

¹A. C. Cramers, J. I. Waffchir, C. J. Gorter, *Physica* **18**, 329 (1952).

²J. J. M. Beenakker, K. W. Taconis, E. A. Lynton, Z. Deokoupil, J. van Soest, *ibid.*, p. 433.

³T. P. Ptukha, *Zh. Eksp. Teor. Fiz.* **40**, 1583 (1961) [*Sov. Phys.-JETP* **13**, 1112 (1961)].

⁴B. Carreri, I. Reuss, I. M. Beenakker, *Nuovo Cimento* **13**, 148 (1959).

S. V. Maleev. Magnetic Dipole Forces and Dynamics of Critical Fluctuations Above the Curie Point in Ferromagnetics. Usually, only exchange forces are considered in studies of critical fluctuations in ferromagnets. This approximation is not adequate for description of the relaxation of homogeneous magnetization or the absorption of long-wave electromagnetic oscillations, since the exchange Hamiltonian conserves the total spin of the system. This conservation law is violated by magnetic interaction of atomic spins. The latter is anisotropic and long-range. Above the Curie point, this causes the spin Green's function to decompose into two parts, longitudinal and transverse with respect to the wave vector k . Because of the long-range action of the dipole forces at small k , these two parts are connected by the Krivoglaz relation

$$G = G_{\perp} \frac{1}{1 + \omega_0 G_{\perp}}, \quad \omega_0 = \frac{4\pi |\mu g|^2}{v_0},$$

with $\omega_0 G_{\perp} = 4\pi\chi$, where χ is the ordinary susceptibility. Near T_C , the susceptibility increases without limit, so that only the fluctuations perpendicular to the momentum k increase without limit in the temperature range where $4\pi\chi \gg 1$, and the parallel fluctuations are limited; but if $4\pi\chi \ll 1$, the fluctuations are isotropic. Thus, because of the long range of the dipole forces, there exists a temperature range (it might be called the dipole range) in which these forces, despite their smallness, cannot be considered in perturbation theory. As a result, the critical dynamics of the ferromagnet in the dipole range undergoes a radical change. A new characteristic momentum $q_0 = a^{-1} \sqrt{\omega_0/T_C}$ at which G_{\parallel} and G_{\perp} become equal makes its appearance. For fluctuations with momentum larger than q_0 , there is the usual dynamic similarity with the same critical exponent $Z \approx 5/2$ as in the range $4\pi\chi \ll 1$. At the same time, a dynamic similarity regime with the new critical exponent $Z_d \approx 1$ appears for fluctuations with momentum k smaller than q_0 , and the characteristic energy of the critical fluctuations takes the form

$$\Gamma_k = T_c q_0^{3/2} \kappa f(k/\kappa) \sim \begin{cases} T_c q_0^{3/2} \kappa, & k \ll \kappa, \\ T_c q_0^{3/2} k, & k \gg \kappa, \end{cases}$$

where κ is the reciprocal radius of the critical fluctuations. Since $\kappa \sim \tau^{2/3}$ ($\tau = (T - T_C)/T_C$), as we should expect, the homogeneous relaxation time $t = \Gamma_0^{-1}$ increases without limit. In the range $4\pi\chi \ll 1$, the value of Γ_0 calculated from perturbation theory is then proportional to $\omega_0^2/T_C \tau$, so that the homogeneous relaxation time behaves nonmonotonically as τ decreases, reaching a minimum in the temperature range where $4\pi\chi \sim 1$.

O. M. Sumbaev, E. V. Petrovich, Yu. P. Smirnov, I. M. Band, and A. I. Smirnov. Use of a Method of Small X-Ray Line Shifts to Investigate the Electronic Structure of Crystal Chemical Bonds. An effect in which the energies of K-series x-ray emission lines vary with the chemical state of the emitting atom (a chemical shift) has been observed experimentally in the range of

heavy elements ($30 < Z < 75$). It has been shown that the effect is directly related to the specific nature of the changes in the valence shells of the atom on formation of the chemical bond, and is explained by a mutual screening mechanism.

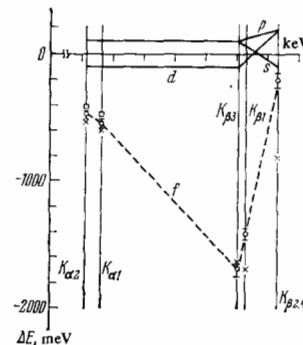
The general classification of experimental data on the chemical shifts (ΔE) of the $K_{\alpha 1}$ x-ray lines of the heavy elements (metals) in oxides or compounds with oxygen-group elements has been considered. It has been established that all of these experimental data, which cover more than 30 elements and 50 compounds, are described approximately by a relation of the type

$$\Delta E = i \sum_l m_l C_l,$$

where i is the Pauling ionicity, $m = \sum_l m_l$ is the valence,

m_l is the number of valence electrons with a given orbital quantum number l , and C_l is the energy change of the $K_{\alpha 1}$ line on complete removal of one valence electron of type l (s, p, d, f) from the atom, with $C_s = C_p \equiv C_{s,p} = 80 \pm 10$ meV, $C_d = -115 \pm 10$ meV, and $C_f = -570 \pm 30$ meV over the entire range of Z considered. The dependence of the effect on the distribution of the valence electrons over the l sublevels, i.e., on the valence configurations, and the differences in the signs and absolute values of the coefficients $C_{s,p}$, C_d , and C_f are alone sufficient to permit use of the effect as an experimental method of studying valence configurations. However, the scope of the method can be expanded by measuring the $K_{\alpha 1}$ shifts of both (electropositive and electronegative) partners in the compound and, most importantly, by using the other intense lines of the K series: $K_{\beta 1, 3}$ and $K_{\beta 2, 4}$. The experimentally measured shifts of the $K_{\alpha 1}$, $K_{\beta 1}$, and $K_{\beta 2, 4}$ lines on stripping of s (p), d, or f electrons from the atoms are compared with theoretical calculations made within the framework of the Hartree-Fock-Slater method. Quite good agreement between the experimental and calculated shift vs. line-type relations is noted, especially in the case of 4f electrons. It is important that these relationships are found to be quite characteristic, differing for s(p), d, and f electrons and remaining unchanged in general outline in a broad range of Z (see figure). They serve as electron "facsimiles" of a sort, from which it is possible in a number of cases to judge with certainty which electron is involved in the phenomenon under study. If we compare the shapes of the experimental and calculated (experimental standard) "facsimiles," the ionicity is no longer needed, thus illustrating the advantages of the multiparameter (more precisely, three-parameter) character attained in the method. Study of the valence state of the formally bivalent thulium monochalcogenides TmTe, TmSe, and

Typical shift vs. line type ($K_{\alpha 1, 2}$, $K_{\beta 1, 3}$, and $K_{\beta 2, 4}$) relations observed on removal (incorporation into an ionic chemical bond) of one s (p), d, or f electron and serving as "facsimiles" of valence electrons.



TmS is examined as a case in which this method is used. It is concluded from comparison of the experimental and calculated shifts of the $K_{\alpha 1}$, $K_{\beta 1}$, and $K_{\beta 2}$,⁴ lines that the thulium ion in TmTe is basically in the bivalent state; an admixture of the bivalent state of thulium was observed for the first time in TmSe. The compound TmS is trivalent, with the structure $S = \text{Tm} - \text{Tm} = \text{S}$, the metal-metal bond apparently formed by the 5d electron.

The typical instrument for measurement of small x-ray line shifts in heavy atoms is a special Cauchois crystal diffraction spectrometer with two-meter focal length and a scintillation counter as a detector. The shift range that can be measured is 0.05 to 1.0 eV, and the relative error of the measurements $\sigma(\Delta E)/E \approx 10^{-7}$, where $\sigma(\Delta E)$ is the rms error. It should also be noted that another experimental technique based on silicon or germanium semiconductor detectors can also be used. Such instruments now deliver accuracies $\sigma(\Delta E)/E \approx 10^{-6}$.

The basic results have been published in the papers: Zh. Eksp. Teor. Fiz. 48, 445 (1965) [Sov. Phys.-JETP 21, 295 (1965)]; 50, 861 (1966) [23, 572 (1966)]; 53, 796 (1967) [26, 489 (1968)]; 54, 1352 (1968) [27, 724 (1968)]; 55, 745 (1968) [28, 385 (1969)]; 56, 536 (1969) [29, 296 (1969)]; 57, 1139, 1716 (1969) [30, 622, 927 (1970)]; 61, 1756 (1971) [34, 935 (1972)]; 65, 1157 (1973) [38, 573 (1974)].

Yu. S. Grushko, L. I. Molkanov, I. M. Band, and A. V. Olef'nik. Combination of the X-Ray Chemical Shift Method and the Mossbauer Effect in Study of Electron Valence Structure. A new experimental method has been developed successfully in recent years for study of electronic valence structure—the x-ray-line chemical-shift method^[1]. Similar information can be obtained from the Mossbauer effect.

The present paper is devoted to a comparison of the results obtained for various iodine compounds by these two methods. The chemical shifts of the $K_{\alpha 1}$, $K_{\beta 1}$, and $K_{\beta 2}$,⁴ lines were measured for a considerable number of iodine compounds. In addition, self-consistent Dirac-Slater calculations were made for 22 different electron configurations of the iodine ion, and the chemical shifts of the x-ray lines with respect to the $5s^2p^5$ configuration and the electron densities at the nucleus were computed.

Figure 1 shows the calculated results for the $K_{\alpha 1}$ line shift. A similar picture is observed for the $K_{\beta 1}$ line. It is seen that a certain permissible set of configurations corresponds to a given experimental shift and can be represented as a practically straight line with the numbers of 5s and 5p electrons as coordinates; we shall call this line the configurational trajectory. The same can be said of the $K_{\beta 1}$ line. The results of calculation of the electron density at zero can be represented graphically in much the same way as was done for the x-ray chemical shift, and the experimental isomeric shifts can be compared, by appropriate calibration, to the electron density at the nucleus and, as in the case of the x-ray chemical shifts, the configurational trajectories can be obtained from the Mossbauer effect. Obviously, all trajectories should intersect at the same point, whose coordinates correspond to the 5s and 5p populations that satisfy the entire aggregate of data analyzed. We should note that the presence of 5d elec-

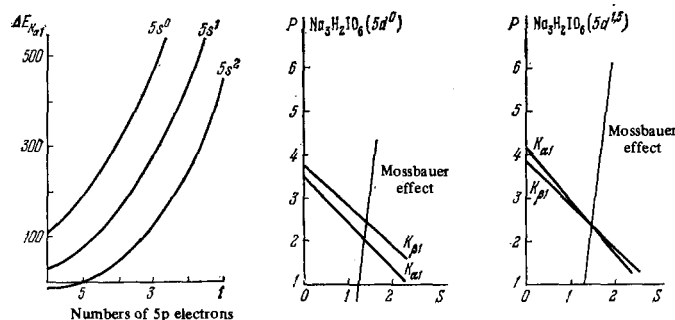


FIG. 1. ($\Delta E - \bar{I}$ meV).

FIG. 2

trons in the valence configuration substantially alters the coordinates of the trajectory intersection point, and that the change can be taken into account quantitatively with the aid of the results of the self-consistent calculation. Figure 2 gives an example of this analysis for sodium paraperiodate. It is seen that if we assume participation of only s and p electrons in the valence configuration, it is impossible to obtain a consistent configuration for the $K_{\alpha 1}$ and $K_{\beta 1}$ lines and the isomeric shift in $\text{Na}_3\text{H}_2\text{IO}_6$. But the assumption that 1.5 5d electrons participate in the configuration yields a single consistent configuration. The same analysis for KICl_2 and KICl_4 indicates that the experimental results agree satisfactorily without participation of 5s and 5d electrons in the configuration. This last result is consistent with the now generally accepted notion that the bonds in integraloid compounds are of pure p character. This configurational analysis, which was carried out for all of the compounds studied, indicated that it is necessary to assume participation of 5d electrons in the valence configuration for oxygen compounds of iodine.

The idea that d electrons participate in the chemical bonds of high-valence compounds of nontransition elements has been suggested by many authors, but we have apparently obtained the first quantitative data. For some of the compounds, the configurations obtained were used to calculate the quadrupole splitting constants of the ground state of the iodine-127 nucleus, which were then compared with the experimental values from the Mossbauer effect and NQR. The experimental and calculated values agree satisfactorily within the limits of error.

It can be stated in conclusion that combination of the x-ray chemical shift and Mossbauer effect methods enables us to acquire additional information on electron valence structure that does not follow from either of the methods taken alone.

¹O. I. Sumbaev, Zh. Eksp. Teor. Fiz. 57, 1716 (1969) [Sov. Phys.-JETP 30, 927 (1970)]; P. L. Lee, F. Boehm and P. Vogel, AEC Research and Development Report CALT-63-190.

G. M. Drabkin, A. I. Sibilev, V. V. Klyubin, T. G. Braginskaya, and G. E. Shmelev. Spatial Correlation Effects of Fluctuations in a Liquid Binary Mixture and its Electrical Conductivity Near a Phase-Transition Point. The sensitivity of the spatial coherence modulus of light scattered at small angles to changes in the fluctuation dispersion of the triethylamine-water system under phase-transition conditions has been demonstrated experimentally. The spatial coherence modulus of the scattered light increases with increasing optical thickness of the sample, a fact explained by the