

Our method, in contrast to the ordinary Hanle effect, is based on an effect linear with the magnetic field and so allows the direct measurement of very short lifetimes. This is of interest in studying the scattering processes in the polariton bottleneck.

*On leave from Institute of Experimental Physics, University of Warsaw, Poland.

†Laboratoire associé au Centre National de la Recherche Scientifique.

¹A. Bonnot, R. Planel, C. Benoît à la Guillaume, and G. Lampel, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, 1972*, edited by The Polish Academy of Sciences (PWN—Polish Scientific Publishers, Warsaw, 1972), p. 1327.

²G. L. Bir and G. E. Pikus, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, 1972*, edited by The Polish

Academy of Sciences (PWN—Polish Scientific Publishers, Warsaw, 1972), p. 1341.

³A. Bonnot, R. Planel, and C. Benoît à la Guillaume, *Phys. Rev. B* **9**, 2, 690 (1974).

⁴R. Planel, A. Bonnot, and C. Benoît à la Guillaume, *Phys. Status Solidi (b)* **58**, 251 (1973).

⁵G. Fishman, C. Hermann, and G. Lampel, *J. Phys. Colloq.* **35**, C3-13 (1974).

⁶G. L. Bir and G. E. Pikus, *Zh. Eksp. Teor. Fiz.* **64**, 2210 (1973) [*Sov. Phys. JETP* **37**, 1116 (1973)].

⁷G. L. Bir, B. S. Rasbirin, and I. N. Ural'tsev, *Fiz. Tver. Tela* **14**, 433 (1972) [*Sov. Phys. Solid State* **14**, 360 (1972)].

⁸E. Gross, S. Permogorov, V. Travnikov, and A. Selkin, *Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971), p. 238.

⁹P. Wiesner and U. Heim, *Phys. Rev. B* **11**, 3071 (1975).

¹⁰R. Planel, M. Nawrocki, and C. Benoît à la Guillaume, to be published.

¹¹V. A. Kiselev, B. S. Razbirin, and I. N. Ural'tsev, *Phys. Status Solidi (b)* **72**, 161 (1975).

¹²H. J. Stocker and H. Kaplan, *Phys. Rev.* **150**, 619 (1966).

Transferability of Phase Shifts in Extended X-Ray Absorption Fine Structure*

P. H. Citrin, P. Eisenberger, and B. M. Kincaid

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 14 January 1976)

Phase shifts in extended x-ray-absorption fine-structure (EXAFS) measurements have been empirically determined for atom pairs. For photoelectron energies > 100 eV it is shown that these phase shifts, because they are essentially independent of chemical environment, can be used with EXAFS spectra to determine interatomic distances typically to accuracies of 0.02 \AA .

Except for the case of an isolated atom, the x-ray absorption coefficient above threshold will be modulated as a result of interference between photoexcited outgoing electron waves and those same waves that have been backscattered from nearby neighboring atoms.¹ In a single-distance system this modulation, called the extended x-ray-absorption fine structure (EXAFS), is determined by two quantities—the interatomic distance and the phase shift describing the scattering effects from the absorbing and neighboring atoms. *The accuracy of interatomic distance determinations using the EXAFS technique is therefore inherently limited by the accuracy to which the phase shift is known.* *Ab initio* calculations of this quantity,²⁻⁴ while encouraging, have been only qualitatively successful. In this Letter we report the empirical determination of phase

shifts for atom pairs. The results are used to test the concept of chemical transferability: Phase shifts are sufficiently insensitive to chemical environment so as to be transferable from one system to the next.⁵ The rationale for transferability is that for electron energies above 100 eV the scattering process is dominated by the core electrons, which are essentially unaffected by changes in the chemical environment. For the first time we shall show that transferability enables phase shifts from one system to be used for very accurate distance determinations in another system. Such a general procedure⁵ is essential if the EXAFS technique is to make a significant contribution to structure studies; without it, accuracies better than 0.1 \AA would be difficult, if not impossible, to achieve.

The EXAFS χ is defined as the normalized dif-

ference between x-ray absorption coefficients for a free atom and that atom in a polyatomic system, i.e., $\chi = (\mu - \mu_0)/\mu_0$. In a system of single distance R the EXAFS arising from an initially bound s electron photoexcited into the continuum with wave vector $k \gg R^{-1}$ is given by^{2-4, 6, 7}

$$\chi(k) = A(k) \sin[2kR + \delta(k)]. \quad (1)$$

$A(k)$ is an amplitude function which takes into account the probability for electron backscattering, the mean electron escape depth from the absorbing atom, and the vibrational fluctuations of the surrounding atoms. The argument of the EXAFS sinusoid contains the distance information. $\delta(k)$ is the *total* phase shift which equals the *sum* of twice the phase shift for the outgoing photoelectron from the ionized absorbing atom α , $2\delta_a^\alpha(k)$, plus the phase shift for the backscattered photoelectron from the neutral neighboring atom(s) β , $\delta_{sc}^\beta(k)$. Since an EXAFS experiment always measures the total phase shift δ , it is not possible to show explicitly that the individual phase shifts δ_a and δ_{sc} are themselves chemically transferable. It is possible, however, to demonstrate transferability inductively by performing the following tests on atom *pairs*. Denoting different chemical environments of atoms α , β , and γ by capital letters, we shall prove that indeed

$$\delta^{\alpha\beta}(A) = 2\delta_a^\alpha(B) + \delta_{sc}^\beta(C), \quad (2)$$

by showing, in order of increasing stringency, that

$$\delta^{\alpha\alpha}(U) = \delta^{\alpha\alpha}(V), \quad (3)$$

$$\delta^{\alpha\beta}(W) = \delta^{\alpha\alpha}(U) + \delta^{\beta\beta}(X) - \delta^{\beta\alpha}(W), \quad (4)$$

$$\delta^{\alpha\gamma}(Z) = \delta^{\alpha\beta}(W) + \delta^{\beta\gamma}(R) - \delta^{\beta\beta}(X), \quad (5a)$$

$$= \delta^{\alpha\alpha}(U) + \delta^{\beta\gamma}(R) - \delta^{\beta\alpha}(W), \quad (5b)$$

$$= \delta^{\alpha\beta}(W) + \delta^{\gamma\gamma}(S) - \delta^{\gamma\beta}(T). \quad (5c)$$

These equations are expected to hold for all photoelectron kinetic energies much greater than valence-electron binding energies.

The absorption experiments were performed using synchrotron radiation from SPEAR and instrumentation that has been described elsewhere.⁴ Since some of the compounds were highly reactive or nonvolatile at room temperature, a vacuum pumped and trapped 30-cm glass cell with thin Teflon windows was constructed to allow for vacuum transfer of materials and heating of the cell. The windows were differentially heated to prevent possible condensation. Partial pressures were vacuum and temperature adjusted to ap-

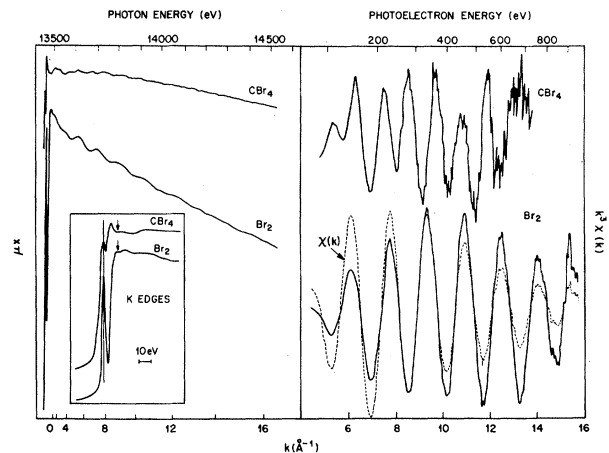


FIG. 1. Left, absorption versus photon energy for Br_2 and CBr_4 , raw data. $k=0$ indicated by arrows in insert. Right, $\chi(k)$ versus photoelectron energy, background removed, and data multiplied by k^3 . Also shown is Br_2 data without k^3 multiplier.

proach optimum signal-to-noise ratios of 2–3 absorption lengths. Data collection methodology has already been described.⁴

As illustrative examples of data analysis procedures we show in Fig. 1 the raw data, $\mu x = \ln(I_0/I)$ (μ is the absorption coefficient, x is the absorption length, and I_0/I is the incident/transmitted photon intensity) plotted against photon energy for samples of Br_2 and CBr_4 .⁸ The absorption edge defined as $k=0$ is consistently chosen at the average energy between the first allowed excitation and the continuum limit according to atomic calculations,^{4,9} indicated by arrows for the Br edges in the insert in Fig. 1. This procedure for choosing $k=0$ minimizes random (but not systematic) errors and is justified because energy level differences between (final-state) ionized absorbing atoms in different (initial-state) chemical environments are expected to be small. Equation (1) is only valid for $kR \gg 1$ so the data are truncated at $k=4 \text{ \AA}^{-1}$. A polynomial background is subtracted from the truncated data to isolate the oscillatory EXAFS from the structureless atomic absorption background. The resulting $\chi(k)$, multiplied by k^3 to compensate for amplitude reduction, is shown in Fig. 1 for CBr_4 and Br_2 .

Given the known interatomic distance, R , and a variable amplitude function, $A(k)$, a nonlinear least-squares fitting routine is then used to determine the total-phase-shift function $\delta(k)$ from the $k^3\chi(k)$ data. The functional form for $\delta(k)$ is unknown, containing both the k -dependent phase

shifts of the outgoing p wave and the contribution of large numbers²⁻⁴ of backscattered l waves ($l \geq 0$). In our fitting program we have assumed an arbitrary form of $\delta(k) = a + bk + ck^2$. It is noteworthy that the simpler form of $\delta(k) = a + bk$, which has been assumed in previous EXAFS studies,⁶ gives less satisfactory fits to the data.

The most direct test of transferability is to determine the phase shift for an atom pair in one molecule of known distance and then use it to determine the interatomic distance in another molecule containing the *same* atoms but in a *significantly different* chemical environment [see Eq. (3)]. The molecules chosen for this test were Br_2 and CBr_4 .¹⁰ In diatomic bromine the atoms are covalently bonded and are separated by $2.283 \pm 0.005 \text{ \AA}$,¹¹ whereas in tetrahedral CBr_4 the Br atoms are not directly bonded, have a net charge, and are separated by $3.171 \pm 0.005 \text{ \AA}$.¹¹ By studying CH_3Br and CH_2Br_2 we have observed that above $k \sim 6 \text{ \AA}^{-1}$ the C-Br scattering in CBr_4 is negligible compared to Br-Br scattering, thus making CBr_4 an essentially single-distance system.

Phase shifts obtained from our computer fits for the Br-Br atom pairs in Br_2 and CBr_4 are plotted in Fig. 2 as dashed and solid lines, respectively. Although the curves are separated by only ~ 0.3 rad, the real test of transferability is to take $\delta^{\text{BrBr}}(\text{Br}_2)$ as a fixed input parameter and, using the same fitting routine but with variable R , solve for the Br-Br distance from the EXAFS data of CBr_4 . Doing this a Br-Br distance of $3.18 \pm 0.015 \text{ \AA}$ is obtained, in excellent agreement with the known value of 3.171 \AA ¹¹ (errors are discussed below). Note that *we have used the absolute magnitude of $\delta(k)$ in our distance determination and not simply the linear or quadratic terms in k* . In view of the different distances and chemical environments of the Br atoms in the two molecules, the concept of phase-shift transferability appears to be a valid one.

A somewhat more stringent test of transferability is described by Eq. (4) where the phase shifts for three different atom pairs and chemical environments are permuted to give a fourth atom-pair phase shift. This "predicted" phase shift can then be used to determine a distance for that pair, which in turn can be compared with the known value. The molecules used for this test were Br_2 , Ge_2H_6 , and BrGeH_3 . The latter two molecules are essentially diatomic because backscattering from H atoms is negligible. In Fig. 2 we have plotted the total phase shift for the Br-

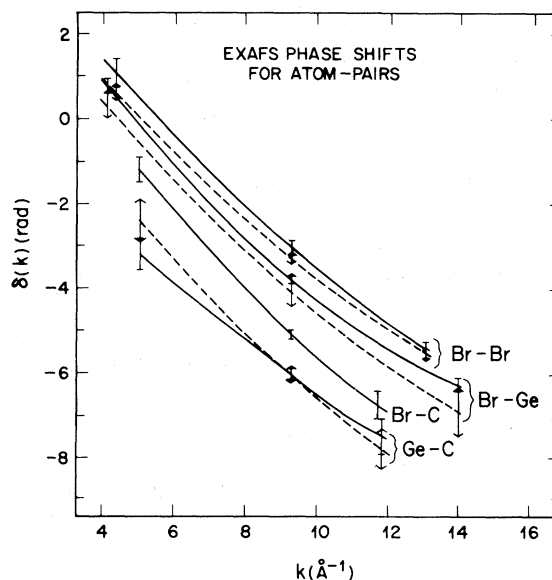


FIG. 2. Total EXAFS phase shifts $\delta(k)$ for various atom pairs $\alpha\text{-}\beta$ (α , absorbing atom, β , scattering atom) assuming quadratic k dependence. Solid curves with horizontal-topped error bars are empirical assuming known $\alpha\text{-}\beta$ distance, dashed curves with arrow-topped error bars are "predicted" assuming phase-shift transferability. Note that the size of the error bars for a given δ are variable (see text) and δ depends on both the absorbing and scattering atoms.

Ge atom pair as well as the predicted phase shift for that pair (shown as a dashed line) determined by $\delta^{\text{BrGe}} = \delta^{\text{BrBr}} + \delta^{\text{GeGe}} - \delta^{\text{GeBr}}$. Applying the predicted phase shift to the data of BrGeH_3 and solving for the Br-Ge distance gives $2.32 \pm 0.025 \text{ \AA}$, which should be compared with the known value of $2.298 \pm 0.005 \text{ \AA}$.¹¹ Considering that our result involves the arithmetic manipulation of three different phase shifts, one of which contributes an error of $\pm 0.02 \text{ \AA}$,¹² the agreement is entirely gratifying.

The last test of transferability, Eq. (5), is actually a more general case of Eq. (4) in that it involves the determination of a fourth phase shift from atom pairs in four different chemical environments. Thus, one obtains a predicted phase shift for an atom pair without even using a compound containing those atoms. In testing this scheme we have used C as the scattering atom, one which is quite different from the intermediate Z atoms Br and Ge. The Ge-C distance in H_3GeCH_3 is predicted using the phase shifts for BrCH_3 , Br_2 , and H_3GeBr according to $\delta^{\text{GeC}} = \delta^{\text{GeBr}} + \delta^{\text{BrC}} - \delta^{\text{BrBr}}$, Eq. (5a). The empirical and predicted phase shifts for Ge-C are included in Fig. 2. Following the procedures above we predict a

Ge-C distance of $1.95 \pm 0.015 \text{ \AA}$, again in excellent agreement with the known value of $1.945 \pm 0.005 \text{ \AA}$.¹¹ This result is particularly significant because it tests transferability for the important class of low- Z atoms which are the dominant scatterers in biological compounds.

Inspection of Fig. 2 shows that while the various phase shifts for atom pairs are similar, they are indeed different in slope and, significantly, in magnitude. To illustrate the importance of correctly including the scattering-atom phase-shift contribution to δ , we have solved for the Br-Br distance in Br_2 using $\delta^{\text{BrC}}(\text{BrCH}_3)$ (also shown in Fig. 2). The resulting distance was in error by 0.09 \AA . Allowing a to vary as in previous EXAFS studies,⁶ the distance was in error by 0.04 \AA . Similar errors result in using $\delta^{\text{GeBr}}(\text{H}_3\text{GeBr})$, illustrating the importance of the absorbing-atom phase-shift contribution to δ . It is clear, therefore, that since the absolute magnitude and k dependence of δ depend on both the absorbing- and scattering-atom phase shifts, procedures ignoring one or the other are inherently limited in structural accuracy.

All the phase shifts in this study have been determined for a limited and consistently chosen energy region, $k \geq 4 \text{ \AA}^{-1}$, where we expect transferability to be valid. The choice of $k=0$ for the Br and Ge compounds was also consistently made above the appropriate Rydberg states⁹; different values are of course required for different absorbing atoms. Our procedures for determining δ involved the assumption of a quadratic functional form. This, along with the finite range of data used in the fits, the systematic uncertainties in interatomic distances,^{11, 12} and the uncertainties in the choice of $k=0$ ⁹ and other estimated errors in the fitting process, results in the *variable-sized* error bars shown in Fig. 2. We found that the above uncertainties in the fitting procedures gave a typical fitting precision of ± 0.5 rad for a given δ , amounting to a fitting precision of no worse than $\pm 0.01 \text{ \AA}$ in distance. If the systematic uncertainties in interatomic distance are included the total distance errors are found to be between 0.015 and 0.025 \AA ; it is this total uncertainty that we quote in all our "predicted" determinations.

From this and previous^{2-4, 6} work it is obvious that an improved theoretical understanding of the k dependence of EXAFS phase shifts is needed. By purely empirical means, however, we have

shown that phase-shift transferability is a viable procedure, applicable to a rather wide range of atom pairs in significantly different chemical environments. We expect that this result will enable EXAFS spectroscopy to become an important structural technique for determining interatomic distances to $\pm 0.02 \text{ \AA}$ in systems whose distances are either currently unknown or indeterminable by conventional methods.

The authors are indebted to C. G. MacLennan for her assistance in computer programming, B. Salzberg and other members of the Stanford Synchrotron Radiation Project staff for their invaluable help, and J. Griffiths for supplying some of the Ge compounds.

*Partially supported by National Science Foundation Grant No. DMR73-07692, in cooperation with the Stanford Linear Accelerator and the U. S. Energy Research and Development Administration.

¹For a recent review of this subject see L. V. Azároff and D. M. Pease, in *X-Ray Spectroscopy*, edited by L. V. Azároff (McGraw-Hill, New York, 1974), Chap. 6.

²C. A. Ashley and S. Doniach, *Phys. Rev. B* **11**, 1279 (1975).

³P. A. Lee and J. B. Pendry, *Phys. Rev. B* **11**, 2795 (1975).

⁴B. M. Kincaid and P. Eisenberger, *Phys. Rev. Lett.* **34**, 1361 (1975).

⁵In E. A. Stern, D. E. Sayers, and F. W. Lytle, *Phys. Rev. B* **11**, 4836 (1975), an experimental test of transferability was attempted for the Ge-Ge atom pair in Ge and GeO_2 solids, from which the unnecessarily restrictive, and thus erroneous, conclusion was made that transferability is valid *only* for compounds of a "given class of binding."

⁶Stern, Sayers, and Lytle, Ref. 5.

⁷D. E. Sayers, E. A. Stern, and F. W. Lytle, *Phys. Rev. Lett.* **27**, 1204 (1971).

⁸The signal to noise is poorer for the relatively less volatile CBr_4 solid due to less than optimum absorption.

⁹For atomic Br the continuum is calculated (see Ref. 4) to be ~ 13 eV above the $4p$ Rydberg state; for Ge this energy is ~ 10 eV.

¹⁰Note that the absorbing Br atom (which is actually a cation) is *different* from the neutral scattering Br atom in the Br-Br pair; in other words, $\alpha-\alpha$ in Eq. (3) is no less general a case than $\alpha-\beta$.

¹¹*Tables of Interatomic Distances and Configurations in Molecules and Ions*, Supplement 1956-1959, Special Publication No. 18, edited by L. E. Sutton *et al.* (The Chemical Society, London, 1965).

¹²The Ge-Ge phase shift is in greater error since the Ge-Ge distance in Ge_2H_6 is uncertain to $\pm 0.02 \text{ \AA}$ (see Ref. 11).