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The Measurement of Anomalous Scattering factors near the Ga *K* Absorption Edge in GaP

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By the use of an SSD diffractometer and continuous X-rays, the energy dependences of $\Delta f'$ and $\Delta f''$ values of Ga have been studied on GaP with energy resolution of about several eV around the Ga *K* edge; the values of $\Delta f''$ were determined by the measurement of the absorption coefficient, and then the values of $\Delta f'$ have been obtained from the precisely measured ratio of Friedel-pair reflexions from a (111) single-crystal plate of polar GaP. Fine structures have been found in $\Delta f''$ and therefore in $\Delta f'$ corresponding to those of the absorption coefficient. The present work has shown that the measured values of $\Delta f'$ more or less reasonably agree with the curves calculated from the dispersion relation.

1. Introduction

The anomalous scattering factor is not only interesting from the physical point of view but also very important for determining phases, as is well known in crystallography. Generally speaking, the values of the anomalous scattering factor, especially near the absorption edge, have seldom been measured except when convenient characteristic radiations happen to have energy values nearly similar to an absorption edge of a certain atom. Therefore, hardly any systematic measurement has been carried out on anomalous scattering factors, particularly in the energy region near the edge. As for the data so far published, the agreement among measured values themselves and also between measured values and calculated values has usually been poor, as was summarized by James (1954) or more recently compared, for instance by Bonse & Materlik (1972).

However, the advent of an energy-dispersive or an SSD (solid-state detector) diffractometer has enabled us to carry out the measurements easily, even in the energy region very near the absorption edge. The energy resolution in the present work was about ± 2 or 3 eV, being determined by the beam divergence of the slit system used (Fukamachi, Hosoya & Terasaki, 1973).

2. Intensity ratio of a Friedel pair

As was reported by Cole & Stemple (1962), the intensity ratio between Friedel-pair reflexions of a polar crystal is given by the structure factor F or the intensity I as

$$R_h = |F_h|^2/|F_{\bar{h}}|^2 = I_h/I_{\bar{h}}\,, \qquad (1)$$

being independent of the perfection of the specimen crystal, at least when the reflexion is in a symmetrical Bragg case. As will be separately published, this is valid when the primary extinction alone is taken into consideration, but not exactly valid when the secondary extinction is considered as well. However, at least in the energy region higher than the edge, the absorption is so heavy that the intensity is less subject to secondary extinction, which already does not much affect high-index reflexions such as are used in the present work.

Holloway (1969) confirmed the validity of this relation with characteristic radiations, and more recently the present authors have confirmed the validity with continuous radiation in the energy region very near the edge (Fukamachi, Hosoya & Okunuki, in preparation), both for nearly perfect crystals. The above ratio R_h can be measured with very high accuracy because various factors common to a pair of reflexions are cancelled. It is to be noted that the deviation from uniform polarization, if any, in the white radiation is also cancelled. In the present work, the absorption correction has no effect either, because of the geometry concerning the shape of the sample and the reflexion used. As mentioned in the above, even extinction does not matter in favourable cases.

3. Principles of measurement

As often carried out, the value of $\Delta f''$ has been determined by the measurement of the linear absorption coefficient μ. Then the above-mentioned ratio R_h has been measured. In the present work, the 555 Friedel-pair reflexions from GaP with the zincblende-type structure have been used. When the positions (0,0,0) and $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$ are assumed to be occupied by Ga and P atoms, respectively, the structure factors are expressed as

$$|F_{555}|^2=16[(f^0_{Ga}+\Delta f''_P\,.\,T_2+\Delta f'_{Ga})^2 + \{\Delta f''_{Ga}-(f^0_P+\Delta f'_P)\,.\,T_2\}^2]T_1^2\,, \quad (2)$$

$$|F_{\bar{5}\bar{5}\bar{5}}|^2=16[(f^0_{Ga}-\Delta f''_P\,.\,T_2+\Delta f'_G)^2 + \{\Delta f''_{Ga}+(f^0_P+\Delta f'_P)\,.\,T_2\}^2]T_1^2, \quad (3)$$

where

$$T_1=\exp(-B_{Ga}s^2)\,,$$
$$T_2=\exp\{-(B_P-B_{Ga})s^2\}\,;$$

B_{Ga} and B_P are the temperature factors of Ga and P, respectively, and

$$s=\sin\theta/\lambda\,.$$

By substitution of (2) and (3) into (1), the following equation is obtained:

$$A(\Delta f'_{Ga})^2+B\Delta f'_{Ga}+C=0\,, \quad (4)$$

where

$$A=(1-R_h)\,,$$
$$B=2[f^0_{Ga}+\Delta f''_P\,.\,T_2-R_h(f^0_{Ga}-\Delta f''_P\,.\,T_2)]\,,$$

and

$$C=(f^0_{Ga}+\Delta f''_P\,.\,T_2)^2-R_h(f^0_{Ga}-\Delta f''_P\,.\,T_2)^2 + \{\Delta f''_G-(f^0_P+\Delta f'_P)T_2\}^2 - R_h\{\Delta f''_{Ga}+(f^0_P+\Delta f'_P)\,.\,T_2\}^2.$$

The measurements of the linear absorption coefficient μ give the value of $\Delta f''_{Ga}$. The factors B_{Ga} and B_P were assumed to have the values given by Pepe, Masri, Bienfait & Dobrzynski (1974). If the normal atomic scattering factor f^0_{Ga} and f^0_P and the anomalous scattering factors $\Delta f'_P$ and $\Delta f''_P$ are assumed to have calculated values, the values of $\Delta f'_{Ga}$ are given by the measurements of R_h values for each energy value. Namely, equation (4) generally has two solutions for $\Delta f'_{Ga}$, one of which can be chosen because of its physical significance. Naturally it is not desirable to use the calculated values for the quantities of $\Delta f'_P$ and $\Delta f''_P$ in the equation. However, the values of $\Delta f'_{Ga}$ and $\Delta f''_{Ga}$ are to be determined in the energy region distant from the absorption edge of P atoms. Therefore, the errors in calculated values of $\Delta f'_P$ and $\Delta f''_P$ are not so large as affect the results seriously.

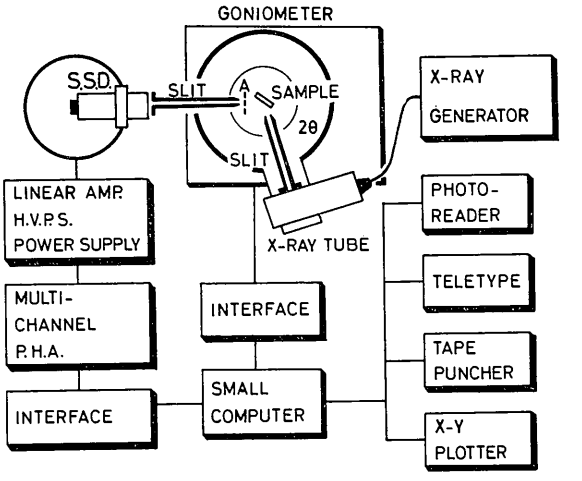

Fig. 1. Schematic diagram of an SSD diffractometer system used for the present work. SSD: Ge(Li), ORTEC Model 8113 or Si(Li) HORIBA; 4096 channel PHA: TOSHIBA USC-1, Model 10; small computer: AICOM-C4 (8k words); goniometer: JEOL DX-GOEDZ; X-ray generator: JEOL DX-GE-100S.

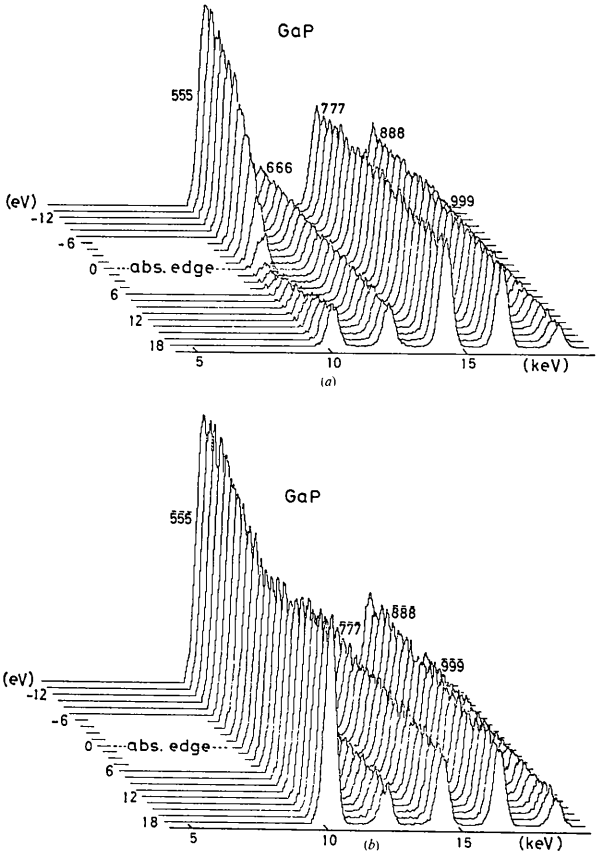

Fig. 2. The comparison of *hhh* and $\bar{h}\bar{h}\bar{h}$ diffraction spectra from a GaP single crystal. Each series of spectra was measured by a Ge(Li) detector with energy resolution of ±3 eV and with a step of 1·5 eV by changing the scattering angle.

4. Measurements of spectra

The diffractometer system used for the present work is shown in Fig. 1. The measurements were carried out under the following two sets of slightly different conditions, the conditions in the second case being shown in square brackets.

The tube was rotated instead of the Ge(Li) [Si(Li)] detector with a heavy cryostat. The X-ray tube with a Cu target was operated at 30 kV and 36 [38] mA; the effective focal size was about $0{\cdot}4\times0{\cdot}5$ mm and a pair of the same collimators with circular section limit the beam divergence to less than $\pm0{\cdot}1°$ [$\pm0{\cdot}06°$] eV in scattering angle $2\theta_B$ of 143°34′, the energy resolution being ±3 [±2] eV when the 555 reflexion was brought near the Ga K absorption edge. The measured range was $x=\omega/\omega_K=1\pm0{\cdot}002$ [$1\pm0{\cdot}0006$], where ω_K is the energy of the Ga K absorption edge (Table 1). The GaP sample used was the same (111) plate used in previous work on the determination of polarity sense (Hosoya & Fukamachi, 1973). This sample was measured in the symmetrical Bragg case: a pair of spectra were obtained as shown in Fig. 2. In these measurements, the fluorescence X-rays were subtracted in the same way as already reported (Hosoya & Fukamachi, 1973).

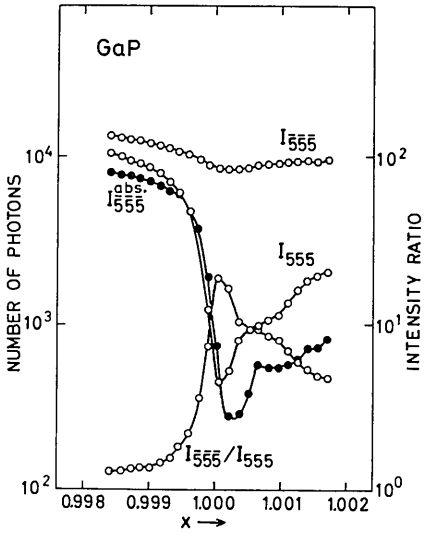

Fig. 3. Open circles show the energy dependences of I_{555} and $I_{\bar{5}\bar{5}\bar{5}}$ and their ratio. Solid circles show the intensities of $I^{abs}_{\bar{5}\bar{5}\bar{5}}$ which were measured after attenuated by a GaP thin foil. The points shown in the region, $x=1\pm0{\cdot}0006$, were measured with high resolution [±2 eV], other points with ±3 eV. The abscissa: $x=\omega/\omega_K$.

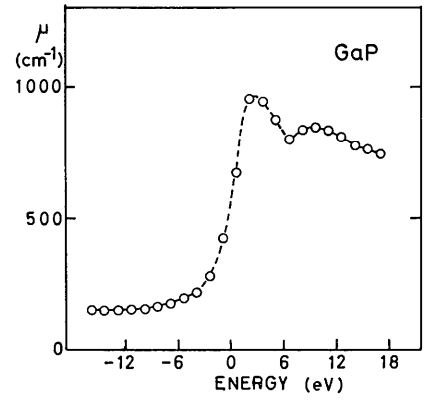

Fig. 4. The measured values of μ_{GaP} near the Ga K edge. The points shown between $\omega_K\pm6$ eV were measured with the high resolution [±2 eV], those elsewhere with ±3 eV.

Table 1. *Numerical values used for atomic scattering factors and other quantities*

Lattice constant of GaP: 5·4506 Å*.
Ga K absorption edge: 10·368 keV.
Reflexion used: 555

f^0_{Ga}: 9·614†	f^0_P: 4·311†
$\Delta f'_P$: 0·19‡	$\Delta f''_P$: 0·26‡
B_{Ga}: 0·35 Å²§	B_P: 0·47 Å²§

* Giesecke & Pfister (1958); † Fukamachi (1971); ‡ Present work; § Pepe, Masri, Bienfait & Dobrzynski (1974).

5. Measurements of the intensity ratio and the absorption coefficient

By the procedures described in the previous section, a pair of hhh and $\bar{h}\bar{h}\bar{h}$ spectra were obtained, where the Bragg angle was chosen so that the reflexion peaks with $h=5$ are near the Ga K absorption edge ω_K. As seen in Fig. 2, the 555 reflexion changes its intensity far more conspicuously than $\bar{5}\bar{5}\bar{5}$. This is because $\Delta f''_{Ga}$ and f^0_P, more or less comparable values in the 2nd term of the right-hand side, are cancelled in (2) but not in (3). Other reflexions in Fig. 2 are not very near the Ga K edge and, therefore, they are not very much affected by a small energy change.

Naturally the even reflexions in this structure satisfy Friedel's law. In pairs with odd indices $h=7$ and 9, the deviation from Friedel's law is also found, although it is not large, with relations $R_{777}>1$ and $R_{999}<1$ as expected. The energy dependences thus obtained are shown by open circles in Fig. 3 for each of the 555 pair reflexions and for their ratio R^{-1}_{555}. The intensity I_{555} and therefore the ratio R^{-1}_{555} were found to show small variations in the region a little higher than the edge, although they are less marked for the latter because of the logarithmic plot. The details will be described later.

A part of GaP sample was cut and thinned to about 33 μm. When this thin plate is inserted at the position A in Fig. 1, the intensity $I_{\bar{5}\bar{5}\bar{5}}$ decreased to the value $I^{abs}_{\bar{5}\bar{5}\bar{5}}$ as shown by the solid circles in Fig. 3. From these ratios, the linear absorption coefficient μ has been determined as shown in Fig. 4, where a sub-maximum is found in the μ curve. This fine structure shows a good correspondence at least qualitatively with that in the μ curve of the same substance measured by a spectroscopic method (Kantelhardt & Waidelich, 1969).

6. Measured values of $\Delta f'$ and $\Delta f''$

The linear absorption coefficient, μ, and $\Delta f''$ are related by the relation

$$\Delta f''=\mu/(4\pi A\,.\,\lambda)\,, \tag{5}$$

where

$$A=(Ne^2\varrho)/(2\pi mc^2M)=2{\cdot}70\times10^{10}\varrho/M\,,$$

N is Avogadro's number, ϱ the density of the specimen, M its atomic weight, and λ the wavelength used (in Å). The necessary value μ_{Ga} was obtained from

$$\mu_{Ga}=\mu_{GaP}-\mu_P\,, \tag{6}$$

where μ_P was determined by the use of (5) with the calculated values of $\Delta f''_P$.

Then the value of $\Delta f'_{Ga}$ for each energy was determined from (4), while the values for f^0_{Ga}, f^0_P, $\Delta f'_P$ and $\Delta f''_P$ shown in Table 1 were used. The values thus obtained for $\Delta f'_{Ga}$ as well as the values $\Delta f''_{Ga}$ are shown in Fig. 5 by solid circles.

7. Calculation of anomalous scattering factors

When an X-ray photon with energy near the absorption edge is scattered by an atom, the atomic scattering factor (Sakurai, 1967) is expressed as

$$f=\sum_n f_{nn}$$
$$-\sum_n\sum_i\left[\frac{(\mathbf{p}\,.\,\boldsymbol{\varepsilon})_{ni}\{(\mathbf{p}\,.\,\boldsymbol{\varepsilon})_{in}\}_p}{\omega_{in}-\omega-i\Gamma_{in}/2}+\frac{(\mathbf{p}\,.\,\boldsymbol{\varepsilon})_{ni}\{(\mathbf{p}\,.\,\boldsymbol{\varepsilon})_{in}\}_p}{\omega_{in}+\omega}\right], \tag{7}$$

where the atomic unit ($\hbar=1$, $m=1$ and $e=1$) is used, ω is the energy of the incident X-rays, $\omega_{in}=E_i-E_n$, E_i and E_n are the energies of electrons in intermediate and ground levels, respectively, Γ_{in} is the spectral width of the intermediate state, $\mathbf{p}$ is the momentum vector of an electron, $\boldsymbol{\varepsilon}$ is the polarization vector of a photon, and the suffix p expresses the component of the parenthesized quantity perpendicular to the scattering vector $\mathbf{k}$.

The first term in (7) is an atomic scattering term normally given by

$$f^0=\sum_n f_{nn}=\sum_n\int\varphi_n^*\varphi_n\exp(i\mathbf{k}\,.\,\mathbf{r})\mathrm{d}v \tag{8}$$

where φ_n is the wave function of an electron in the fundamental state. As for the second term in (7), let us assume that the wavelength of the incident X-rays is long in comparison with the average orbital radius of the electron in study. Then the approximation $\exp(i\mathbf{k}\,.\,\mathbf{r})\simeq1$ holds and the oscillator strength is given by

$$g_{in}=(2/\omega_{in})\,(\mathbf{p}\,.\,\boldsymbol{\varepsilon})_{ni}\{(\mathbf{p}\,.\,\boldsymbol{\varepsilon})_{in}\}_p=2\omega_{in}|x_{in}|^2, \tag{9}$$

where

$$x_{in}=\int\varphi_i^*x\varphi_n\mathrm{d}v\,. \tag{10}$$

If a scatterer is randomly orientated relative to the incident rays, we have

$$g_{in}=(\tfrac{2}{3})\omega_{in}\{|x_{in}|^2+|y_{in}|^2+|z_{in}|^2\}\,. \tag{11}$$

Thus the Thomas–Reiche–Kuhn sum rule

$$\sum_i g_{in}=1 \tag{12}$$

holds.

Because the final states are generally continuous in the case of X-ray excitation, the oscillator strength between ω and $\omega+\mathrm{d}\omega$ is expressed by the oscillator density $\mathrm{d}g/\mathrm{d}\omega$ times $d\omega$. The real part of the second term in (7), which is $\Delta f'$, is expressed by

$$\begin{aligned}\Delta f'&=-\sum_n\sum_i{}'\tfrac{1}{2}\omega_{in}g_{in}\left\{\frac{\omega_{in}-\omega}{(\omega_{in}-\omega)^2+\Gamma_{in}^2/4}\right.\\&\quad\left.+\frac{1}{\omega_{in}+\omega}\right\}\\&=-\sum_n\int_{\omega_n}^{\infty}\frac{\omega_{in}^4-\omega_{in}^2\omega^2+\omega_{in}(\omega_{in}+\omega)\Gamma_{in}^2/8}{(\omega_{in}^2-\omega^2)^2+(\omega_{in}+\omega)^2\Gamma_{in}^2/4}\\&\quad\times\left(\frac{\mathrm{d}g_{in}}{\mathrm{d}\omega_{in}}\right)\mathrm{d}\omega_{in}\,,\end{aligned} \tag{13}$$

where ω_n is the absorption edge of the nth level. Then the corresponding imaginary part is expressed by

$$\begin{aligned}\Delta f''&=\sum_n\sum_i{}'\tfrac{1}{2}\omega_{in}g_{in}\,\frac{\Gamma_{in}/2}{(\omega_{in}-\omega)^2+\Gamma_{in}^2/4}\\&=\frac{\pi}{2}\sum_n\int\frac{\mathrm{d}g_{in}}{\mathrm{d}\omega_{in}}\,\omega_{in}\delta(\omega_{in}-\omega)\mathrm{d}\omega_{in}\\&=\frac{\pi}{2}\sum_n\omega\,\frac{\mathrm{d}g_n}{\mathrm{d}\omega}\,,\end{aligned} \tag{14}$$

where the relation $\lim_{\varepsilon\to0}\{\varepsilon/(x^2+\varepsilon^2)\}=\pi\delta(x)$ has been used. Therefore, if the oscillator density can be obtained, then $\Delta f'$ and $\Delta f''$ would be calculated by (13) and (14). In fact, such calculations have been carried out by Hönl (1933*a*) for K electrons and by Eisenlohr & Müller (1954*a*,*b*) for L electrons. Wagenfeld (1966) calculated the linear absorption coefficient for M electrons, and therefore their oscillator strength can be calculated from his results, as will be shown later. However, all of these authors assumed that the X-ray energy is far enough from the relevant absorption edges. The same approach cannot be applied to the present case where the energy region of our concern is the very vicinity of the edge. Therefore, the more or less conventional method was taken for determining the oscillator density from the photoelectric absorption.

As is well known, the refractive index n of the scattering substance is related to the atomic scattering factor f as

$$n=1-2\pi(c/\omega)^2Nr_0f\,. \tag{15}$$

The imaginary part of n is related to μ as follows:

$$\mu=(2\omega/c)\,\mathrm{Im}\,(n)=4\pi(c/\omega)Nr_0\Delta f''. \tag{16}$$

If the atomic absorption coefficient μ_a is used instead of μ,

$$dg/d\omega=(c/2\pi^2)\mu_a=(c/2\pi^2)\sum_n \mu_{an}(\omega)\,. \qquad (17)$$

In the energy region not very near the edge, the value of μ_a at the level n is expressed by

$$\begin{aligned}\mu_{an}(\omega)&=(\omega_n/\omega)^{q_n}\mu_{an}(\omega_n) \quad \text{for} \quad \omega>\omega_n\,,\\ &=0 \quad \text{for} \quad \omega<\omega_n\,,\end{aligned} \qquad (18)$$

where q_n is an exponent with an empirical value, and the suffices n of q_n and ω_n signify the electron level. In such a region, the direct calculations mentioned above are not very much different from those given by (18). Assuming that the value of μ is well expressed by (18), the oscillator strength g_n of electrons in the n shell is given by

$$g_n=\int_{\omega_n}^{\infty}(c/2\pi^2)\mu_{an}(\omega)d\omega=\frac{c}{2\pi^2}\frac{\omega_n}{q_n-1}\mu_{an}(\omega_n)\,. \qquad (19)$$

This value g_n is given by

$$g_n=N_n(1-\sum_m g_{nm})\,, \qquad (20)$$

where N_n is the number of electrons in the nth level and g_{nm} is the virtual oscillator strength for the occupied level, to which the transition is prohibited, and can be calculated from the wave functions of the fundamental level, φ_n. The values for g_n and q_n used are from those used by Cromer (1965), which are listed in Table 2.

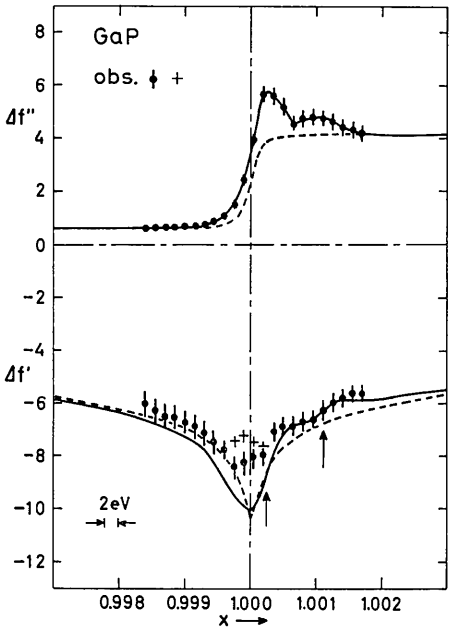

Fig. 5. Measured values of $\Delta f'$ and $\Delta f''$ of Ga in GaP. For the meaning of the solid and broken curves, the text should be referred to. Points shown by crosses were measured with low resolution, ± 3 eV.

Table 2. *Numerical values used for calculating anomalous scattering factors*

	n	ω_n(keV)	q_n^*	g_n^*
	$1s$	10·368	2·75	1·29
	$2s$	1·30	2·33	1·37
Ga	$2p_0$	1·134	2·5	1·79
	$2p_\pm$	1·117	2·5	3·58
P	$1s$	2·142	2·75	1·49

* Cromer (1965).

In short, the value $dg/d\omega$ was estimated (i) by adopting the measured value of $\mu_{an}(\omega)$ at the edge, and elsewhere (ii) by finding g_n from (20), then $\mu_{an}(\omega_n)$ by (19) and finally $\mu_{an}(\omega)$ by (18) to get (17). From these $\mu_a(\omega)$ values, the values of $dg/d\omega$ were obtained. There is no problem in obtaining $\Delta f''$ with (14), while the integration in (13) should be carried out to obtain $\Delta f'$ values. This integration was done numerically by the use of the classical radiation-damping factor $2\omega^2/3c^3$ for Γ_{in}. The results are shown in Fig. 5 for comparison with the present measured data. The solid curves were obtained when the measured $\mu_a(\omega)$ values were used around the edge and elsewhere the approximation (18) was used. Therefore the solid curve for $\Delta f''$ naturally coincides with the measurements. Because of this derivation, the solid curve for $\Delta f'$ reproduces the behaviour of the measured values to some extent. However, the discrepancy between the calculated and measured $\Delta f'$ values is relatively large in the region very near the edge. On the other hand, the broken curves did not show any fine structure, because they were obtained by assuming the relation (18) for the whole energy region.

8. Discussion

The present data for $\Delta f'$ seem to show a comparatively good agreement with the values calculated by the use of the measured $\Delta f''$ values and the dispersion relation, although the agreement is worse near the very edge. Since the fine structure of the absorption curve was known near the edge, the corresponding structure may be supposed to exist for $\Delta f'$, as shown in Fig. 5 by arrows. This seems to have first been experimentally confirmed in the present work.

Apart from the region near the very edge, the discrepancy in $\Delta f'$ is systematic and there is, at most, 5 to 8% between the calculations and the measurements. Possible reasons for this seem to be as follows:

(1)* When the value $\Delta f''$ was obtained from the measured μ values, that the part due to photoelectric absorption in μ depends upon the scattering angle to some extent (Hönl, 1933*b*) was entirely neglected.

(2) The absorption due to TDS and Compton scattering was also entirely neglected. This may make the μ value overestimated to some extent. However,

* This is due to Professor S. Miyake.

when the oscillator strength of the K electrons is determined, the contribution from other electrons is subtracted as background. Therefore, the effect of this approximation may be small.

(3) The dipole approximation seems to be sufficient for K electrons of Ga but may not be so for other electrons, for which the quadrupole and octopole terms need be taken into account.

(4) In § 3, the temperature factors obtained by Pepe *et al.* (1974) were used. Their errors, if any, will affect the measured value of $\Delta f'_{\mathrm{Ga}}$, though they may be small in magnitude.

In the energy region of $\omega_K \pm 2$ eV, $|\Delta f'_{\mathrm{obs}}|$ is smaller than $|\Delta f'_{\mathrm{cal}}|$ by about 20%. This apparent discrepancy partly comes from the experimental fact that the energy resolution was about ± 2 eV. This limitation in resolution is mainly due to the lack of luminosity of the X-ray focus used, and therefore would be improved if only a more suitable X-ray source, such as synchrotron radiation, could be used. Another more intrinsic reason for the discrepancy may be that the classical radiation damping factor was used in the above calculations. The value of Γ_{in} is about 1 eV for the present case and corresponds to about $\frac{1}{4}$ of the half width of the step of measuring μ around the edge. However, it cannot be said whether the Γ_{in} value is too small, because the energy resolution is not high enough. If the resolution for the maximum value of Γ_{in} is used, then the discrepancy between $|\Delta f'_{\mathrm{cal}}|$ and $|\Delta f'_{\mathrm{obs}}|$ decreases to about half of that in Fig. 5. Further calculation is not useful until the experimental resolution in energy has been improved.

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