of three $J=\frac{7}{2}$ holes coupled to a spin of $J=\frac{7}{2}$. Using $\langle r_n{}^2\rangle = R_0{}^2A^{2/3}$ with $R_0=1.2\times10^{-13}$ cm, we obtain $Q=+0.09$ b. This is considerably smaller than the measured quadrupole moment, and conceivably is due to configuration mixing or small deformations of the nuclear core. The only other shell-model state likely to contain the 61 st proton is $d_{5/2}$, but this is not allowed because the configuration $(d_{5/2})^3$ coupling to $I=\frac{7}{2}$ is forbidden by the Pauli principle.

On the assumption that the nuclear core of Pm^{151} is highly deformed, there are two possible state assignments for the 61 st proton that give the correct spin and parity. When the notation of Mottelson and Nilsson is used,[5] these are $\frac{5}{2}+[413]$ and $\frac{5}{2}+[402]$. We have calculated the nuclear moments of these states for different values of the deformation parameter δ. The value obtained for the level $\frac{5}{2}+[402]$ is about 3.7 nm and is insensitive to the deformation. The level $\frac{5}{2}+[413]$ gives a moment of 0.91 nm with a deformation parameter of $\delta\approx0.4$. This is in better agreement with the measured value and seems to us to be the proper state assignment. The collective-model value for the quadrupole moment can be obtained from the expression

$$Q=Q_0\frac{3K^2-I(I+1)}{(I+1)(2I+3)}, \tag{4}$$

where $Q=\frac{4}{5}ZR_0{}^2\delta$. Using these expressions, we obtain for the quadrupole moment $Q=+2.1$b. The theoretical sign of Q/μ is positive, which agrees with the sign inferred from the data.

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Measurement of the Atomic Scattering Factor of Ne, Ar, Kr, and Xe

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To test the accuracy of the Hartree-Fock (HF) method and the reliability of x-ray measurements of the atomic scattering factor f, we have determined the scattering of Mo $K\alpha$ radiation by Ne, Ar, Kr, and Xe gases. Values of f were obtained on an absolute basis with an accuracy of about $\frac{1}{4}\%$. Results at small angle yield the mean-square radius of the electron cloud $\langle r^2\rangle_{\mathrm{av}}$ and the dispersion correction. For Ne, Ar, and Kr, the values of $\langle r^2\rangle_{\mathrm{av}}$ are in good agreement with HF calculations. For Xe, the experimental value is significantly lower. Susceptibility results yield about 6% lower values in each case. Our derived values of the dispersion correction are each more negative than those obtained from published absorption coefficients. At higher angles, our f values differ by less than 0.2 electron unit from the HF values for all the gases; even for Xe the approximate HF values presently available are more nearly accurate than the Thomas-Fermi-Dirac (TFD) values. We conclude that a 4% discrepancy between theory and experiment found by Batterman, Chipman, and DeMarco for metal powders arose from solid-state effects or from difficulties in sample preparation.

INTRODUCTION

EXPERIMENTS[1] have indicated that electron densities in free atoms as calculated by the Hartree-Fock (HF) method do not yield scattering factors in agreement with those measured by x-ray diffraction from powdered metal samples of Al, Fe, and Cu. Several explanations may be advanced to explain this discrepancy: (1) terms neglected in the HF formulation are large enough to be significant, (2) the basic equation relating x-ray scattering and charge density is incorrect when accuracies of the order of 1% are required, (3) the experiment on metal powders[1] did not satisfy all the conditions for which the scattering equation was derived, (4) the change in charge density as the atoms are formed into the solid is sufficient to explain the results. As a matter of fact, the experiment showed that the scattering factor for Al was actually lower than that calculated for the Ne core in Al, and Batterman *et al.*[1] concluded that it was unlikely that such a large change could be brought about by binding effects.

Since the x-ray scattering from gas does not entail such experimental difficulties as extinction, porosity, or surface roughness, there is much less chance of an error of type (3) above in the case of scattering from a gas. Furthermore, one is not restricted to the Bragg reflections alone for a gas and it is possible to make measurements down to low angle. It is then possible to check (2) because the scattering factor in the forward

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[1] B. W. Batterman, D. R. Chipman, and J. J. DeMarco, Phys. Rev. **122**, 68 (1961).

direction, after correction for dispersion, should be Z, the total number of electrons. Such experiments were carried out by various workers[2] in the early days of x-ray techniques to an accuracy of about 5% in the scattering factor. Their results differed from the modern HF values by about this amount. In addition, Bartell and Brockway[3] have measured the electron scattering from Ar and find deviations from the HF values of the same order. They do not distinguish, however, whether these deviations arise from experimental error, from a breakdown of the Born approximation used to interpret their results, or from an inadequacy of the HF method.

This earlier work is, thus, not sufficiently accurate to help us to understand the 4% discrepancy in the scattering factors of the metals as reported by Batterman *et al.*[1] We, therefore, have remeasured the x-ray scattering factors of Ne, Ar, Kr, and Xe with an accuracy of better than $\frac{1}{2}\%$. The analysis of the data is complicated by the dispersion correction and we have found discrepancies of the order of two or three times the experimental error. Nevertheless, we feel that the HF scattering factor is essentially adequate to our accuracy. In the case of Xe, the fractional deviation is slightly less than that in the other gases, but the greater precision possible in this case allows us to distinguish clearly the difference between the experimental results and the HF prediction.

EXPERIMENTAL

The apparatus was constructed so as to alternately measure the scattering of monochromatic x rays from the sample and from helium. The effect of the angular spread of the incident and scattered beams was then taken into account to yield a scattering factor which, after correction for the scattering of helium, could be compared to that calculated theoretically.

A Norelco diffraction unit was so modified that a monochromator and a gas sample could be accommodated. The arrangement is shown schematically in Fig. 1. X rays from the line focus of a molybdenum anode tube impinged on LiF monochromating crystal. The crystal was so cut and bent that Mo $K\alpha_1$ radiation was brought to a focus in the plane of the receiving slit. Since the tube was operated at a maximum of 31 kV, there was no harmonic contamination. A portion of the monochromated beam was scattered into the monitor counter by the Mylar foil. Several Zr absorber foils, only one of which is shown in the figure, served as attenuators and could be inserted or removed from the beam as required. The absorption of each foil was measured directly and the absorption of a series of foils, adequate to attenuate the main beam to a countable rate, could then be inferred. The sample chamber was machined in a large brass plate which was supported along the axis of the Norelco goniometer. The chamber was about 1 cm thick. Windows of 0.0005-in. Al foil were secured to each face with O-rings. Because of the preferred orientation in these foils, it was possible to align them in such a way that two of the three lowest order Bragg reflections were virtually eliminated. We chose to orient our foils so that (200) and (220) were suppressed at the expense of considerable reflection from (111). This reflection created so much background from 14° to 22° that it was not feasible to take data in this angular range. In order to limit the volume from which background scattering could occur, a beam stop was placed as close to the sample as possible within the restriction that it must not shield the data counter from the sample. A receiving slit, which defined the solid angle through which scattering was observed, was placed in the approximate position of a standard Norelco receiving slit. The slit was approximately 1-cm square and it could be removed, as could the beam stop, when it was desired to make a measurement of the direct beam intensity. The detectors were scintillation counters used in conjunction with pulse-height analyzers. Because the aluminum windows could not withstand any appreciable pressure differential, it was not possible to construct a vacuum arrangement to eliminate background scattering. Instead, a large polyvinyl chloride bag, indicated by dashed lines in the figure, was placed around all parts of the setup from which scattering might enter the data counter. Helium was allowed to flow through the bag in such a way that its outlet pressure was maintained slightly above atmospheric; the sample was similarly flowed through its chamber. Scattering experiments as a function of sample flow rate showed that there were no gas leaks and that there was no appreciable bowing of the windows arising from pressure differences.

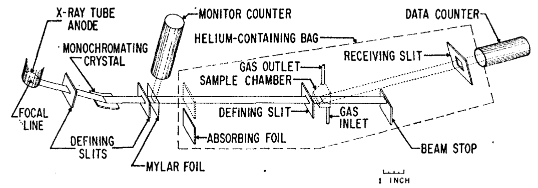

FIG. 1. Schematic diagram of the apparatus.

A Zr-Sr balanced filter, placed in front of the data counter, was used in the case of Kr because the fluorescence was not resolved from the ordinary scattering by the pulse height analyzer. This procedure avoided changing radiations, which would have entailed considerable effort. However, the Kr fluorescence was about five times as intense as the scattering, so that it was advantageous to make the filter elements quite thick. We chose our filters to have an absorption of

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[2] Work previous to 1933 is summarized in A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand, Inc., Princeton, New Jersey, 1935). Later work of G. Herzog, Helv. Phys. Acta **6**, 508 (1933) and E. Laurila, Ann. Acad. Sci. Fennicae, Series **AI 27** (1944) does not significantly alter the results shown in Compton and Allison. We are indebted to Dr. R. P. Hurst for calling the Laurila reference to our attention.

[3] L. S. Bartell and L. O. Brockway, Phys. Rev. **90**, 833 (1953).

TABLE I. Experimental values of the total scattering, given by f_{eff}^2, and the values of the effective scattering angle, δ_{eff}, for the goniometer settings δ, used.

δ	Ne		Ar		Kr		Xe	
(Deg)	δ_{eff}	f_{eff}^2	δ_{eff}	f_{eff}^2	δ_{eff}	f_{eff}^2	δ_{eff}	f_{eff}^2
3	3.76	97.7	3.69	314.3	3.73	1207	3.73	2783
4	4.59	95.9	4.53	307.8	4.57	1188	4.56	2741
7	7.33	90.1	7.28	281.3	7.31	1102	7.31	2547
10	10.22	81.6	10.18	246.9	10.20	1000	10.21	2322
14	14.13	70.2	14.09	199.9	14.13	855	14.14	2000
22	22.05	46.1	22.03	129.9	22.08	632	22.09	1500
27	27.02	35.3	27.03	104.1	27.07	522	27.07	1275
32	32.01	27.5	32.03	87.7	32.06	442	32.06	1091

about 80 for Kr fluorescence. Such a large value of absorption places stringent requirements on the uniformity of the filter; we found that our Zr foils varied by about 1% in thickness, giving rise to about 4% variation in the absorption. We corrected for this effect by shimming with pieces of Mylar, but the over-all filter was believed to be uniform to only about 1% in absorption. In addition, the Sr itself fluoresced. This effect was taken into account by making the assumption that the Sr fluorescent power was proportional to the Mo $K\alpha$ power. In view of these considerations, the accuracy of the Kr measurements was less than for the other gases as will be detailed below.

The detection system was studied in detail for possible spurious effects. It was found by measuring the apparent absorption of a single foil as a function of count rate that a simple dead time was adequate to explain the counting efficiency as a function of intensity, up to a count rate of about 8000 counts/sec. At higher count rates, there was a shift in the pulse-height distribution and no measurements were made at such high rates. The pulse-height distribution also shifted depending upon the position in the scintillation crystal which was activated. The limits of the pulse-height analyzer were so set that a negligible fraction of the pulses were lost on this account. It was, on the other hand, not possible to set the lower limit at such a position that unavoidable drift in effective gain did not change the count rate significantly because of the background at these low levels. (Effective gain includes changes in such parameters as the photomultiplier high voltage, the value of the base line of the pulse-height analyzer, as well as actual changes in gain.) Such changes could be taken into account, however, by measuring the change in count rate effected by decreasing the gain a fixed fraction. The actual value of effective gain at any time could be established by measuring the position of the peak of the pulse-height distribution of the direct beam.

It is important to have a strictly monochromatic beam, not only because of the scattering parameter, $(\sin\theta)/\lambda$, but especially because of wavelength dependence of the absorption of the foils used to attenuate the main beam. We studied the wavelength distribution of our beam with the help of Al, Zr, and Y foils, pulse-height analysis, single-crystal diffraction scans, and direct observation of the dispersion of the monochromating crystal. From the latter, it was possible to distinguish the α_1 and α_2 lines. The defining slits were so adjusted that only about 4% of the beam was α_2. From the other experiments it was possible to determine that there were no very hard nor very soft components, arising from diffuse scattering or fluorescence. We found, however, that there was a small component of continuous radiation just beyond the Y edge which was apparently being Bragg reflected from the extreme of the mosaic distribution in our monochromating crystal. We were unable to devise any direct, sensitive method of investigating the intensity in the main beam between the Zr edge and the Mo $K\alpha$ wavelength; on the other hand, if the mosaic distribution were approximately symmetrical, this effect would be small enough so as not to affect our results.

Because of the spread in incident beam directions and because of the appreciable area of the receiving slit, it was necessary to make a calculation which related the measured scattering at each setting of the counter to the theoretical value at some particular value of the scattering parameter $(\sin\theta)/\lambda$. This relation was established in the following way. A beam scanner was placed in the region usually occupied by the receiving slit and the beam stop. This scanner defined narrow pencils of x rays whose intensity could be measured as a function of displacement (in angle and position) from the central ray. The central ray was that ray which passed through, and normal to the axis of the goniometer, and through the center of the receiving slit when the scattering angle as measured by the goniometer setting δ was zero. Then, with an assumed function given by Eq. (1) using theoretical estimates of f_{eff} [see Eq. (3)], and using data from the beam scanner discussed above, we calculated the average intensity (by machine integration over the incident beam, over the scattering volume, and over the receiving slit area) to be expected at the counter for several selected values of δ. In a second calculation, we obtained the intensity which would have fallen at the center of the receiving slit if all of the incident power had been confined to the central ray and all of the scattering had taken place on the axis of the goniometer. We defined δ_{eff} as the angle at which the intensity from the second calculation equaled the intensity from the first calculated at angle δ. The correction for divergence was then applied by measuring the gas scattering at receiving slit positions given by δ, but plotting the intensity so obtained at $\delta_{\rm eff}$. After the experiment it was possible to modify the assumed function and iterate the procedure, but this was found to be unnecessary. All our results are given as though the entire scattering took place at the angle $\delta_{\rm eff}$. Table I gives the values of $\delta_{\rm eff}$ for the values of δ used. One may note that the difference from gas to gas is such as to yield an error in the scattering factor of only a few tenths of a percent, even though the scattering functions are quite different for the various gases.

To carry out an actual run, the sample of spectroscopic grade rare gas[4] was allowed to flow through the sample chamber until the scattered intensity became constant with time. (It was not possible to pump out the chamber because of the thin windows.) After making measurements at the selected values of δ, the sample was replaced with He and "background" measurements were made. These measurements were then corrected to those which applied to the gas sample by allowing for the additional absorption present in the latter case and by making use of the theoretical scattering function for He.[5] The corrected results were then interpreted in terms of the formula[6]

$$P_s/P_b=N(e^2/mc^2)^2 t\Omega PAGf_{\rm eff}^2\,, \tag{1}$$

where P_s is the power scattered into the receiving slit, P_b is the power in the direct beam, N is the number of atoms per unit volume, (e^2/mc^2) is the classical electron radius, t is the thickness of the sample, Ω is the solid angle intercepted by the receiving slit, P and A are polarization and absorption factors, discussed below, $f_{\rm eff}$ is the effective scattering factor [see Eq. (3)], and the factor G corrects for the finite size of the atoms. This factor is less than 0.1% for every case considered here. The polarization factor P is given by $(1+\cos^2 2\theta_M \times\cos^2 2\theta_S)/(1+\cos^2 2\theta_M)$, where θ_M is the Bragg angle for the monochromating crystal and $2\theta_S$ is the scattering angle from the sample. In actual fact, divergences in the incident and scattered beams give rise to an additional term involving the sine of the angle between the two scattering planes, but this term is negligible for all rays in our experiment. The absorption factor arises because the scattered rays traverse a longer path in the sample and in the exit window than do the direct rays.

To summarize, one averages the scattering function, given by the right-hand side of Eq. (1), over the spread in scattering angle yielding $\delta_{\rm eff}$ as a function of δ. Then, evaluating all angularly dependent parameters in Eq. (1) at $\delta_{\rm eff}$, we calculate the measured value of $f_{\rm eff}$ from the experimental value of the ratio P_s/P_b.

TABLE II. Experimental values of the mass-absorption coefficient and the imaginary part of the scattering factor derived therefrom.

	Ne	Ar	Kr	Xe
μ/ρ	20 ± 0.4	12.2 ± 0.3	79.9 ± 0.2	38.39 ± 0.13
$\Delta f''$	0.02	0.20	2.8	2.2

RESULTS

Table I gives our results in the form of $f_{\rm eff}^2$ versus $\delta_{\rm eff}$. In order to compare these values to those calculated theoretically from the formula[6]

$$f=\int_0^\infty 4\pi r^2\rho(r)\frac{\sin kr}{kr}dr\,, \tag{2}$$

one must make use of the relation

$$f_{\rm eff}^2=(f_0+\Delta f')^2+(\Delta f'')^2+(Z-\mathfrak{F})/B^2. \tag{3}$$

In these expressions, f_0 is the value of the scattering factor at very high frequency, $\rho(r)$ is the radial density of electrons, k is the parameter 4π $(\sin\theta)/\lambda$ with 2θ the scattering angle and λ the wavelength, $\Delta f'$ and $\Delta f''$ are the real and imaginary parts of the dispersion correction, and $(Z-\mathfrak{F})/B^2$ is the Compton scattering. The Breit-Dirac correction factor appears here as B^2 rather than B^3 because with scintillation counting we measure power in photons per second rather than in conventional units.

To obtain f_0 from our results, we proceeded as follows: We used our experimental values of μ/ρ to evaluate $\Delta f''$ according to the relation $\Delta f''=(\mu/\rho) \times(M/N_0)(mc^2/e^2)/2\lambda$, with μ/ρ the mass absorption coefficient, M the molecular weight, and N_0 Avogadro's number. These values are given in Table II. Incidentally, it is likely that these values of μ/ρ are the most accurate available for the three heavier gases. Values for the Compton scattering were estimated from the literature.[7] Experimental values for $\Delta f'$ were then determined from an extrapolation of our values of $f_0+\Delta f'$ to zero scattering angle where $f_0=Z$; this procedure is described more fully in the following section. The values of $\Delta f'$ so obtained are presented in Table V, and other necessary quantities given in Table III.

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[4] The total impurities were less than 0.05%; the atomic numbers of the impurities were such that the error introduced was also less than 0.05%.

[5] C. M. Womack, Jr., J. N. Silverman, and F. A. Matsen, Acta Cryst. 14, 744 (1961).

[6] R. W. James, *The Optical Principles of the Diffraction of X Rays*, (G. Bell and Sons, London, 1954).

[7] For Ne: A. J. Freeman, Acta Cryst. **12**, 274 (1959); For Ar: Values were interpolated from those for Ca^{++}, K^+, and Cl^- from A. J. Freeman, *ibid.* **13**, 190 (1960); For Kr and Xe: We evaluated the scattering neglecting exchange from the Hartree-Fock scattering factors. These values were then lowered for the effect of exchange based on exact calculation for Kr at $(\sin\theta)/\lambda=0.3$ which Dr. Freeman and Dr. Watson kindly carried out for us. These estimates were adequate for these heavier gases for which the Compton scattering is a small fraction of the total.

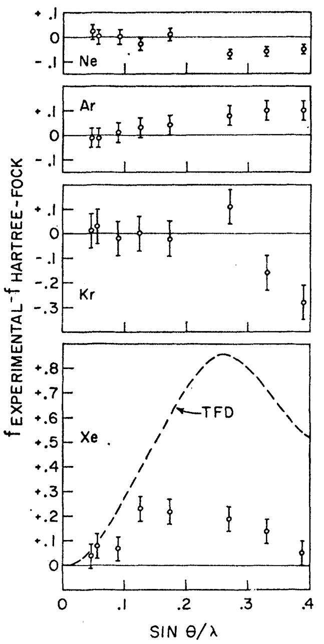

FIG. 2. Deviations of our values of scattering factor from those calculated using the Hartree-Fock scheme. In the case of Xe, the dashed curve shows the TFD prediction.

The experimental values for f_0 which are obtained from the data as described above, are in close agreement with theory. Rather than plotting this information as a curve of f versus $(\sin\theta)/\lambda$, we have chosen to plot in Fig. 2 the difference between the measured values of f_0 and the HF values.[8] The relevant HF values themselves are given in Table III. In addition, for Xe, we have shown the values predicted by the Thomas-Fermi-Dirac (TFD) method.[9]

Examination of Table III and Fig. 2 shows that the maximum fractional deviation of the experimental results from the HF values ranges from $1\frac{1}{2}\%$ for Ne to $\frac{1}{2}\%$ for Xe. However, only in the case of Xe is the deviation more than twice our estimate of the error. Even in this case we cannot say whether or not the HF technique is inadequate for two reasons. Firstly, Freeman and Watson were not able to choose so complete a basis set for Xe as for the atoms with fewer electrons. Secondly, as these authors and others have emphasized, relativistic corrections are important for high-Z atoms. It might be noted that the difference between the experimental and the HF values for f is in the same direction and is of the same order of magnitude as that calculated by Ibers[10] for the difference between relativistic and nonrelativistic Hartree values for Hg. Under any circumstances, even with these limitations, the HF values are better than the TFD ones.

It is especially interesting to compare theory with experiment in the low-angle region, for here both results may be expressed in terms of a single parameter $\langle r^2\rangle_{\text{av}}$ as may be seen by expanding Eq. (2).

$$f_0 = Z - (k^2/6)\langle r^2\rangle_{\text{av}} + \cdots. \tag{4}$$

Furthermore, the molar diamagnetic susceptibility is given[11] by

$$\chi_m = -(e^2/mc^2)N_0\langle r^2\rangle_{\text{av}}/6, \tag{5}$$

giving an additional comparison. Values for $f_0+\Delta f'$ obtained as described above, were first corrected for higher order terms omitted in Eq. (4). This was done by using the HF calculations to determine $\delta f = f_0 - Z + k^2\langle r^2\rangle_{\text{av}}/6$. We may then define that part of f_0 which includes terms through quadratic as $f_{0q} = f_0 - \delta f$. Figure 3 shows our experimental values of $Z - (f_{0q} + \Delta f')$, obtained using the subsidiary quantities

TABLE III. Values of subsidiary quantities used to assess our results.

	δ_{eff}	$(\sin\theta)/\lambda$	$(Z-\mathfrak{F})/B^2$	$f_0+\Delta f'$	δf	f_{HF}
Ne	3.76	0.0462	0.2	9.87	0.00	9.86
	4.59	0.0564	0.3	9.78	0.01	9.79
	7.33	0.0901	0.7	9.46	0.03	9.47
	10.22	0.1256	1.2	8.97	0.10	9.01
	14.13	0.1734	2.0	8.26		8.26
	22.05	0.2696	3.7	6.51		6.59
	27.02	0.3293	4.6	5.54		5.61
	32.01	0.3887	5.4	4.70		4.76
Ar	3.69	0.0454	0.6	17.71	0.02	17.62
	4.53	0.0557	0.8	17.52	0.03	17.43
	7.27	0.0895	1.7	16.72	0.15	16.61
	10.18	0.1251	2.7	15.63	0.50	15.50
	14.09	0.1730	4.3	13.99		13.85
	22.03	0.2693	6.7	11.10		10.92
	27.03	0.3294	7.8	9.81		9.61
	32.03	0.3889	8.8	8.88		8.68
Kr	3.73	0.0459	1	34.61	0.02	35.41
	4.57	0.0562	1	34.34	0.04	35.12
	7.31	0.0899	2	33.05	0.23	33.88
	10.20	0.1253	4	31.43	0.81	32.24
	14.13	0.1734	6	29.00		29.83
	22.08	0.2699	9	24.80		25.50
	27.07	0.3299	11	22.43		23.40
	32.06	0.3893	12	20.54		21.63
Xe	3.73	0.0458	1	52.70	0.03	53.06
	4.56	0.0561	1	52.30	0.07	52.62
	7.31	0.0898	4	50.38	0.43	50.71
	10.21	0.1254	6	48.07	1.51	48.24
	14.14	0.1735	8	44.58		44.76
	22.09	0.2701	14	38.48		38.69
	27.07	0.3299	16	35.41		35.67
	32.06	0.3892	18	32.68		33.03

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[8] For Ne: B. H. Worsley, Can. J. Phys. **37**, 967 (1959). Freeman's values (Ref. 7) do not differ significantly and are not given at as small intervals of $(\sin\theta)/\lambda$. The values given in the *International Tables for X Ray Crystallography*, edited by C. H. MacGillavry and G. D. Rieck (Kynoch Press, Birmingham, 1962) which include correlation, also cannot be distinguished within our accuracy. For Ar: J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, Acta Cryst. **8**, 478 (1955). Dr. Freeman has informed us that these results are in substantial agreement with those based on more recent wave function, R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961). For Kr: Values of A. J. Freeman and R. E. Watson, in *International Tables for X Ray Crystallography*, edited by C. H. MacGillavry and G. D. Rieck (Kynoch Press, Birmingham, 1962), For Xe: Approximate Hartree-Fock results of A. J. Freeman and R. E. Watson (unpublished).

[9] L. H. Thomas and K. Umeda, J. Chem. Phys. **26**, 293 (1957).

[10] J. A. Ibers, Acta Cryst. **11**, 447 (1958).

[11] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

TABLE IV. Values of $\langle r^2\rangle_{\mathrm{av}}$ derived in various ways; atomic units.

	Exptl	H-F	Susc	TFD	(1.06)(Susc)
Ne	9.4	9.41	8.9		9.4
Ar	26.0	26.03	24.6	27.9	26.1
Kr	39.4	39.4	36.6	44.8	38.8
Xe	60.8	62.7	57.4	58.0	60.9

of Table III, plotted against $[(\sin\theta)/\lambda]^2$. The slope of these lines yields $\langle r^2\rangle_{\mathrm{av}}$ and the intercept is $-\Delta f'$. The solid lines are drawn with a slope corresponding to the HF values of $\langle r^2\rangle_{\mathrm{av}}$.[12] Also shown are dashed lines with slopes corresponding to the reported values of diamagnetic susceptibility.[13] The HF slopes are seen to be in agreement with the present experimental values for every case but Xe, while the susceptibility values are too low in every case. Table IV gives values of $\langle r^2\rangle_{\mathrm{av}}$ from several sources, including for comparison values given by the TFD model.[14]

That the values of δf used are approximately correct is verified both by the lack of curvature shown in the lines through the points in Fig. 3 and by the agreement of the slope with the HF values in the cases of the lighter gases where the latter are expected to be the most accurate. It will further be useful for later discussion to note that the values of δf are negligible for our lowest angle points and therefore do not affect our measured values of $\Delta f'$ appreciably.

Values of the dispersion correction, $\Delta f'$, obtained from the graphs of Fig. 3 are given in Table V, along with values obtained from the literature.[15] These latter were obtained by assuming an analytic form for the wavelength dependence of the absorption coefficient and then integrating the equation,[6]

$$\Delta f' = \left(\frac{mc}{2\pi^2 e^2}\right) \int \frac{(\mu/\rho)(M/N_0)d\omega'}{(\omega/\omega')^2 - 1}, \tag{6}$$

which determines the values of $\Delta f'$ in the forward direction. Because the analytic form does not fit the measured values of μ/ρ exactly, we have numerically evaluated the integral in Eq. (6) using literature values for the absorption coefficients,[16] obtaining the values listed in the third column of Table V.

TABLE V. Values of the dispersion correction derived in various ways.

	Exptl	Literature	from μ/ρ
Ne	-0.01	0.03	0.03
Ar	0.10	0.2	0.20
Kr	-0.81	-0.6	-0.6 ?
Xe	-0.40	-0.45	-0.21

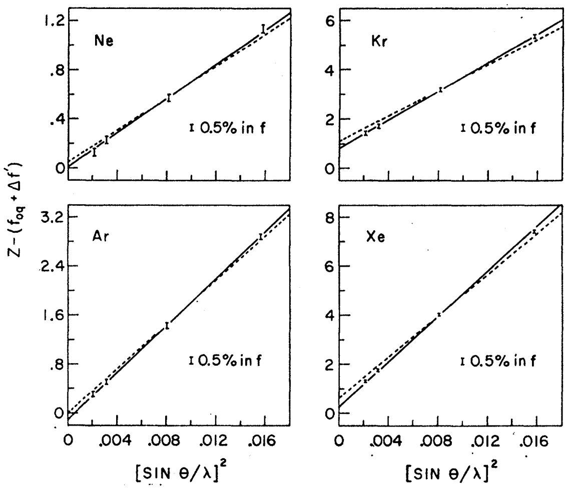

FIG. 3. Experimental values of $Z-(f_{0q}+\Delta f')$ plotted against $[(\sin\theta)/\lambda]^2$. The solid lines are drawn with a slope corresponding to the Hartree-Fock values of $\langle r^2\rangle_{\mathrm{av}}$ and the dashed lines with a slope corresponding to the susceptibility values of $\langle r^2\rangle_{\mathrm{av}}$. The intercept gives the value of $\Delta f'$.

It is clear that there is not consistency among the first three columns of Table IV or of Table V. It is, therefore, necessary to investigate possible sources of error in these values.

Our experimental values were obtained from at least three separate sets of measurements taken on different days. The spread in the data at any point was, on the average, slightly greater than would be expected from statistics alone. This effect was greatest for Ne where the counting times were the longest, leading us to attribute the additional random error to "drift" undetected by our monitor system. The error bars on our plotted experimental points include random error rising from counting statistics and from "drift," and also the known systematic errors. The latter includes the value of the absorption of the attenuating foils and our estimate of the error entailed in the measurement of the dimensions of the apparatus, of the temperature, and of the pressure. There are perhaps additional systematic errors, arising from the wavelength distribution, the pulse-height distribution, and, for Kr, the unbalance of the filters, which are not included.

Considering first the values of $\langle r^2\rangle_{\mathrm{av}}$, one can see that our results would be very little affected by the presence

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[12] A convenient summary of the values of $\langle r^2\rangle_{\mathrm{av}}$ is given in B. Dawson, Acta Cryst. **14**, 1120 (1961). The values which we actually used correspond to the HF values given in Table III.

[13] A summary of all early work has been given by W. Klemm, Z. Anorg. Allgem. Chem. **244**, 377 (1940). We have used, however, the values of C. Barter, R. G. Meisenheimer, and D. P. Stevenson, J. Phys. Chem. **64**, 1312 (1960), which are slightly higher in most cases. The listing of the "most probable values," R. E. Glick, *ibid.* **65**, 1552 (1961) does not differ greatly.

[14] L. H. Thomas and K. Umeda, J. Chem. Phys. **24**, 1113 (1956).

[15] For Ne, we have used the formula given by James (Ref. 6) for K electrons. For Ar, Kr, and Xe we have used the values of C. H. Dauben and D. H. Templeton, Acta Cryst. **8**, 841 (1955), supplemented in the case of Xe by values derived from H. Eisenlohr and G. L. J. Müller, Z. Physik **136**, 511 (1954).

[16] At shorter wavelengths, we used the averaged values of J. A. Victoreen, J. Appl. Phys. **20**, 1141 (1949) as modified in the *International Tables for X-Ray Crystallography*, edited by C. H. MacGillavry and G. D. Rieck (Kynoch Press, Birmingham, 1962). At longer wavelengths, these were supplemented by smoothed values from B. L. Henke, R. White, and B. Lundberg, J. Appl. Phys. **28**, 98 (1957).

of a systematic error which was angularly independent, such as, for example, an error in the direct beam intensity. This consideration, coupled with the good agreement with the HF values, leads us to believe that our values of $\langle r^2\rangle_{\text{av}}$ are, indeed, reliable and that the values from the susceptibility are in error.

Although there are known to be corrections to Eq. (5),[11] none of them would be expected to apply to the rare gases and suspicion must be directed at the experimental susceptibility values. Examining these values, one finds that there are differences among observers which are large compared to their individual quoted errors in every case but for Ar. In this one case, the agreement was approximately 1%. In the only recent measurement, Barter *et al.*[13] took advantage of this situation and calibrated their apparatus with Ar. Thus, the results of Barter *et al.* may be viewed as giving merely the ratios of the susceptibilities. We found that if all their values were raised by 6% there was then reasonable agreement with our values as shown in the last column of Table IV. We offer no explanation, however, as to why the results of many previous workers were in error in absolute value.

We have mentioned that the dispersion correction is not sensitive to δf, but this correction would be affected by a systematic error. In fact, if one considered the values of $\Delta f'$ which we obtained from the absorption coefficients to be more reliable than the literature values, the discrepancy could essentially be removed by assuming that our scattering results were systematically in error by about 1% in intensity ($\frac{1}{2}$% in f). However, as may be seen from an examination of the error bars in Fig. 3, we feel that our error is appreciably smaller than the discrepancy in $\Delta f'$. Therefore, we examined with some care the values of the absorption coefficients. Because of the proximity of the absorption edge in the case of Kr, the published values of the absorption coefficients differed sufficiently to account for the difference between -0.8 and -0.6 and are, thus, marked with a question mark in Table V. In the case of Ne, our results are not of high enough accuracy to warrant detailed consideration. For Ar and Xe, however, the difference appears to be real, and it is our opinion that the published absorption coefficients at short wave length are too small.

CONCLUSIONS

We have shown that the method of x-ray scattering gives the correct scattering factor extrapolated to zero angle within an uncertainty of approximately $\frac{1}{2}$%, which is about the uncertainty in the dispersion correction. In addition, to approximately the same accuracy, the Hartree-Fock formulation gives correct scattering factors up to $(\sin\theta)/\lambda = 0.4$ for free atoms with atomic numbers up to the neighborhood of Xe at least. Therefore, the 4% discrepancy noted by Batterman *et al.*[1] for the metals is presumed to arise from solid-state effects or from difficulties in sample preparation. Furthermore, the HF wave functions for the outer electrons, which are the ones which determine the fall off of f_0 at low angle, depend on the wave functions of the inner electrons through the self-consistent field and there is thus the presumption that the wave functions for the inner electrons are also nearly correct. On the other hand, the TFD scattering factors appear less accurate than the HF values made available by present day computer techniques for atoms up to the rare-earth region.

Our results do not correlate perfectly with published values for the susceptibility or of the x-ray absorption coefficients for the gases studied, and, assuming that the theory leading to these correlations is correct, we have concluded that the susceptibility and absorption coefficient data should be modified.

Note added in proof. Recently M. J. Cooper, Phil. Mag. **7**, 2059 (1962) has reported that the scattering from Cr metal is lower than the HF free atom values by approximately the same amount found for other cases in Ref. 1.

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