orbitals, but their *location.* If we simply count the number of orbitals on each site, then we find that the moments on the Cl located on the x and y axes cancel. Thus, although the charge is transferred equally from the Cl, there is a net magnetic moment only on the Cl at $\pm z$, and in fact all 30% of the transferred moment ends up on these two Cl. This will have a very large effect on the form factor both because of the large percentage of the moment on the Cl and also because the Cl are located far from the origin. To see if this can explain the observed form factor we assumed that a fraction M_{Cl} of the total moment resides on the Cl, and this has a spatial distribution which is simply given by Gaussian distributions with width σ centered at $\pm(0, 0, u)$. We then least-squares

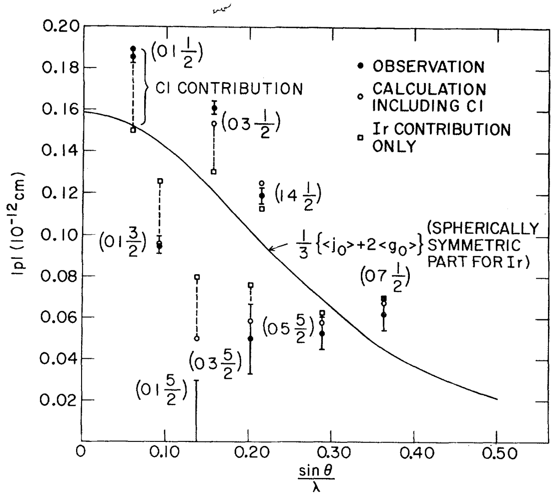

FIG. 3. Detailed comparison between the observations and calculations, with the various contributions to the calculated magnetic amplitude shown explicitly.

fitted this model to the data, and the calculated form factor values are shown in Fig. 1 as the open circles. Considering the rather crude approximation for the Cl moments, the fit is remarkably good, with a $\chi^2 = 1.6$ ($\chi^2 = 1.0$ is ideal), while the fit without the Cl moments gave $\chi^2 = 17$. For clarity Fig. 3 shows the various contributions to the calculated form factor for a selected number of points. The final best-fit parameters are $\mu = 0.80\mu_B$ for the total moment, $M_{Cl} = 0.28$, and $\sigma = 0.06a$, which compare very favorably with the estimated[1,8] values of $\mu = 0.89\mu_B$ at $T = 0$ K, and $M_{Cl} \sim 0.3$. With the success of this simple model, it would certainly be desirable to have a more rigorous calculation of the magnetization density for the $IrCl_6$ complex.

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Magneto-optical Study of Gd Using Synchrotron Radiation

J. L. Erskine*

Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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The first measurements of magneto-optical effects in metals at energies above the quartz trasmission limit are reported. The discussion focuses on the results for Gd which exhibits a $4f$ transition threshold that confirms the result of recent optical studies. Details of the magneto-optical spectrum suggest that this technique provides a sensitive probe of core-state splittings as well as other features of optically excited states in ferromagnetic metals.

Recent work on ferromagnetic metals has stimulated new interest in the application of magneto-optical techniques as a probe of their electronic structure. In particular, interest in the $4f$ core levels of rare-earth metals is apparent from the x-ray-photoemission (XPS) studies of $4f$-core-state excitations[1] and from the $4f$-electron-binding-energy calculations that have recently appeared.[2] Additionally, several new experimental techniques that probe the spin polarization of conduction-band electrons in ferromagnetic metals have been developed. These techniques (spin-polarized photoemission and field emission, and spin-dependent tunneling) have raised new questions regarding the ground-state electronic structure of ferromagnets as well as the nature of the new probes.[3] The new interest in magneto-optical techniques stems from the fact that the same parameters, i.e., core-state splittings, $4f$ thresholds, spin polarization, and band properties, can, in principle, be obtained from magneto-optical studies. In addition, at energies