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ELECTRICAL CONDUCTIVITY OF DILUTE SOLUTIONS OF TRANSITION METALS IN PLATINUM

Yu. N. TSIOVKIN and N. V. VOLKENSHTEĬN

Institute of Metal Physics, Academy of Sciences, U.S.S.R.

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Measurements were made of the resistance of the solid solutions (0.5 at.%) in platinum of the transition metals of the 3d group and of some of the 4d group. It is shown that the "residual" resistance of the solutions does not vary monotonically with the charge of the impurity. The maximum value of the "residual" resistance of the solutions of the 3d metals in Pt corresponds to the Ti impurity, while for the investigated solutions of the 4d metals, the maximum corresponds to the Zr impurity. The results obtained are discussed on the basis of the existing theory of localized states.

SEVERAL interesting features of the physical properties of dilute solid solutions of transition metals are attracting increasing attention of both experimentalists and theoreticians. Friedel[1] has suggested that the localized energy states E_{loc} of impurity centers, close to the Fermi level energy of the solvent E_f, should play an important role in the electrical conduction and in the thermoelectric and magnetic properties of solid solutions. According to Friedel's theory, the scattering of electrons by impurity centers, represented by a perturbing potential ΔV corresponding to an effective impurity change ΔZ (ΔZ is the difference between the number of outer electrons of the solvent N and the impurity N_q), may be of the resonance type. The curve $\Delta\rho = f(E)$, where $\Delta\rho$ is the difference between the resistivities of the solution and the solvent, should have a maximum at $E = E_{loc}$. This theory has successfully explained the well-known experimental results of Linde[2], who investigated the resistance of dilute solutions of transition metals in a matrix of a non-transition metal.

Friedel's ideas about the role of localized states in various physical phenomena were developed later by a number of workers.[3-5] Clogston, Matthias et al.[5] have shown theoretically that the localized states of impurity centers in a solution do indeed appear near the Fermi level energy of the solvent and their appearance depends on the density of states in the conduction band of the solvent. This was confirmed by Clogston, Matthias et al. experimentally in a study of the magnetic properties of the solid solutions of iron in Mo—Nb, Mo—Re and some other alloys. It has been established that the existence of the magnetic moment of the Fe impurity atom depends on the electron density in the solvent; moreover, the value of the magnetic moment increases when there is a decrease in the density of states near the Fermi level energy of the solvent. Investigations of the electrical conductivity,[6] carried out on the same alloys, have shown that the "impurity" resistance (the difference between the resistances of the solution and the solvent) increases strongly at the electron densities corresponding to the appearance of the magnetic moment. Our measurements of the magnetic properties of dilute solid solutions of the 3d metals in Pt[7] have shown that a strong magnetic moment is exhibited by the Cr, Mn, Fe, and Co impurities. Nickel, dissolved in Pt, does not exhibit a magnetic moment. Since it is assumed that in these cases the magnetic moment of an impurity atom is governed by the presence of localized states, it is interesting to investigate the resistance of these solutions.

RESULTS OF MEASUREMENTS AND DISCUSSION

We investigated the temperature dependence of the resistance of the solutions (0.5 at.%) of Sc, Ti, V, Cr, Mn, Fe, Co. Ni, Y, Zr, Nb, and Mo in Pt in the temperature range 273—373°K.

As a measure of the "residual" resistance associated with the scattering of the conduction electrons by impurity centers, we selected the quantity

$$\alpha = \frac{R_s(0)}{R_s(T)} - \frac{R_m(0)}{R_m(T)},$$

where $R_s(0)$ and $R_m(0)$ are the residual resistances of the solution and the matrix, found by linear extrapolation of the dependence of R(T) to zero temperature; $R_s(T)$ and $R_m(T)$ are the resistances of the solution and the matrix at $T = 373°K$. The value of α was calculated per 1% of the impurity. This selection of the quantity α to represent the "residual" resistance made it possible to eliminate the error associated with the geometry of the sample. The investigated samples were in the form of strips 0.08 mm thick, 2—3 mm wide and 15—30 mm long. The main error in α was associated with the accuracy of the determination of the impurity concentration, which was deduced from the initial charge. An analysis of the possible losses of the impurity showed that the maximum error in the determination of the impurity concentration (Mn and Sc) could reach 3—4%.

Figure 1 shows the dependence of the "residual" resistance α of the solutions of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, and Mo in Pt on the effective impurity charge $\Delta Z = N - N_q$.

Figure 2 shows similar curves, taken from Linde's work,[2] for transition and non-transition metals dissolved in Cu. It is evident that the "residual" resistance of the transition metal solutions both in Cu and Pt varies nonmonotonically, in contrast to the resistance due to the presence of non-transition metals in Cu. The "residual" resistance maximum for the solutions of the 3d transition metals both in Pt and Cu corresponds to the Ti impurity, and for the investigated solutions of the 4d metals in Pt, it corresponds to the Zr impurity. The conclusions about the 3d-metal solutions in Cu may be found to be somewhat premature, since the "residual" resistance curve (Fig. 2) lacks the points for the solutions of Sc and V. Vassel[8] has investigated the "residual" resistance of the 3d metals in Cu, including Ca and V. The value of the "residual" resistance of the solution of Ca in Cu is considerably lower than the corresponding value for the Ti solution, but the "residual" resistance of the solution of V in Cu is close in value to the "residual" resistance of the solution of Ti in Cu. It seems to us that the value of the "residual" resistance of the solution of V in Cu is somewhat exaggerated due to the difficulty of preparing a solid solution.[9] If we assume, as has been done in the paper of Cohen and Heine,[10] that the introduction of an impurity into Cu leads to some disturbance of the filled d band, then Cu becomes the analog of Ni in respect of its effective valence. The displacement to the right of the "residual" resistance curve of the 3d metals in Cu (Fig. 2) by unit effective charge produces a qualitative similarity of the dependence of the "residual" resistance on the impurity charge for the 3d-metal solutions in Pt and Cu.

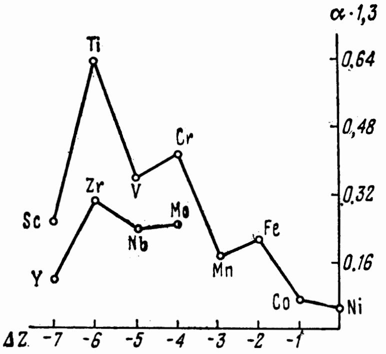

FIG. 1

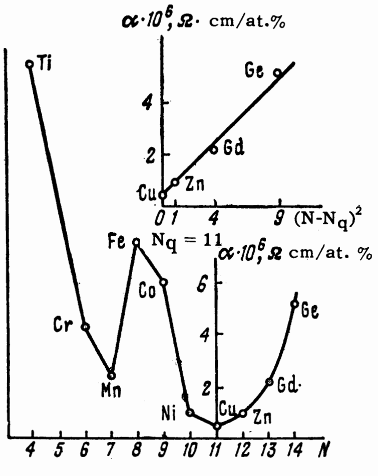

FIG. 2

We note that Cr, Mn, Fe and Co, dissolved both in Pt and Cu, exhibit a magnetic moment.[11] Therefore, it is natural to expect that the qualitative explanation of the curves is the same for both cases.

The fact that the maximum of the dependence of the "residual" resistance on the charge occurs at the Ti impurity permits us to conclude that the width of the d band both in Cu and Pt should be approximately the same, since, according to Friedel,[12] this maximum corresponds to the appearance of a localized level near the Fermi level energy of the solvent. Anderson[3] has shown that the localized magnetic moment is always obtained at the level $E_{loc} \approx E_f$. Consequently, the "residual" resistance of the solutions of Fe, Co, Mn, and Cr is always found to fit the resonance curve $\Delta\rho = f(E)$. The intra-atomic exchange interaction in the impurity, which splits the E_{loc} into two sublevels corresponding to the right-handed and left-handed spin orientations, tends to keep this resistance on the resonance curve.

As is evident from the curves in Figs. 1 and 2, the "residual" resistance of the 3d-metal solutions in Pt and Cu varies nonmonotonically with ΔZ. This may be explained qualitatively by assuming that the possible value of E_{loc} is proportional to the depth of the potential well, characterized by an effective charge ΔZ. Then the possible value of E_{loc} should decrease when ΔZ decreases. Let us assume that E_{loc} for Sc in platinum lies above E_f; this means that the corresponding level will be vacant and the outer electrons of the Sc atom will be lost to the conduction band. The "residual" resistance maximum of the solutions of Ti corresponds to $E_{loc} \approx E_f$. In this case, the outer electrons may be either lost to the conduction band or become localized. In all probability, the poor solubility of V in the noble metals[9] is due to the weak interaction of its outer electrons with the conduction band.

In the case of the solutions of Cr, Mn, Fe, and Co, the position of the E_{loc} level with respect to the E_f level should be affected considerably by the intra-atomic exchange interaction, which splits the E_{loc} level into two sub-levels corresponding to the right-handed and left-handed spin orientations.

If we assume that the intra-atomic exchange interaction increases on going from Cr to Ni, then the superposition of the two mechanisms—the increase in the exchange interaction when ΔZ decreases and the decrease in the possible value of E_{loc}—may lead to a situation such that one of the E_{loc} sub-levels periodically approaches or retreates from E_f. The magnetic moment of the solution of 0.5 at.% Ni in Pt is not localized. This may mean that the two sub-levels are above E_f so that they tend to remain vacant and the outer electrons of the Ni atom are lost to the conduction band.

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[1] J. Friedel, Canad. J. Phys. **34**, 1190 (1956).

[2] J. O. Linde, Ann. Physik 15, 219 (1932).

[3] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[4] P. A. Wolff, Phys. Rev. **124**, 1030 (1961).

[5] Clogston, Matthias, Peter, Williams, Corenzwit, and Sherwood, Phys. Rev. **125**, 541 (1962).

[6] M. P. Sarachik, J. Appl. Phys. **35**, 1094 (1964).

[7] Yu. N. Tsiovkin and N. V. Volkenshteĭn, FMM **19**, 367 (1965).

[8] C. R. Vassel, J. Phys. Chem. Solids **7**, 90 (1958).

[9] M. Hansen and K. Anderko, Structure of Binary Alloys, (Russ. Transl.) 1962, Part II.

[10] M. H. Cohen and V. Heine, Adv. Phys. **7**, 395 (1958).

[11] C. Vogt, Angew. Chem. **48**, 734 (1935).

[12] J. Friedel, J. phys. rad. **19**, 573 (1958).

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