

## Resistivity of Mo-Nb and Mo-Re Alloys Containing 1% Fe

M. P. SARACHIK, E. CORENZWIT, AND L. D. LONGINOTTI

*Bell Telephone Laboratories, Murray Hill, New Jersey*

(Received 19 March 1964)

The resistivity of a series of Mo-Nb and Mo-Re alloys, with and without 1% Fe, has been measured at room temperature, and between 1.5 and 77°K. Large effects are observed near the alloy composition where the iron acquires a localized magnetic moment. These effects appear both as an excess temperature-independent scattering and in the form of large anomalies at low temperatures. Interpreted in the light of current theories of localized moments, the resistivity results confirm the existence of virtual bound states near the Fermi level. In addition, the anomalous behavior of the resistivity at low temperatures has been directly related to the existence of a localized magnetic moment.

### INTRODUCTION

THE magnetic properties of 1% Fe dissolved in Nb-Mo and Mo-Re alloys have been studied by Matthias *et al.*<sup>1</sup> and Clogston *et al.*<sup>2</sup> Proceeding from Nb to Mo to Re in closely spaced alloy compositions, they found that the iron solute does not exhibit a localized moment in the Nb-rich Nb-Mo alloys. A moment first appears at approximately the equi-atomic composition (Nb<sub>0.5</sub>Mo<sub>0.5</sub>), and persists in the Mo-Re alloys almost to pure Re, as shown in Fig. 1. In the present experiment, the resistivity of these alloys was measured in an effort to relate their magnetic and transport properties. Current theories of localized moments<sup>3</sup> predict that a maximum in the residual resistance due to magnetic impurities should occur for those alloy compositions at which moments first appear. The resistivity of each alloy was also studied as a function of temperature in order to relate the existence of a localized magnetic moment with the appearance of low-temperature resistive anomalies commonly observed in dilute magnetic alloys,<sup>4</sup> and if possible, to find a relation between the size of the moment and the size and temperature dependence of the anomalous scattering.

### EXPERIMENTAL TECHNIQUES

#### A. Sample Preparation

The samples were arc melted in an argon-atmosphere furnace.<sup>5</sup> The ingots were remelted several times during the preparation of the master alloys to ensure homogeneity. The samples were then weighed again and iron added. During the addition of the iron, care was taken not to exceed the melting point of the host alloy more than necessary in order to minimize the loss of iron by evaporation. This was a more serious consideration for

the Mo-Re alloys, and they may therefore contain somewhat less iron than the Mo-Nb alloys. The estimated error in iron concentration is less than 25% in all cases.

Annealing a sample of (Mo<sub>0.8</sub>Re<sub>0.2</sub>)<sub>0.99</sub>Fe<sub>0.01</sub> resulted in its having the same superconducting transition temperature as the Mo<sub>0.8</sub>Re<sub>0.2</sub> alloy without iron. Since at this composition the transition temperature is known<sup>1</sup> to decrease at the rate of 22°K/% Fe, one can only conclude that the annealing process caused the iron to precipitate out of solution. Subsequent samples were therefore not annealed.

The arc-melted buttons were cut with a rubber bonded grinding wheel into rods about 0.025 by 0.025 by 0.5 in, and four platinum leads were mounted by spot welding.

#### B. Resistivity Measurements

The resistivity was measured using a standard four-terminal technique. Current regulation was better than 0.005%, and voltages were measured with a potentiometer using a sensitive microvoltmeter as a detector. Resistance readings were taken at room temperature, 77°K, and between 1.5 and about 60°K depending on the sample. A gallium arsenide diode was used as a temperature-sensing device.<sup>6</sup> The diode was calibrated at the boiling and triple points of nitrogen

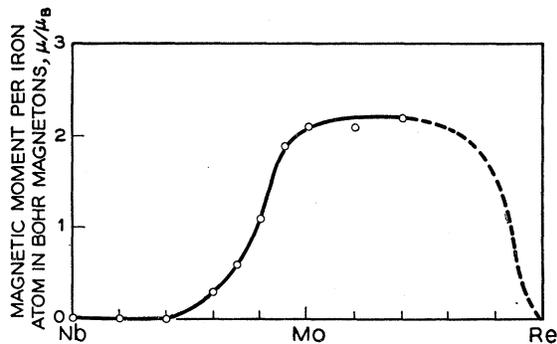


FIG. 1. Magnetic moment of an iron atom dissolved in various Mo-Nb and Mo-Re alloys as a function of alloy composition, according to Clogston *et al.*

<sup>6</sup> B. G. Cohen, *Rev. Sci. Instr.* **34**, 1091 (1963).

<sup>1</sup> B. T. Matthias, M. Peter, H. J. Williams, A. M. Clogston, E. Corenzwit, and R. C. Sherwood, *Phys. Rev. Letters* **5**, 542 (1960).

<sup>2</sup> A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, *Phys. Rev.* **125**, 541 (1962).

<sup>3</sup> P. A. Wolff, *Phys. Rev.* **124**, 1030 (1961).

<sup>4</sup> For a recent review see G. J. Van den Berg and J. de Nobel, *J. Phys. Radium* **23**, 665 (1962).

<sup>5</sup> All starting materials were in the form of solid metals to minimize the gas content. The purities were: rhenium 99.99%, niobium 99.99%, molybdenum 99.95%. Ferrovac iron was used.

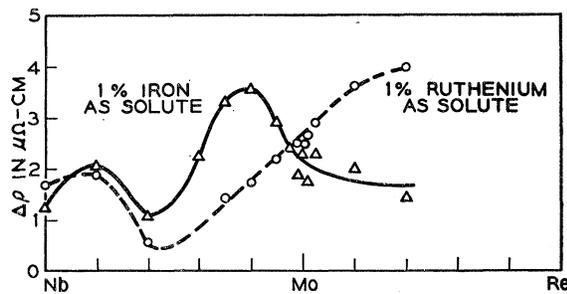


FIG. 2. Differential resistivity for iron and for ruthenium dissolved in Mo-Nb and Mo-Re alloys vs alloy composition.

and hydrogen, and at the boiling point and  $\lambda$  point of helium.

The sample was surrounded by an isothermal copper shield filled with activated charcoal. The temperature was varied between 1.5 and 4.2°K by pumping on helium. Temperatures above 4.2°K were obtained by boiling off the helium and allowing the sample to drift up slowly in temperature. The rate of temperature drift was controlled by a heater surrounding the copper shield.

Absolute resistivity measurements have an estimated error of  $\pm 5\%$ , resulting almost entirely from uncertainties in sample dimensions and surface irregularities. However, relative measurements on a given sample are accurate to 0.2%. The error in the measurement of temperature is approximately  $\pm 1^\circ\text{K}$  between 20 and 63°K (two of the calibration points) and  $\pm 0.2^\circ\text{K}$  elsewhere.

### RESULTS

The resistivity of each alloy was measured with and without iron at 300, 77, and between 1.5 and 60°K. According to Matthiesen's rule it should be true that

$$\Delta\rho \equiv \rho'_{300^\circ\text{K}} - \rho_{300^\circ\text{K}} = \rho'_{77^\circ\text{K}} - \rho_{77^\circ\text{K}}. \quad (1)$$

where  $\rho'$  refers to resistivities of an alloy with iron,  $\rho$  to resistivities without iron, and  $\Delta\rho$  is the increase in resistivity due to the dissolved iron which will be referred to as the "differential resistivity" in the remainder of this paper. The quantity  $\Delta\rho$  should thus be temperature independent<sup>7</sup> except at low temperatures where the resistivity anomalies occur.

The differential resistivity  $\Delta\rho$  is a small difference between two large numbers, each of which has a 5% error. This results in a fairly large uncertainty in  $\Delta\rho$  itself. In order to minimize this error, the following procedure was adopted. The resistivity  $\rho_{300^\circ\text{K}}$  of each alloy without iron was computed from its dimensions and the measured resistance. The differential resistivity was then determined by imposing the condition that

Eq. (1) be obeyed exactly. Thus

$$\Delta\rho = \rho_{300} \left[ \frac{\rho_{77}'/\rho_{300}' - \rho_{77}/\rho_{300}}{1 - \rho_{77}'/\rho_{300}'} \right]. \quad (2)$$

The total error in  $\Delta\rho$  is now  $\pm 5\%$ , and derives mainly from the error in  $\rho_{300}$ , since resistivity ratios are accurate to 0.2%. Resistivities  $\rho_{300}'$  calculated by applying Matthiesen's rule never differed by more than 5% from the values obtained directly from dimensions. This procedure does not alter the essential features of the results. It only serves to reduce the scatter in the data for  $\Delta\rho$ .

The quantity  $\Delta\rho$ , is plotted as a function of alloy composition in Fig. 2.<sup>8</sup> The differential resistivity for 1% Ru dissolved in a similar set of alloys is also presented in Fig. 2 for comparison. Since it is in the same column of the periodic table as Fe, Ru should offer the same charge contrast when dissolved in the Nb-Mo-Re system, but Ru does not exhibit a localized moment. It is clear that a maximum occurs in  $\Delta\rho$  for iron near, but not at the composition where a localized moment first appears, whereas no such behavior is observed in the case of Ru. Preliminary results on this phase of the experiment have been published elsewhere.<sup>9</sup>

The low-temperature results are shown in Figs. 3 and 4. All resistivities are normalized at 4.2°K. The alloys which have no localized moment, namely  $(\text{Mo}_{0.2}\text{Nb}_{0.8})_{0.99}\text{Fe}_{0.01}$  and  $(\text{Mo}_{0.4}\text{Nb}_{0.6})_{0.99}\text{Fe}_{0.01}$ , exhibit no anomalous behavior, as expected. A shallow minimum first appears at  $(\text{Mo}_{0.6}\text{Nb}_{0.4})_{0.99}\text{Fe}_{0.01}$  and deepens as one proceeds towards molybdenum. A decrease in resistivity at low temperature appears at  $(\text{Mo}_{0.95}\text{Nb}_{0.05})_{0.99}\text{Fe}_{0.01}$ , and these alloys exhibit both a maximum and a minimum. For the Mo-Re alloys the decrease at low temperature persists, but the minimum now becomes shallow and disappears.

Figure 5 shows the temperature-dependent part of the resistivity which results from magnetic scattering. It is the total resistivity minus the phonon and residual contributions. Thus,

$$\Delta\rho'(T) = \rho'(T) - \rho(T) - \Delta\rho, \quad (3)$$

where  $\Delta\rho$  is the differential resistivity defined earlier. It should be noted that the temperature of the minimum in  $\rho'$  is just that temperature at which the low-temperature rise in resistivity due to magnetic scattering overcomes the decrease in resistivity due to phonon scattering, and should thus not be regarded as a basic parameter of the problem.

The largest variation in resistivity at low temperature is found to occur for  $(\text{Mo}_{0.8}\text{Nb}_{0.2})_{0.99}\text{Fe}_{0.01}$  and  $(\text{Mo}_{0.9}\text{Nb}_{0.1})_{0.99}\text{Fe}_{0.01}$ .  $\Delta\rho'$  is about 0.6  $\mu\Omega\text{-cm}$  for these alloys, whereas the total resistivity is 6  $\mu\Omega\text{-cm}$  at 4.2°K

<sup>7</sup> One does not expect Matthiesen's rule to be obeyed exactly, but deviations from it should be small compared to experimental error.

<sup>8</sup> The total resistivity varies between approximately 20  $\mu\Omega\text{-cm}$  and 6  $\mu\Omega\text{-cm}$  at room temperature for Nb and Mo, respectively. The differential resistivities are thus a sizable fraction of the total.

<sup>9</sup> M. P. Sarachik, J. Appl. Phys. Suppl. 35, 1094 (1964).

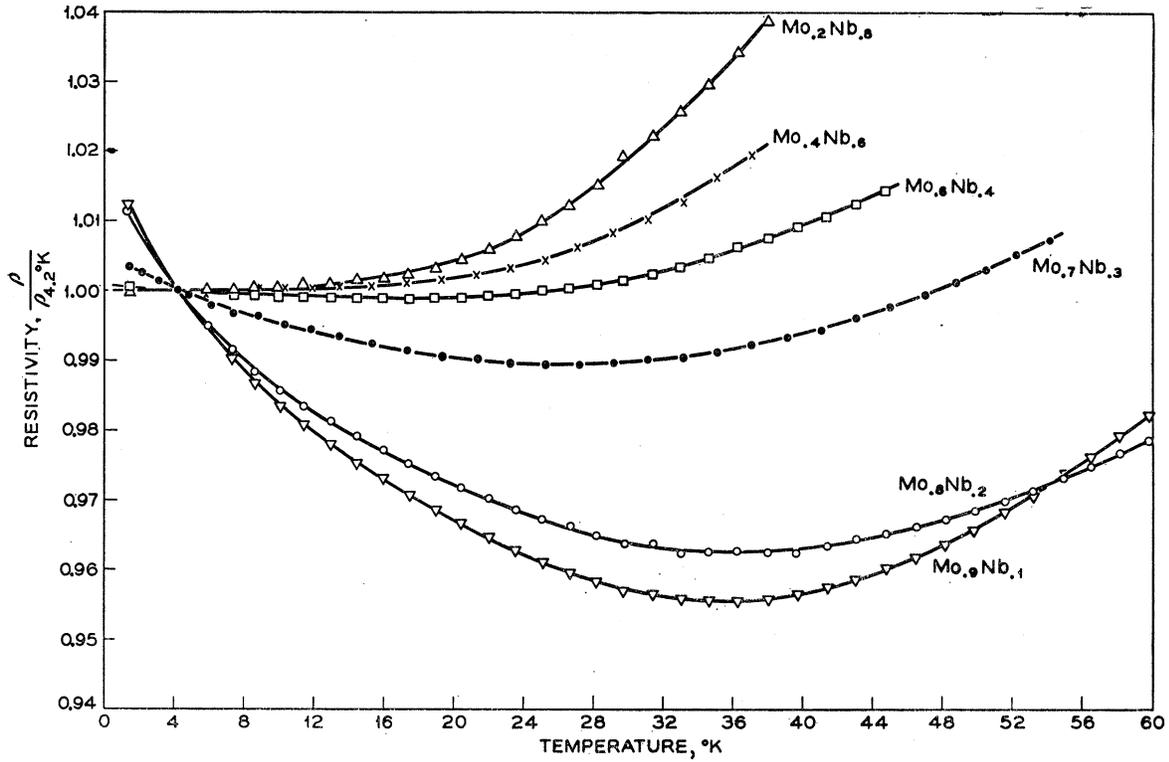


Fig. 3. Resistivity vs temperature for various Mo-Nb alloys containing 1% Fe. Resistivities are normalized at 4.2°K.

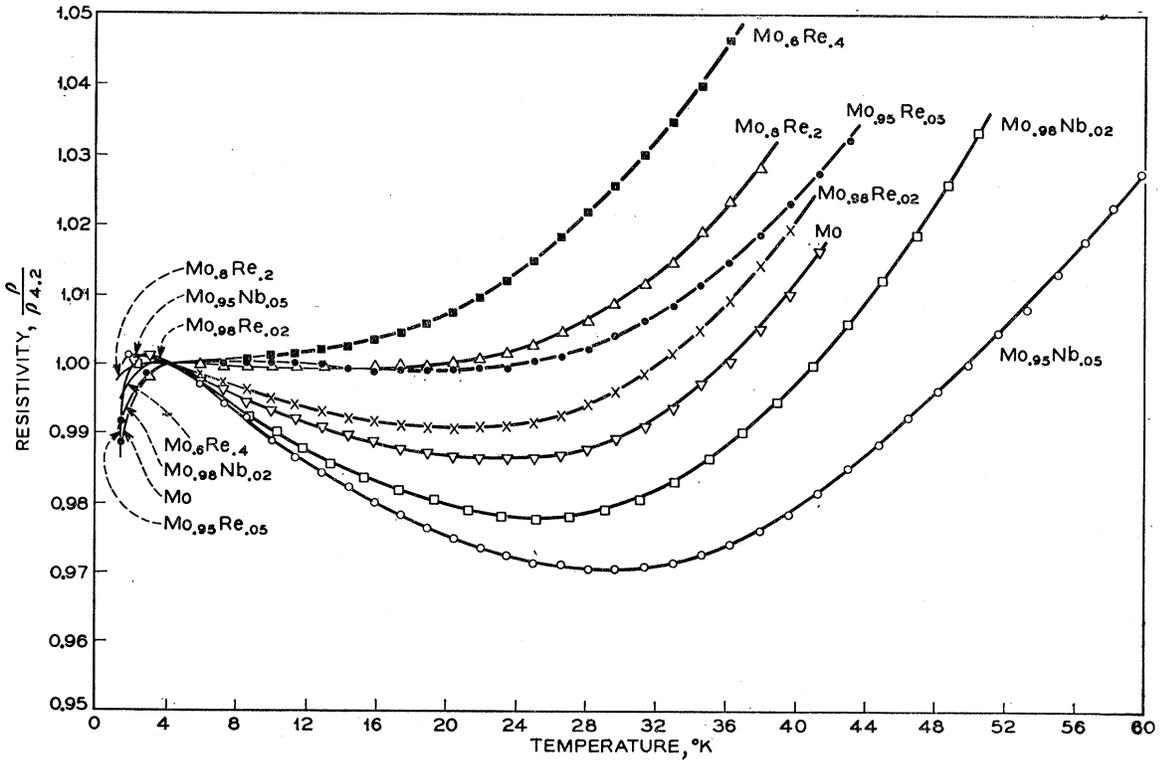


Fig. 4. Resistivity vs temperature for various Mo-Nb and Mo-Re alloys containing 1% Fe. Resistivities are normalized at 4.2°K.

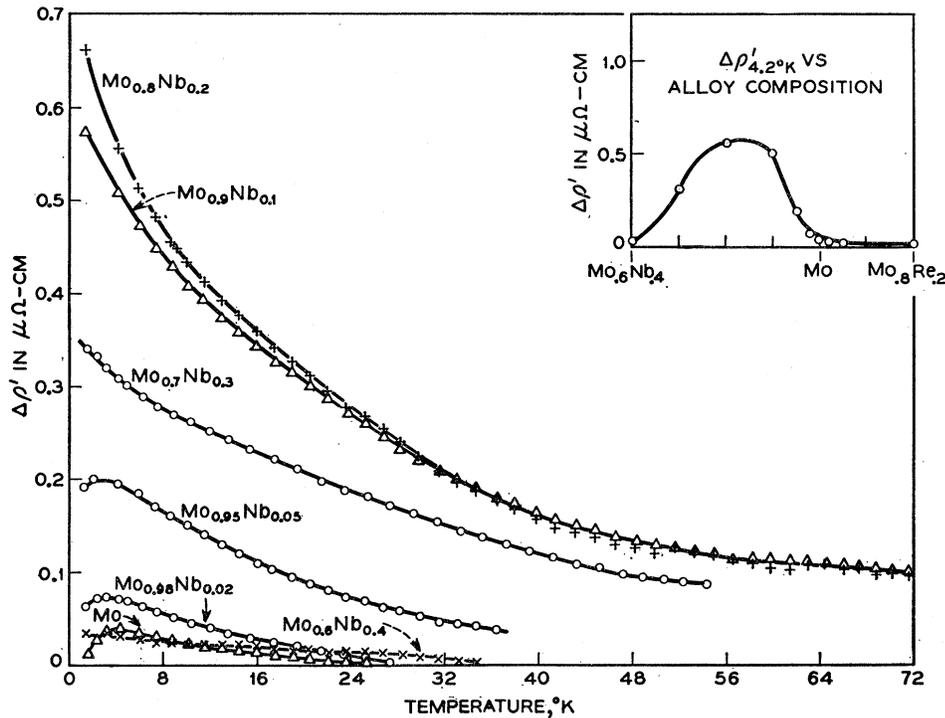


FIG. 5. Resistivity due to magnetic scattering vs temperature for Mo-Nb alloys containing 1% Fe. The resistivity  $\Delta\rho'$  is the total minus the residual and phonon contributions. The insert shows the variation of  $\Delta\rho'$  with alloy composition.

for the latter case. The effect is therefore quite large and is most pronounced near the composition for which the differential resistivity  $\Delta\rho$  has its maximum value.

#### DISCUSSION

The behavior of the differential resistivity  $\Delta\rho$  as a function of the composition of the matrix alloy may be understood in terms of current theories<sup>2,3,10,11</sup> of localized moments as follows: A localized virtual bound state associated with the iron impurity atom forms near the Fermi level of the host alloy. In the niobium-rich alloys this virtual level is a single unmagnetized state. At  $(\text{Mo}_{0.6}\text{Nb}_{0.4})_{0.99}\text{Fe}_{0.01}$  it splits into two spin states, one moving up in energy and the other down, as shown in part (a) of Fig. 6. A small moment is observed corresponding to the difference in population between the two states, and the scattering begins to increase. A maximum in the scattering should occur when the upper state has its peak at exactly the Fermi energy, as shown in Fig. 6, part (b). This is the situation for  $(\text{Mo}_{0.8}\text{Nb}_{0.2})_{0.99}\text{Fe}_{0.01}$ , where one observes a peak in  $\Delta\rho$ . As the levels continue to split [part (c) of Fig. 6], the scattering decreases while the magnetization continues to increase. This is observed experimentally for the Mo-Re alloys. It appears that the behavior of the resistivity is directly correlated with resonant scattering

from a localized state which is crossing the Fermi surface. The fact that the largest scattering occurs not at the composition where a moment sets in, but rather when the moment has already appeared, indicates that the original unmagnetized level was near the Fermi surface but not coincident with it.

An estimate for the differential resistivity can be obtained using the Friedel<sup>11</sup> sum rule:

$$\Delta\rho = (2\pi c/k) \sum_l (2l+1) \sin^2 \eta_l - 2l \sin \eta_l \sin \eta_{l-1} \cos(\eta_l - \eta_{l-1}), \quad (4)$$

for the case of magnetized states, one of which is completely filled. Here  $c$  is the impurity concentration,  $k$  is the radius of the Fermi sphere,  $(2l+1)$  is the degeneracy of the state, and  $\eta_l$  is the phase shift of the  $l$ th spherical component of the wave function of an electron scattered by an impurity with respect to its phase in the absence of the impurity.<sup>12</sup> This expression is strictly valid only for free electrons in a spherical potential. Assuming a twofold degenerate state (the magnetic moment is measured to be roughly 2 Bohr magnetons), one sets  $(2l+1)$  equal to 2.<sup>13</sup> The  $d$ -state phase-shift  $\eta_2$  is taken to be  $90^\circ$  to correspond to the situation depicted in part (b) of Fig. 6, and all other phase shifts are assumed to be zero. Assuming that only one  $s$  electron per atom contributes to the conductivity, and using

<sup>10</sup> P. W. Anderson, Phys. Rev. **124**, 41 (1961).

<sup>11</sup> J. Friedel, Suppl. Nuovo Cimento **7**, 287 (1958); P. de Faget de Casteljaun and J. Friedel, J. Phys. Radium **17**, 27 (1956); J. Friedel, Can. J. Phys. **34**, 1190 (1956); J. Phys. Radium **23**, 692 (1962).

<sup>12</sup> This formula is expressed in Hartree atomic units where  $e = \hbar = m = 1$ . One atomic unit of resistivity is  $21.8 \mu\Omega\text{-cm}$ .

<sup>13</sup> This is not unreasonable, since the crystal field splits the fivefold degenerate  $d$  state into a threefold and a twofold degenerate state.

for  $k$  its free-electron value, the calculated value for  $\Delta\rho$  is  $4.3 \mu\Omega\text{-cm}$ . This compares quite favorably with the measured value of  $3.6 \mu\Omega\text{-cm}$ , considering the crudity of the assumptions.

The detailed behavior of the resistivity at low temperature is still largely an unsolved problem. No unusual behavior occurs for the nonmagnetic alloys, as expected. A shallow minimum first occurs where a localized moment is just appearing. The anomalous behavior is most pronounced at around  $(\text{Mo}_{0.8}\text{Nb}_{0.2})_{0.99}\text{Fe}_{0.01}$ , which is the composition for which we concluded above that one of the spin states is at the Fermi energy. As the levels in question get further from the Fermi surface, the anomalies persist but become much smaller. Thus, there is no correlation between the size of the moment and the size of the anomaly, but there does appear to be a relation between the former and the appearance of a maximum in the resistivity.

It is interesting to compare the progressive shape of these curves with the behavior observed by Coles<sup>14</sup> for different concentrations of iron in molybdenum. At very low concentrations he found a shallow minimum. For intermediate concentrations there is a minimum and a maximum, and for 1.5% Fe the minimum has disappeared, while there is still a decrease in resistivity at low temperatures. If one were to subtract the phonon and impurity scattering, as was done in the analysis in the present work, one would find a low-temperature rise for low concentrations, and then a maximum would appear which comes at higher temperatures, the higher the iron concentration. This is roughly the behavior of the low-temperature resistivity observed as the host alloy is varied between niobium and rhenium in this experiment.

The existence of resistive anomalies in dilute alloys has been directly related in the present investigation with the appearance of a localized magnetic moment. This is in keeping with the widely accepted view that these anomalies are of magnetic origin.

The Korrington-Gerritsen<sup>15</sup> model which was proposed to account for low-temperature anomalies is inconsistent with the present experiment. The states postulated in their model are several orders of magnitude narrower in energy than the localized states proposed by Wolff<sup>8</sup> and Anderson<sup>10</sup> and could not give as broad a resistive resonance as has been observed in the Nb-Mo-Re system. On the other hand, with a suitable choice of parameters, the Brailsford-Overhauser<sup>16</sup> model can correctly describe the observed temperature dependence of the resistivity. However, measurements are in progress on the resistivity of  $\text{Mo}_{0.8}\text{Nb}_{0.2}$  for different amounts

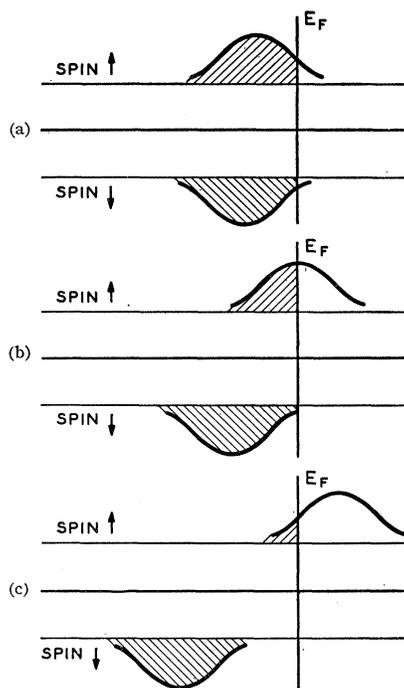


FIG. 6. Schematic diagram of density of states vs energy showing virtual bound states. The humps are the virtual levels, of which the shaded areas are occupied by electrons. (a) State begins to split at  $(\text{Mo}_{0.6}\text{Nb}_{0.4})_{0.99}\text{Fe}_{0.01}$ . (b) Position of levels for maximum scattering at  $(\text{Mo}_{0.8}\text{Nb}_{0.2})_{0.99}\text{Fe}_{0.01}$ . (c) State continues to split. Scattering decreases while magnetization increases, as observed in the Mo-Re alloys.

of iron solute, and preliminary results indicate a linear dependence of the magnetic scattering on concentration. If the iron is indeed in random solid solution, this is in disagreement with the Brailsford-Overhauser model, which predicts a quadratic dependence. Results of resistivity, magnetoresistance, and magnetization measurements on  $(\text{Mo}_{0.8}\text{Nb}_{0.2})_{(1-x)}\text{Fe}_x$  will be published in a later article.

*Note added in proof.* A recent theory by J. Kondo [Progr. Theoret. Phys. (Kyoto) (to be published)] predicts that a minimum exists whenever there is a negative  $s-d$  exchange integral. This theory gives the observed linear dependence on concentration, and apparently gives the correct temperature dependence. I would like to thank Dr. Kondo for sending a preprint of his work prior to publication.

#### ACKNOWLEDGMENTS

The authors wish to thank P. A. Wolff and T. H. Geballe for many valuable discussions. We are particularly indebted to V. Jaccarino for his continued interest and encouragement throughout this project. We would also like to thank B. Cohen for the use of several gallium arsenide thermometers.

<sup>14</sup> B. R. Coles, Phil. Mag. 8, 335 (1963).

<sup>15</sup> J. Korrington and A. M. Gerritsen, Physica 19, 457 (1953).

<sup>16</sup> A. D. Brailsford and A. W. Overhauser, J. Phys. Chem. Solids 15, 140 (1960); Phys. Rev. Letters 3, 331 (1959); Phys. Chem. Solids 21, 127 (1961).