

## EFFECT OF IMPURITIES ON THE X-RAY SPECTRA OF TRANSITION METALS

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Submitted to JETP editor October 10, 1958

J. Exptl. Theoret. Phys. (U.S.S.R.) 36, 1203-1206 (April, 1959)

A method is proposed for an estimate of the effect of impurities on the parameters of transition-metal x-ray emission spectra. The method is applied to the case of dilute alpha-solid solutions with iron as the base.

SYSTEMATIC investigations carried out over the last few years for the study of dilute solid solutions with transition-group metals as a base have shown that a considerable influence is exerted by small impurities (of the order of 0.01 to 0.1% atomic) on some of the physical properties of these solutions. This influence is evidenced by changes in the x-ray emission and absorption spectra parameters, in the optical constants, in the diffusion coefficients, in the coefficient of linear expansion, in the electrical resistivity, etc.

A study of experimental data and a theoretical investigation of the subject have led us to a model of a physical mechanism describing the action of impurities on the electron energy spectrum for the transition metals and on the interatomic binding forces in these metals.<sup>1,2</sup> We examine in the present paper the possibility of applying this model to a quantitative estimate of the wavelength changes in the emitted x-ray spectra.

The model can be described as follows.

Upon entering a metal, an impurity of substitution (or inclusion) loses its outer (valence) electrons, which are distributed in the conduction band of the base metal. The resultant positive charge on the impurity ion may be either greater or less than the positive charge on the remaining atomic cores, i.e., the impurity in the metal will possess an excess positive or negative charge. It turns out that the perturbing potential of this excess charge is active only with a finite radius, because of the shielding effect provided by the conduction electrons. The effective radius of the excitation potential comprises only a few coordination spheres around each impurity atom. The resultant polarization interaction leads to a distortion of the electron shells of the base-metal cores. In transition metals this effect also influences the defective (not fully built up) nd or nf shell. Since the corresponding energy band

overlaps the conduction band, an equilization of electron energies takes place about the Fermi level, i.e., in the immediate vicinity of the impurity, electrons pass from the defective shell into the conduction band (or vice versa, depending on the sign of the excess charge of the impurity). Thus, in the vicinity of the impurity, the effective charge of the base-metal core changes, which is equivalent to the appearance of induced excess charges on these cores. These excess charges are always opposite in sign to the charge of the basic impurity. Therefore, an additional (polar) bond arises between the basic impurity and the surrounding cores. Thus, distinct reinforcement blocks appear and remain until the impurity concentration reaches a value such that the impurities develop strong interactions among themselves.

In Gurov's work<sup>3</sup> an investigation was made of the degree of validity of such a model and the limits within which it could be applied. It was shown that the model holds for those cases when an approximation of strongly bound electrons holds. The concepts thus developed are therefore applicable to all electrons of the atomic core including electrons of the "defective" shell, whereas if applied to the conduction electrons, they can cause considerable discrepancies.

Gurov<sup>3</sup> also showed that if the potential for the excess charge of the impurity drops off rapidly with distance and changes very little at distances on the order of the radius of the first coordination sphere (that is, practically constant over a range on the order of the dimensions of the core), then, the local deformation of the electron spectrum (isolated at each site) can be conveniently described by the "rigid band" approximation,<sup>4</sup> according to which

$$\Delta E = -eW(r), \quad (1)$$

where  $W$  is the potential of the excess impurity charge,  $e$  the absolute charge of the electron, and  $r$  the distance from the core of interest to the impurity. It is common practice to express  $W(r)$ , after Mott,<sup>5</sup> in the following form (for a more precise form see reference 6)

$$W(r) = -(Ze/r)e^{-qr} \quad (2)$$

where  $Ze$  is the excess charge.

On the basis of the concepts described above and Moseley's law we can make an approximate evaluation of the influence of the impurities on the x-ray spectra of the transition metals. To illustrate how this evaluation is carried out, we examine the line shift of the x-ray emission spectrum of iron in dilute  $\alpha$ -solid solution from the positions in the spectrum of pure  $\alpha$ -iron.

We can consider the position of the Fermi level fixed for small impurity concentrations. For this case the change in effective charge takes place as a result of the "local deformation" of the 3d band and because of a corresponding leakage of electrons from the 4s band into the 3d band (or the reverse, as determined by the sign of the excess impurity charge). Thus, the mean change of effective charge,  $\Delta Ze$ , per atom of the system is equal to the total change of effective charge in one block multiplied by the number of blocks,  $N_{\text{imp}}$ , for a given atomic concentration of impurity,  $c$ , and divided by the total number of atoms in the system,  $N$  ( $c = 100 N_{\text{imp}}/N$ ). For an approximate computation, in view of the rapid falling off of potential of the excess impurity charge, the order of magnitude of the total change in effective charge in the block can be determined from the change of effective charge on the atomic cores situated on the first coordination sphere around the impurity. Therefore

$$\begin{aligned} |\Delta Ze| &= \left| \frac{N_{\text{imp}}}{N} \int_{\text{layer}} e \{ \rho_{3d}(r, E_F) - \rho_{3d}^0(r, E_F) \} d\tau \right| \\ &= \left| 0.01 ce \int_{\text{layer}} \Delta E_F (\partial \rho / \partial E)_{E_F} d\tau \right| \\ &= \left| 0.01 c N e^2 W(R_k) n_{3d}^0(E_F) \int_{\text{layer}} |\psi_{3d}(r, E_F)|^2 d\tau \right| \\ &\approx 0.01 ce^3 |Z| \frac{N_k \exp(-qR_k)}{R_k} n_{3d}^0(E_F), \quad (3) \end{aligned}$$

where  $\rho_{3d}$  and  $\rho_{3d}^0$  are the densities of the 3d electrons respectively in the dilute solid solution and in the pure metal,  $n_{3d}^0(E_F)$  is the density (per atom) of the levels at the Fermi surface in the 3d band of the pure metal,  $N_k$  is the number of atomic cores on the first coordination sphere, and  $R_k$  is the radius of this sphere (for  $\alpha$ -iron,  $N_k = 8$ ,  $R_k = 2.4 \times 10^{-8}$  cm). The integration is

taken over a monatomic spherical layer which encompasses the atomic cores on the first coordination sphere; the transformations take into account the fact that in the approximation of strongly bound electrons

$$\int_{\text{layer}} |\psi_{3d}(r, E_F)|^2 d\tau \approx N_k / N; \quad (4)$$

the parameter  $q$  is connected with the effective radius of the blocks and may be approximated with the aid of the Friedel<sup>4</sup> scheme, or else empirically<sup>7,8</sup> from the position of the extremal points of the concentration curves for the diffusion coefficient or for the linear thermal expansion coefficient.<sup>9,10</sup> The concentration corresponding to the extremal point determines the concentration of impurity at which "dense packing" of the blocks takes place. This determines in turn the radius of a block and hence the parameter  $q$ . The theoretical and empirical values are of the same order of magnitude ( $q \cong 0.5$  to  $1.0 \times 10^8$  cm<sup>-1</sup>). Estimates of the concentration that yields optimal action of impurities ( $c = 0.1\%$  atomic), computed by this formula, lead to the following magnitude for the change of effective charge

$$|\Delta Ze| \approx 10^{-2} |Ze| \quad (5)$$

(the density of levels in the 3d band at the Fermi surface in  $\alpha$ -iron is taken from the Landolt-Bernstein tables:  $n_{3d}^0(E_F) \cong 7 \times 10^{11}$  erg<sup>-1</sup>).

We now estimate the change in the lines of the x-ray emission spectrum for iron. Let us take as the excess charge of the impurity a quantity on the order of unity (here and in all that follows, everything is expressed in units of electron charge) i.e., according to formula (5),  $|\Delta Z| \cong 10^{-2}$ .

The entire computation is carried out by means of Moseley's law in the following manner. We write Moseley's law in the form

$$\nu/R = \text{const} \cdot (Z_{\text{nuc}} - \sigma)^2, \quad (6)$$

where  $Z_{\text{nuc}}$  is the absolute nuclear charge and  $\sigma$  is the shielding constant

$$\sigma = \sum_s B_s z_s, \quad (7)$$

where each term indicates the contribution of a particular electron shell to the shielding ( $z_s$  is the charge of the corresponding electron shell). Evidently

$$\Delta(\nu/R) = -\text{const} \cdot 2(Z_{\text{nuc}} - \sigma) \Delta\sigma \quad (8)$$

or

$$\Delta\nu/\nu = -2 \Delta\sigma / (Z_{\text{nuc}} - \sigma). \quad (9)$$

Let us estimate the value of  $\Delta\sigma$ . For the general case we have

$$\Delta\sigma = \sum_s B_s \Delta z_s + \sum_s z_s \Delta B_s. \quad (10)$$

A change in the charge of any one electron shell causes all the  $B_s$  to change, i.e.  $\Delta B_s = F(\Delta z_1, \Delta z_2, \dots)$  for any  $s$ . Moreover, it is evident that upon change in sign of any one  $\Delta z_j$  the signs of all the  $\Delta B_s$  change, i.e., the  $F(\Delta z_j)$  curves have inflection points at  $\Delta z_j = 0$ . Therefore, if we expand  $\Delta B_s$  in powers of  $\Delta z_j$  the series will start with the  $(\Delta z_j)^3$  term. For this reason we can neglect all the  $\Delta B_s$  if  $\Delta z_j \ll 1$ . On the other hand, the terms which have been dropped become the dominant ones for  $\Delta z_j \cong 1$ .

In the scheme that we have investigated, the charge changes only in the 3d-shell, and  $|\Delta z_{3d}| \cong 10^{-2} \ll 1$ , so that

$$\Delta\sigma = B_{3d} \Delta z_{3d}. \quad (11)$$

The coefficient  $B_{3d}$  is determined by Sommerfeld's formula<sup>11</sup>

$$B_{3d} = a_n / a, \quad (12)$$

where  $a_n$  is the radius of the electron shell, with respect to which the screening is under consideration, and  $a$  is the atomic radius.

Let us investigate, for example, the shift of the  $K_{\beta_1}$  iron line (the 1s-3p transition). Here the determining quantity (of greater magnitude) will be  $a_{3p}$ , so that we must determine the radius of the 3p shell. This quantity can be found in the Landolt-Bernstein tables for a free iron atom (the radius of inner shells changes insignificantly for transitions in the metallic state). This radius is equal to  $a_{3p} = 0.2 \times 10^{-8}$  cm (overestimated). For the atomic core of  $\alpha$ -iron (metal), we find from the same tables  $a = 0.4 \times 10^{-8}$  cm, so that

$$B_{3d} \approx 10^{-1}; \quad |\Delta\sigma| = B_{3d} |\Delta z_{3d}| \approx 10^{-3}. \quad (13)$$

It follows from the above that the estimated relative displacement of the  $K_{\beta_1}$  line is (bearing

in mind the fact that  $(Z_n - \sigma) \cong 20$ )

$$|\Delta\nu/\nu| = |-2\Delta\sigma/(Z_{\text{nuc}} - \sigma)| \approx 10^{-4}. \quad (14)$$

Experimental data show a displacement of  $\Delta\nu \cong 0.7$  ev for  $\nu = 7 \times 10^3$  ev, i.e., of the same order of magnitude.

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