approximation in the theoretical derivation.

In summary, we have observed two-magnon RRS in MnF_2 around the magnon sidebands. The mechanism for the two-magnon RRS is different from that for the nonresonant case. With a given excitation frequency ω_l, it selects a particular set of two-magnon modes to be most strongly resonantly enhanced. Consequently, because of the presence of magnon dispersion, the two-magnon line shifts in frequency as ω_l varies, and two two-magnon lines show up when simultaneous resonance with two magnon sidebands occurs. The resonance enhancement agrees quite well with a simple theoretical description.

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Possibly Mixed Valency of Uranium in $UNi_{5-x}Cu_x$

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This paper reports the lattice constant at room temperature and the susceptibility, specific heat, electrical resistivity, and absolute Seebeck coefficient of compounds $UNi_{5-x}Cu_x$ ($0 \leq x \leq 5$) as a function of temperature. It is suggested that the drastic change in the properties of these compounds when x, increasing from 0, comes into the range of 4 to 5 is caused by a change of the uranium ions from a U^{4+} to a mixed U^{4+}-U^{3+} state.

It is already known from susceptibility (χ) measurements,[1] in the temperature range of 4 to 900 K, and from neutron diffraction data[2] that UCu_5 is an antiferromagnet with a Néel temperature (T_N) of 15 K. It is concluded in Ref. 1 from the approximate Curie-Weiss behavior of χ at temperatures above 400 K that the effective moment (p_{eff}) per uranium equals $3.6\mu_B$, and that the uranium ions are in the U^{4+} ($5f^2$) state. A different conclusion is reached by Brodsky and Bridger,[3] where the data bear upon the susceptibility and resistivity (ρ) of UNi_5 and UCu_5 (2 to 300 K), namely that χ in UCu_5 at $T > T_N$ follows a modified Curie-Weiss law with $p_{eff} \approx 2.3\mu_B$, corresponding to the U^{2+} ($5f^4$) state. For UNi_5, a similar analysis led to $p_{eff} \approx 0.15\mu_B$. Not much different results were obtained on samples either as cast or annealed at 1210 K for 5 days. On the other hand, annealing was reported to have a large influence on ρ-T data obtained on UCu_5.

In this paper it is suggested that in UCu_5 the uranium ions are neither tetravalent nor divalent but mixed tetravalent and trivalent. Indications of a mixed-valency state are derived not only from the lattice constant a of cubic ($AuBe_5$ type) pseudobinary compounds $UNi_{5-x}Cu_x$ ($0 \leq x \leq 5$) but also from the specific heat C_p, ρ, and Seebeck coefficient S. Another indication is the hypersensitivity of ρ of UCu_5 to deviations from stoichiometry and annealing. The choice of the valency states U^{4+} and U^{3+} is based on χ data. The samples investigated, unless stated otherwise, were as cast. They were checked by x-ray analysis to be single phase.

The variation with x of the lattice constant is shown in the inset of Fig. 1. It is seen that for values of x up to 3 the increase of a proceeds linearly, while there is an additional increase of a for $x > 3$. The increase of the unit-cell volume when going from UNi_5 to UCu_5 amounts to 11.2%.

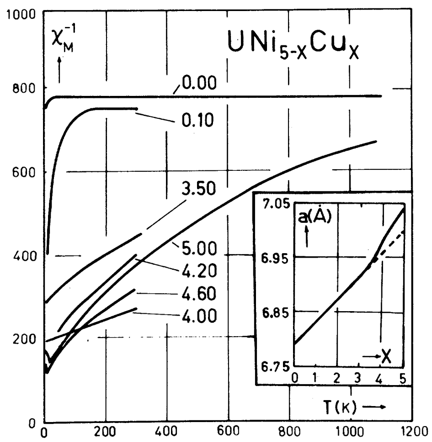

FIG. 1. The reciprocal susceptibility per mole of $UNi_{5-x}Cu_x$ compounds as a function of temperature. The inset shows the lattice constant as a function of x.

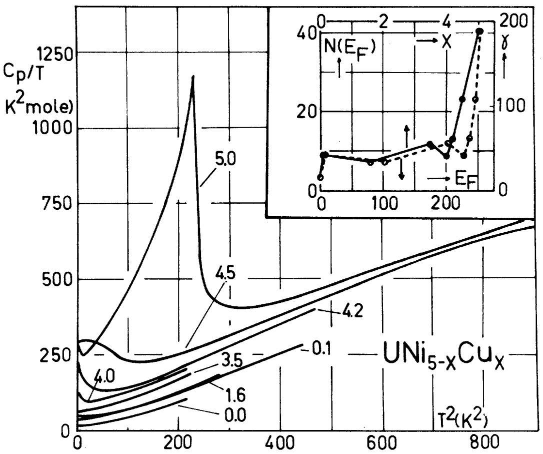

FIG. 2. The specific heat, plotted as C_p/T versus T^2, for compounds $UNi_{5-x}Cu_x$. The inset shows the density of states $N(E_F)$ [(eV mole)$^{-1}$] and the electronic-specific-heat coefficient γ (mJ/mole K^2) as a function of x and of the Fermi energy E_F in meV. Errors in γ are too large to take the fine structure in the schematic curves of the inset seriously.

This is somewhat larger than the corresponding increase of 9.3% obtained in going from $GdNi_5$ to $GdCu_5$. Gadolinium has about the same metallic radius as uranium but does not give rise to a valency change. The extra increase of the lattice constant of compounds $UNi_{5-x}Cu_x$ for $x > 4$ is considered to be indicative of a partial decrease in valency of the uranium ions.

The susceptibility of UNi_5, when disregarding impurity effects at very low temperatures, is in our experimental result perfectly constant up to the highest temperature measured (1100 K, see Fig. 1). This strongly suggests that χ in UNi_5 is dominated by Van Vleck paramagnetism of uranium ions with an even quantum number J for which crystal-field splitting has led to a nonmagnetic ground state. Evidently, the energy distance between the ground state and the lowest magnetic state is large compared to 1100 K. An appreciable contribution to χ of the nickel atoms apparently is absent because of sufficient filling of the nickel $3d$ band. The obvious choice of the valency state of uranium in UNi_5 compatible with the χ data obtained on UNi_5 and with the proposed partial decrease in valency of uranium in the series $UNi_{5-x}Cu_x$, when going from UNi_5 to UCu_5, is the tetravalent state. The transition from nonmagnetic UNi_5 to magnetic UCu_5 then arises from the appearance of U^{3+} ions which have a magnetic ground state for any crystal field (Kramers ions). The antiferromagnetic ordering in UCu_5 implies that the fluctuation frequency of the U^{4+}-U^{3+} mixed-valency state[4] is of the order of kT_N with $T_N \approx 15$ K. An analysis of the paramagnetic susceptibility of UCu_5 on the basis of a mixed-valency state subject to large crystal fields cannot be given because an adequate theory apparently is not available. The validity of the Curie-Weiss analysis presented in Ref. 1 is doubted because it implies a negative asymptotic Curie temperature with a magnitude as high as 700 K. The conclusion drawn in Ref. 3 with regard to the valency of uranium does not seem unambiguous because, e.g., also U^{3+} in large crystal fields with either the doublet Γ_6 or the quartet $\Gamma_8{}^1$ as the ground state leads to an apparent effective moment of about $2.3\mu_B$.

The specific heat of compounds with $0 \leq x < 4$ (see Fig. 2) is characterized by lattice coefficients α of the order of 0.3 mJ/mole K^4 and electronic coefficients γ of the order of 40 mJ/mole K^2. These parameters have much the same values as encountered for the RNi_5 compounds with R = La, Ce, and Pr.[5] We suggest that the values of γ in $UNi_{5-x}Cu_x$ ($0 \leq x < 4$) and in RNi_5 are not determined by localized $5f$ and $4f$ electronic states, respectively, which overlap with the Fermi level, but by an almost filled Ni $3d$ band. This suggestion is supported by the fact that the γ values per gram atom of Ni, which are a factor of about 5 smaller than those derived per mole of the compounds, come close to that found for various Ni alloys. In Fig. 2 the γ values have been converted into values for the density of band states at the Fermi level $N(E_F)$ for one spin orientation. The x scale has been regauged approximately in an energy scale. This has been done on the supposition that substitution of one Cu for one Ni in UNi_5 results in an increase of the valence-electron concentration of one electron per formula unit. One arrives at an approximate bandwidth corresponding to the interval $0<x<4$ of about 0.25 eV.

For compounds with $4 \lesssim x \leqslant 5$, the acquisition of γ values from the C_p data is seriously hampered by the occurrence of two types of anomalies. In UCu_5, one of these anomalies is the λ-type peak, marking the Néel temperature at 15.2 K. It may be remarked that the entropy developed in the magnetic transition appears to have the abnormally low value of $0.59R\ln 2$ per mole. The other anomaly is the upturn of C_p/T versus T^2 at low temperatures. This latter anomaly is probably the onset of a Schottky-type peak, at a temperature of the order of 0.5 K, due to the hyperfine splitting of the uranium nuclear-ground-state multiplet in the presence of magnetic ordering (see Shenoy *et al.*[6] for the hyperfine fields in similar compounds). For the compounds with $4 \leqslant x < 5$ the contribution of the two anomalies to C_p has not been resolved. A reasonable approach to obtain approximate values for γ is the following: Assume that the lattice contribution to C_p at finite temperature is almost equal for all compounds. In a C_p/T-versus-T^2 plot this implies the same shape of the nonanomalous part for all curves. Simple translation of a "normal" curve (e.g., $x = 0.1$) delivers γ values for all compositions. These values of γ, given in Fig. 2, are obviously subject to large errors. However, with x increasing from 4 to 5, the tendency towards high γ values is, in our opinion, a real effect, although the error in the individual γ values may be large ($\sim 20\%$). The corresponding rise of $N(E_F)$ takes place in a narrow energy interval of 25 meV. We consider this rise of $N(E_F)$ indicative of a mixed-valency state of the uranium ions. In such a mixed state the excitation energy (E_{exc}) between the two ionic states approaches a value of the order of the width Δ of a virtual bound state, which becomes situated close to the Fermi level and gives occasion to very high values of $N(E_F)$.[4,7] Also the too-low entropy developed in the antiferromagnetic transition in UCu_5 could be a consequence of the mixed-valency state of the uraniums.

The data obtained for ρ of a number of compounds, after correction for lattice-scattering

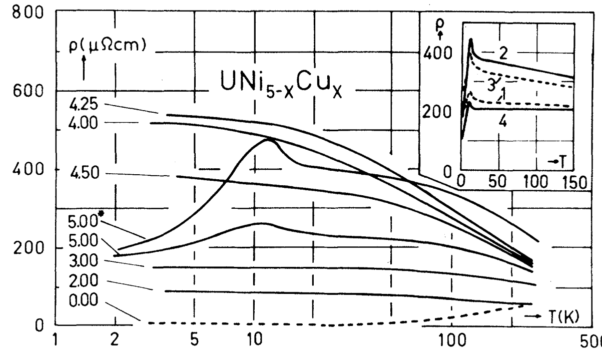

FIG. 3. The resistivity ρ of as-cast samples of $UNi_{5-x}Cu_x$ ($x>0$) as a function of $\log_{10}T$, corrected for the term $\rho(T)-\rho(0)$ obtained on UNi_5 (broken line). For UCu_5, the results after annealing at 850°C for 1 week are marked with an asterisk. The inset demonstrates the effect of annealing and of deviation from stoichiometry on ρ ($\mu\Omega$ cm) versus T (K): curve 1, UCu_5 as cast; curve 2, UCu_5 annealed at 850°C for 1 week; curve 3, $UCu_{4.9}$ as cast; curve 4, $UCu_{5.1}$ as cast.

effects, are presented in Fig. 3 as a function of $\log_{10}T$. The correction is obtained by subtraction of the quantity $\rho(T)-\rho(0)$ measured on UNi_5 (broken line). In compounds with $0 \leqslant x < 4$, ρ behaves more or less as expected for a metal with a relatively large value of $N(E_F)$. The ρ behavior of compounds with $x = 4.00$, 4.25, and 4.50 bears resemblance to the Kondo resistivity of dilute transition-metal alloys.[8] At low temperatures $\rho \propto 1 - (T/T^*)^2$, where $T^* \approx 30$ K, while at higher temperatures $\rho \propto -\log_{10}T$. The Kondo temperature T_K is estimated to be of the order of 100 K. Such a Kondo-like behavior of the resistivity would not be expected if either U^{4+} or U^{3+} ions, magnetically equivalent to Pr^{3+} or Nd^{3+}, respectively, were the carriers of a well-localized magnetic moment. It rather points to the occurrence of a mixed-valency state of the uranium ions which inherently invokes a Kondo effect with $T_K \approx T_F \exp(-E_{exc}/\Delta)$, where kT_F is the Fermi energy.[7]

The sensitivity of ρ to deviations from stoichiometry and to annealing is demonstrated in the inset of Fig. 3. Furthermore, it has been found that $\rho(300\text{ K})$ of as-cast $UCu_{5.1}$ *increases* by 20% and of as-cast $UCu_{4.9}$ *decreases* by 15% upon annealing. A possible explanation of the discrepancy between our results and those given in Ref. 3, for ρ of the as-cast UCu_5 sample and also of the effect of annealing on ρ, could be that our sample has a small excess whereas the sample of Ref. 3 a small deficiency of copper. It is conceivable that the mentioned deviations from stoichi-

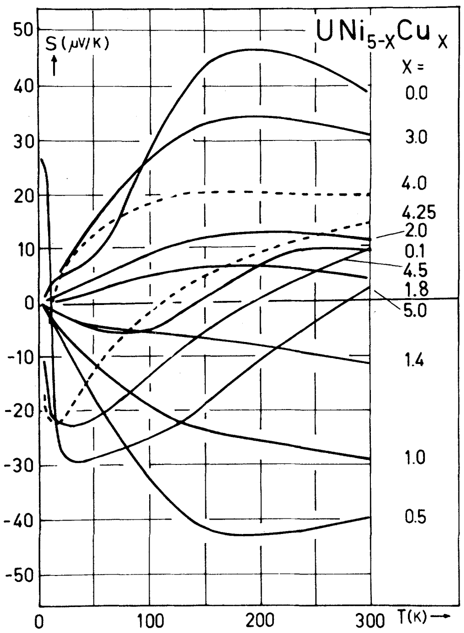

FIG. 4. The absolute Seebeck coefficient of compounds $UNi_{5-x}Cu_x$ as a function of temperature.

ometry introduce different internal pressures which are modified by annealing. These internal pressures change the U^{4+}-U^{3+} ratio in the mixed state, thereby influencing largely the magnitude of the resistivity. A further study is needed to clarify the situation.

S-versus-T behavior of the various compounds differs quite markedly (Fig. 4). In all compounds with $0 \leq x < 4$, except for UNi_5, S is linear in T at low temperatures. This suggests that the diffusion term in S dominates. A phonon-drag term in S probably is dominant only in UNi_5 at low temperatures, while in the other compounds it is evidently suppressed by the alloying effect.[9] The low-temperature ($T < 100$ K) behavior of S, governed by degenerate statistics, can be shown to agree reasonably with the variation of $N(E_F)$, derived from the electronic-specific-heat data (Fig. 2). This is because the diffusion term in S due to electrons residing in a broad s band and scattered predominantly to a narrow d band is in first approximation linear in T with a coefficient proportional to the first specific-energy derivative of $N(E_F)$. S-versus-T behavior in the second group of compounds ($4 \leq x \leq 5$) is quite different. The marked oscillation of S in UCu_5 from high positive to high negative values in a small temperature interval around about 11 K is probably connected with antiferromagnetic ordering. The large negative peaks of S versus T in all compounds (except for $x = 4.00$) in the range $15 \text{ K} \lesssim T_s \lesssim 35$ K are typical of a Kondo thermopower, with $T_s \lesssim T_K$, in the presence of a positive impurity potential.[8] It can be argued, just as done for the case of ρ, that such a behavior is consistent with the presence of a uranium mixed-valency state.

In summary, it is suggested in this paper that a change in composition of compounds $UNi_{5-x}Cu_x$ from $x = 0$ to $x = 5$ leads to a transition from a U^{4+} to a mixed U^{4+}-U^{3+} state. This mixed-valency state possibly lies at the origin of the anomalies observed in the Cu-rich compounds: an extra increase in lattice constant, an extremely high electronic specific heat, a resistivity varying in the paramagnetic range in proportion to $\log_{10} T$ at high temperatures and to $1 - (T/T^*)^2$ at low temperatures and being extremely sensitive to deviations from stoichiometry, and, finally, a Seebeck coefficient showing large negative peaks at low temperature.

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