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ABSTRACT

Magnetic form factor calculations have been performed using 4f wave functions obtained from relativistic Hartree-Fock-Slater calculations for free, and Wigner-Seitz, gadolinium atoms and ions. Only small differences exist between our results for free Gd^0 and free Gd^{3+} , and between free-atom and Wigner-Seitz results for Gd^0 ; however, significant changes are observed as the amount of exchange is varied in the Hartree-Fock-Slater calculation. Comparing our results with previous calculations and the recent experiments of Moon et al. led us to conclude that conduction electron screening produces only minor effects on the form factor, with the major difference between experiment and previous calculation probably being due to indirect relativistic screening.

INTRODUCTION AND GENERAL DISCUSSION

Recent neutron diffraction experiments by Moon et al.¹⁻³ have provided an exceedingly precise, and complete, measurement of the magnetic form factor for metallic gadolinium. As described in their work, these authors logically separated the measured form factor into localized and diffuse parts, and reasonably assigned these parts to, respectively, metallic gadolinium's 4f electrons and its conduction electrons. Each of these form factor components has its unique features, and each possesses its yet not fully extracted information concerning the metallic and magnetic behavior of the responsible electrons. For example, Moon et al. definitely established that the diffuse form factor corresponds to a spatial electronic distribution of long-range and oscillatory character, qualities universally ascribed to rare-earth conduction electrons; however, information contained in their inferred spatial spin density maps must await for its extraction future band structural calculations, probably of the spin-polarized type. Moon et al. also presented a comparison of the localized form factor with the calculations of Blume et al.,⁴ which were based on nonrelativistic Hartree-Fock 4f wave functions calculated by Freeman and Watson⁵ for the free Gd^{3+} ion. An inspection of this comparison shows the experimental results consistently, and significantly, fall below the calculated form factor, implying that the metallic 4f charge distribution is more expanded than the distribution obtainable via Freeman and Watson's Gd^{3+} calculation. The purpose of the present note is to explore some of the possible mechanisms responsible for this expanded 4f distribution.

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It is tempting to ascribe the above differences between measured and calculated local form factor to conduction electron screening. That is, the failure of Freeman and Watson's Gd^{3+} 4f wave function to precisely describe the metallic 4f charge density could conceivably be due to the metal's conduction electrons providing some additional screening of the nuclear charge, as seen by the 4f electrons, and thus leading to a spatial expansion of the 4f wave function. Even though such an effect must qualitatively be present, its quantitative plausibility has heretofore not been definitely established. Another mechanism which could conceivably spatially expand the metallic 4f distribution over that calculated by Freeman and Watson is indirect relativistic screening, that is, additional screening seen by the 4f electrons due to the relativistic contraction of the wave functions for some of the other electrons present. Although Blume et al. have argued, using previously calculated relativistic and nonrelativistic Hartree calculations for Hg, that this relativistic effect should be small, it is our feeling that its actual quantitative effect on form factors for the rare earths is yet to be established. Other effects which could possibly affect the comparison between calculated and measured form factor include core polarization, conduction electron interband mixing with 4f electrons, and correlation effects beyond the Hartree-Fock formalism. Moon et al.³ have argued against the quantitative significance of either core polarization or interband mixing, and, agreeing with their reasoning, no further mention of these effects will be made in this brief report.

In order to provide information which could help isolate the mechanism(s) actually responsible for the above discussed difference between observed and calculated local form factor, we decided to perform a detailed series of form factor calculations using 4f wave functions obtained from relativistic Hartree-Fock-Slater calculations for free and Wigner-Seitz gadolinium atoms and ions. Some of the results emerging from this calculational study will be presented herein, comparisons made with the measured local form factor, and discussion given concerning the pertinence of these results in isolating quantitatively significant effects on the local form factor.

CALCULATIONS

Since metallic gadolinium behaves magnetically as if the individual-site f-shells formed $8S_{7/2}$ states, with the free-atom 5d and 6s electrons forming the conduction band, the 4f form factor is isotropic and expressible as

$$F_{4f}(\kappa) = \langle j_0(\kappa r) \rangle = \int_0^{\infty} \rho_{4f}(r) j_0(\kappa r) dr. \quad (1)$$

Here, κ is the magnitude of the neutron's scattering vector, $j_0(x)$ is the zeroth-order spherical Bessel function, and $\rho_{4f}(r)$ is the radial charge distribution for the 4f electrons. Throughout, we have normalized $\rho_{4f}(r)$ so $F_{4f}(0) = 1$. For our results using free-atom wave

functions, Eq. (1) has been used directly; however, for those results using Wigner-Seitz wave functions, the upper limit on the integral in Eq. (1) was changed to r_s . Here r_s is the radius of the Wigner-Seitz sphere, and determined to have $4\pi r_s^3/3$ be the volume per metallic site. However, due to the smallness of $\rho_{4f}(r_s)$ and the oscillating behavior of $j_0(kr)$, this refinement has little numerical significance.

Since a relativistic formalism necessitates the use of a j - j coupling scheme, relativistic calculations for 4f electrons yield two, two-component, wave functions, one for $j = 5/2$ and one for $j = 7/2$. Thus, for the quantity $\rho_{4f}(r)$ appearing in Eq. (1) we used an occupation weighted average over the two j wave functions: $\rho_{4f}(r) = [\rho_{5/2}(r) + \rho_{7/2}(r)]/7$, with $\rho_{5/2}$ and $\rho_{7/2}$ being the respective charge densities formed in the usual fashion from the two components for a given j value. Again, this refinement has little numerical significance in the final form factor results, since the differences between $\rho_{5/2}$ and $\rho_{7/2}$ are quite minor.

Another common feature present in our calculations was the use of 4f wave functions calculated using a statistical approximation to the exchange potentials, since the wave functions were generated using the readily available Oak Ridge relativistic Hartree-Fock-Slater computer code.⁶ Although there exist studies⁷⁻⁹ which indicate the preferred amount of exchange to use in such calculations if one desires to reasonably approximate Hartree-Fock results, we originally felt it worthwhile to vary the amount of exchange between the Kohn-Sham ($=2/3$) and Slater ($=1$) limits. In this manner we were able to study the effect of the amount of exchange on the resulting form factor, and this effect is significant.

Some results from our form factor calculations are presented in columns C through G of Table I. Included for comparison with our results, in column A of Table I, is the form factor calculated by Blume et al. for Gd^{3+} . Column B of Table I is a fit obtained by Moon et al. to their observed local form factor by adjusting the parameters of an analytic 4f wave function of the same functional form as the Hartree-Fock 4f wave function of Freeman and Watson. So for our purposes here, column B can be considered as "experimental" results, having effective errors, as a function of κ , equivalent to those quoted by Moon et al.³

DISCUSSION

As mentioned earlier, and as is seen from comparing columns A and B of Table I, the observed local form factor falls consistently below the calculated result of Blume et al. One possibility for this difference is conduction electron screening. The tails of gadolinium conduction electrons between the nucleus and, say, the peak of the 4f wave function are expected to behave screeningly very similarly to 5d or 6s wave functions. So it should be possible to gain some insight into the quantitative magnitude of conduction electron screening from form factors for $Gd^0(f^7d^1s^2)$ and $Gd^{3+}(f^7)$. Columns C and D of Table I

Table I. Gadolinium form factors obtained using various 4f wave functions. Column A is the previous work of Blume et al. Column B is the fit obtained by Moon et al., who adjusted the parameters of an analytic 4f wave function to fit their observed local form factor. The remaining columns resulted in the present investigation using 4f wave functions from relativistic Hartree-Fock-Slater calculations. Columns C and D are for, respectively, free $Gd^0(4f^7d^1s^2)$ and free $Gd^{3+}(4f^7)$, both obtained using the standard Latter correction to the exchange potential at large r and an amount of exchange = 0.933. Columns E through G were calculated using Wigner-Seitz results and amounts of exchange of 0.933 for E, 0.800 for F, and 0.667 for G.

κ	A	B	C	D	E	F	G
0.00	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.05	0.986	0.983	0.984	0.985	0.984	0.983	0.931
0.10	1.945	0.934	0.940	0.941	0.938	0.934	0.928
0.15	0.881	0.861	0.872	0.875	0.870	0.861	0.850
0.20	0.802	0.772	0.788	0.793	0.786	0.774	0.760
0.25	0.714	0.677	0.697	0.702	0.696	0.681	0.665
0.30	0.623	0.582	0.604	0.609	0.604	0.589	0.572
0.35	0.534	0.491	0.515	0.519	0.515	0.500	0.483
0.40	0.449	0.409	0.431	0.435	0.432	0.417	0.402
0.45	0.371	0.335	0.356	0.360	0.356	0.343	0.328
0.50	0.301	0.270	0.290	0.292	0.290	0.277	0.265
0.60	0.187	0.166	0.182	0.184	0.183	0.173	0.164
0.70	0.105	0.092	0.106	0.107	0.106	0.100	0.093
0.80	0.051	0.043	0.054	0.054	0.054	0.050	0.046
0.90	0.016	0.012	0.020	0.020	0.020	0.018	0.016
1.00	-0.004	-0.007	-0.001	-0.001	-0.001	-0.002	-0.003
1.10	-0.015	-0.016	-0.012	-0.013	-0.012	-0.013	-0.013
1.20	-0.020	-0.021	-0.018	-0.018	-0.018	-0.018	-0.017
1.30	-0.021	-0.022	-0.020	-0.020	-0.020	-0.020	-0.019

provide this information and are for, respectively, a free Gd atom and a free Gd^{3+} ion. An inspection of these results shows the extra screening produced by the 5d and 6s electrons does slightly affect the 4f form factor, but the magnitude of the effect is much smaller than the difference between columns A and B. Thus, we conclude that conduction electron screening is not the major mechanism for the difference between columns A and B. This conclusion is reinforced by comparing columns C (for a free atom) and E (for a Wigner-Seitz atom), which shows that imposing Wigner-Seitz boundary conditions has a very small effect on the 4f form factor. This implies the screening caused by 5d and 6s electrons is almost unchanged by a change in the environment outside the peak of the 4f wave function.

Columns E through G of Table I are form factors obtained by imposing Wigner-Seitz boundary conditions on $Gd^0(4f^7d^1s^2)$, with the only variable being the amount of statistical exchange used in the calculation. Inspection of these results shows the resulting form factors

to be quite sensitive to the amount of exchange. Furthermore, column F is seen to be much closer to the "experimental" results, column B, than the previous calculation of Blume et al., column A. Also, undoubtedly we would have obtained a slightly better agreement with the "experimental" results by using an exchange value between 0.667 and 0.800, say about 0.75. It is interesting to note that such a value of exchange giving the "best fit" to the "experimental" results would fall in the neighborhood of, but probably be slightly larger than, the value of about 0.70 expected from numerical experiments⁷⁻⁹ performed in order to have atomic Hartree-Fock-Slater calculations agree, both energetically and charge-density-wise, with atomic Hartree-Fock results. Thus, such a hypothetical calculation giving the "best fit" should not necessarily result in a form factor which would be identical to one eventually calculated for a relativistic, Wigner-Seitz, Hartree-Fock, $Gd^{0}(f^{7}d^{1}s^{2})$ atom, although we expect only minor differences. This means we are not able, at present, to eliminate entirely the possibility of correlation producing a small effect on the form factor. Be as it may, since the amount of exchange required to obtain a "best fit" falls in the range 0.667 to 0.800, we believe the close agreement between columns B and F of Table I strongly suggests that indirect relativistic screening does play a measurably significant role in gadolinium's local form factor. This belief is also reinforced by the much larger differences seen when either column F or G is compared with column A than when F or G is compared with B. Of course, if indirect relativistic screening effects are present in gadolinium's local form factor, one would also expect to be able eventually to establish their presence in form factors for the other rare-earth metals.

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