# Neutron diffraction and ac-susceptibility studies of $U(Ni_{0.1}Cu_{0.9})_2Ge_2$

Moshe Kuznietz, Haim Pinto, Hanania Ettedgui, and Mordechai Melamud
*Nuclear Research Centre–Negev, P.O. Box 9001, 84 190 Beer-Sheva, Israel*
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Polycrystalline samples of the solid solution $U(Ni_{0.1}Cu_{0.9})_2Ge_2$ have been investigated by neutron diffraction and ac susceptibility. This material exhibits the tetragonal $ThCr_2Si_2$-type crystallographic structure. It orders ferromagnetically at $T_C=115\pm5$ K, undergoing another transition at $T_0=100\pm5$ K to a ferrimagnetic phase with a wave vector $\mathbf{k}=(0,0,\frac{2}{3})$ and with $(++-)$ stacking of ferromagnetic planes of uranium magnetic moments [$(1.9\pm0.2)\mu_B$ at 10 K] along the tetragonal axis. The magnetic properties of $U(Ni_{0.1}Cu_{0.9})_2Ge_2$ are discussed in reference to the tentative magnetic phase diagram (temperature versus composition) of the $U(Ni_{1-x}Cu_x)_2Ge_2$ system.

## I. INTRODUCTION

In recent years we have been engaged in the study of magnetic ordering in $UM_2Ge_2$ compounds and $U(M,M')_2Ge_2$ solid solutions ($M,M'$=Co, Ni, Cu) by neutron diffraction, supported by ac-susceptibility measurements.[1–4] We have already studied the compound $UCo_2Ge_2$ (Refs. 1 and 2), the system $U(Co,Cu)_2Ge_2$ (Ref. 3), and the solid solutions $UNiCuGe_2$ and $UCoNiGe_2$ (Ref. 4). All materials investigated ($UCoNiGe_2$ excepted[4]) show the common tetragonal crystallographic structure, of the $ThCr_2Si_2$ type, with space group $I4/mmm$ ($D_{4h}^{17}$), and two formula units per unit cell.

We have recently extended our previous studies of $UCu_2Ge_2$ (Ref. 3) and $UNiCuGe_2$ (Ref. 4) to the system of $U(Ni_{1-x}Cu_x)_2Ge_2$ solid solutions, formed between the compounds $UNi_2Ge_2$ and $UCu_2Ge_2$.

$UNi_2Ge_2$, studied by neutron diffraction, was reported[5] to order antiferromagnetically below $T_N=80$ K with a wave vector $\mathbf{k}=(0,0,1)$ and magnetic moments along the tetragonal axis (AF-I).

$UCu_2Ge_2$, studied by neutron diffraction, was reported[5,6] to order ferromagnetically below $T_C=100$ K, transforming at $T_0=25$–$40$ K to an antiferromagnetic (AF) phase with a wave vector $\mathbf{k}=(0,0,0,5)$, and magnetic moments along the tetragonal axis (AF-IA). The transition at $T_0$ was observed once more in high-field magnetization,[7] but not in zero-field electrical resistivity measurements.[7] The ferromagnetic transition was observed at $T_C=107$ K in our ac-susceptibility and neutron-diffraction study.[3] However, the transition at $T_0$, requiring the appearance of superlattice lines, was not observed in our zero-field neutron-diffraction study.[3] $UNiCuGe_2$, studied by us using neutron diffraction,[4] was found to order antiferromagnetically below $T_N=140$ K with the AF-I structure.

A short report on the magnetic phase diagram of the $U(Ni_{1-x}Cu_x)_2Ge_2$ system has recently been published.[8] We report here the full results obtained for the solid solution $U(Ni_{0.1}Cu_{0.9})_2Ge_2$.

## II. EXPERIMENTAL DETAILS

A polycrystalline sample of the solid solution $U(Ni_{0.1}Cu_{0.9})_2Ge_2$ was prepared by arc-melting of stoichiometric amounts of the constituents in argon atmosphere. The obtained buttons were annealed at 750 °C in vacuum for 120 h. Following the annealing, the buttons were crushed into fine powders and examined by x-ray diffraction at room temperature (295 K). The solid solution prepared exhibits a major $ThCr_2Si_2$-type phase, and minority ($<1\%$) impurity phases.

Neutron- ($\lambda=2.45$Å) diffraction measurements were done with the KANDI-II diffractometer at the IRR-2 reactor, using a 20-g sample in cylindrical aluminum container. The measurements were performed in a Displex closed-cycle helium cooler made by Air Products Inc. at room temperature (RT) and low temperatures (LT) down to 10 K. Data was taken up to $2\Theta=105°$. In Fig. 1 the data up to 56° are shown.

ac-susceptibility measurements, in the 80–300 K temperature range, were done on a 0.62-g sample. The ac magnetic field was rather weak (1–10 Oe). Calibration of the ac-susceptibility values was done with a 300-mg polycrystalline sample of $Gd_2O_3$ for which the $\chi_M$ value at 293 K is $51\,000\times10^{-6}$ emu/mol (with $\Theta=-15$ K and $\mu_{\rm eff}=7.9\mu_B$).

## III. RESULTS

### A. Neutron diffraction

The RT neutron diffractogram of $U(Ni_{0.1}Cu_{0.9})_2Ge_2$ contains $\{hkl\}$ reflections with $h+k+l$=even. The RT lattice parameters of $U(Ni_{0.1}Cu_{0.9})_2Ge_2$, obtained from the neutron- and x-ray-diffraction measurements, and the RT fitted position parameter of the germanium atom, from the neutron measurements, are $a=4.060\pm0.010$Å, $c=10.150\pm0.020$Å, $z=0.379\pm0.001$. The LT fitted position parameter of the germanium atom ($0.378\pm0.001$) falls within the error of the respective RT value.

The LT neutron diffractogram (at 10 K) of

 

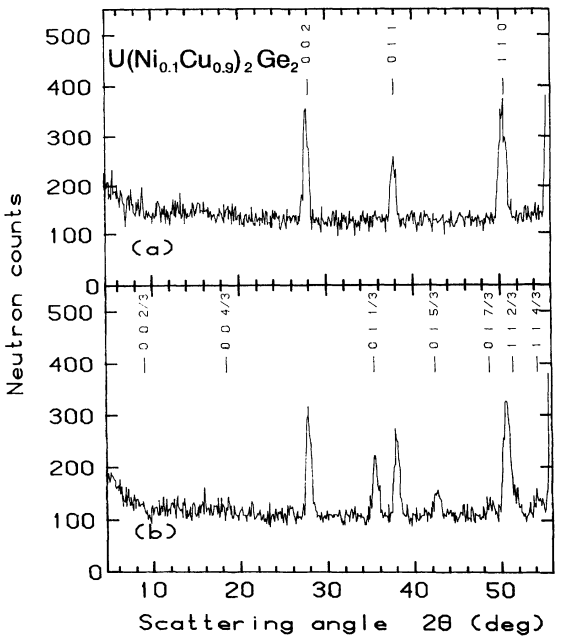


FIG. 1. Neutron- ($\lambda=2.45$Å) diffraction patterns of a polycrystalline sample of $U(Ni_{0.1}Cu_{0.9})_2Ge_2$. For clarity, only data up to $2\Theta=56°$ is shown: (a) at 295 K indicating a $ThCr_2Si_2$-type single phase; (b) at 10 K showing satellite magnetic reflections at $\{hk(l\pm\frac{2}{3})\}$ positions around nuclear $\{hkl\}$ reflections and absence of $\{00(l\pm\frac{2}{3})\}$ reflections.

$U(Ni_{0.1}Cu_{0.9})_2Ge_2$ [Fig. 1(b)] shows superlattice reflections which can be indexed as $\{hk(l\pm\frac{2}{3})\}$ satellites of the RT nuclear $\{hkl\}$ reflections. We observe clearly the two satellites $\{01\frac{1}{3}\}$ and $\{01\frac{5}{3}\}$ around the nuclear $\{011\}$ reflection, the single sattellite $\{11\frac{2}{3}\}$ of the nuclear $\{110\}$ reflection, and only the lower-scattering-angle satellites $\{01\frac{7}{3}\}$ and $\{11\frac{4}{3}\}$ of the nuclear $\{013\}$ and $\{112\}$ reflections, respectively. These additional reflections at LT correspond to a wave vector $\mathbf{k}=(0,0,\frac{2}{3})$ and $++-$ ferrimagnetic stacking along the tetragonal axis of ferromagnetic layers of uranium moments. The absence of $\{00(l\pm\frac{2}{3})\}$ reflections indicates that the ordered magnetic moments are along the tetragonal axis.

A least-squares analysis has been applied to the neutron-diffraction data, fitting the RT reflections (as well as LT nuclear reflections) to the $ThCr_2Si_2$-type crystallographic structure ($I4/mmm$ space-group symmetry), and the LT superlattice magnetic reflections to the squared-up ferrimagnetic $++-$ structure, corresponding to a wave vector $\mathbf{k}=(0,0,\frac{2}{3})$. The observed integrated and calculated intensities in the RT and LT neutron diffractograms up to 105° of $U(Ni_{0.1}Cu_{0.9})_2Ge_2$ are listed in Table I. The calculated residuals, $R$, are 3.5 and 4.3 %, for the RT and LT least-squares fits, respectively. $R$ is defined by

$$R=100\left\{\left[\sum\left[\frac{I_{\rm obs}-I_{\rm calc}}{\sigma}\right]^2\right]\Big/\left[\sum\left[\frac{I_{\rm obs}}{\sigma}\right]^2\right]\right\}^{1/2}, \quad (1)$$

where $\sigma$ is the experimental error in $I_{\rm obs}$, and the summations are over all observed reflections.

From the integrated intensities of the additional magnetic reflections we derive the value $(1.9\pm0.2)\mu_B$ for the uranium-ordered magnetic moment at 10 K, as described in Ref. 1. This moment value is comparable with the moment values in other $U(Ni_{1-x}Cu_x)_2Ge_2$ solid solutions.[8]

Temperature dependence of the total integrated intensity of the magnetic $\{01\frac{1}{3}\}$ reflection, shown in Fig. 2, as well as of the magnetic $\{01\frac{5}{3}\}$ reflection (not shown), indicate that the ferrimagnetism disappears at $T_0=100\pm5$ K, and that the ferrimagnetic structure is of the same type $(++-)$ up to this transition.

In the temperature range 95–115 K, the ac-susceptibility measurements indicate ferromagnetism (see Sec. III B). Because of the small ordered moment in this range, close to $T_C$, our neutron measurements are not sensitive enough to detect such ferromagnetism. The slight increase in the intensity above 100 K is due to the rise in background in the paramagnetic phase. Also shown in Fig. 2 is the temperature variation of the U sublatice ordered moment in the ferrimagnetic phase.

### B. ac susceptibility

The temperature dependence of $\chi_M$, the molar ac susceptibility, at 80–300 K in a polycrystalline sample of $U(Ni_{0.1}Cu_{0.9})_2Ge_2$, is plotted in Fig. 3. The $\chi_M$ value at RT, $4600\times10^{-6}$ emu/mol, is comparable to the $\chi_M$ values at RT in other $U(Ni_{1-x}Cu_x)_2Ge_2$ solid solutions.[8] Two sharp susceptibility peaks, with $\chi_M$ values of $60\,800\times10^{-6}$ emu/mol at $T_C=115\pm5$ K and, $39\,700\times10^{-6}$ emu/mol at $T_0=95\pm5$ K, are observed, corresponding to the onset of a ferromagnetic phase and the transition to a ferrimagnetic phase ($++-$, discussed above), respectively. The transition at $T_0$ is consistent (within experimental error) with the transition observed by neutron diffraction, as the temperature for the disappearance of the magnetic $\{01\frac{1}{3}\}$ reflection (Fig. 2).

Also shown in Fig. 3 is the inverse susceptibility of $U(Ni_{0.1}Cu_{0.9})_2Ge_2$ in the paramagnetic state. An almost

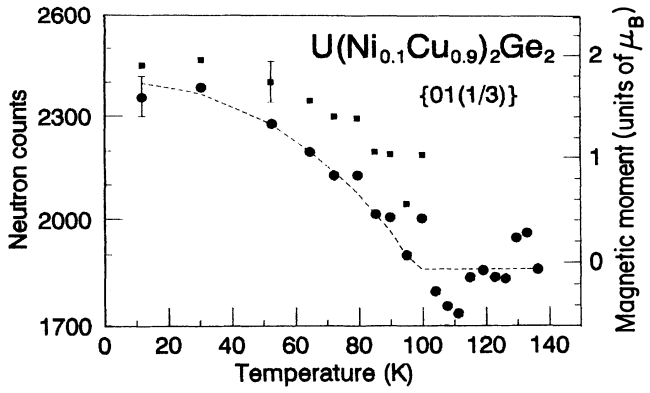


FIG. 2. Temperature dependence of the integrated intensity of the magnetic $\{01\frac{1}{3}\}$ reflection in a polycrystalline sample of $U(Ni_{0.1}Cu_{0.9})_2Ge_2$, indicating $T_0=100\pm5$ K. Each data point (circles) is an average of three consecutive scans of the $\{01\frac{1}{3}\}$ reflection, taken at increasing temperatures. The dashed line is a guide to the eye. Also shown is the deduced U sublattice magnetic moment (squares).

straight line is obtained, of which the linear part above 200 K intersects with the temperature axis at $\Theta$, the paramagnetic Curie temperature. The value obtained, $\Theta=(+90)-(+100)$ K, is close to $T_C$, indicating ferro-ferrimagnetic order.

The effective paramagnetic moment, $\mu_{\text{eff}}$, is obtained (in $\mu_B$, Bohr magnetons) from the linear part of the inverse-susceptibility curve via the relation

$$\mu_{\text{eff}}=2.83[(T-\Theta)\chi_M(T)]^{1/2}\ , \tag{2}$$

where $\chi_M$ is given in emu/mol and $(T-\Theta)$ is given in K. With the measured molar susceptibility at RT (293 K) and the respective value of $\Theta$, a value of $\mu_{\text{eff}}=(2.7\pm0.2)\mu_B$ is obtained, which is comparable to the $\mu_{\text{eff}}$ values in other $U(Ni_{1-x}Cu_x)_2Ge_2$ solid solutions.[8]

## IV. DISCUSSION

$U(Ni_{0.1}Cu_{0.9})_2Ge_2$ exhibits the $ThCr_2Si_2$-type crystallographic structure ($I4/mmm$ symmetry) characteristic of

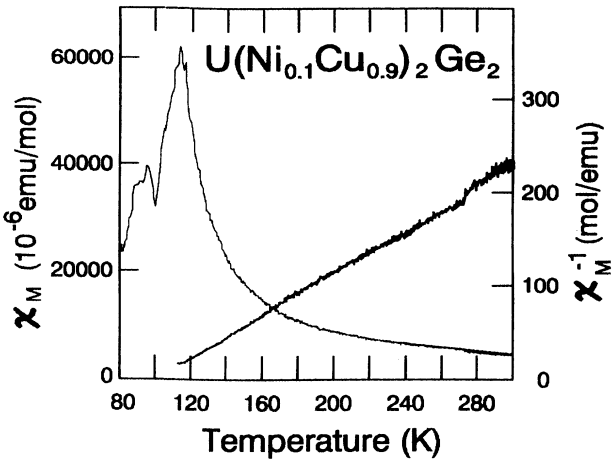


FIG. 3. Temperature dependence of the molar ac susceptibility (at 80–300 K, thin curve) and its inverse (in the paramagnetic state, thick curve) in a polycrystalline sample of $U(Ni_{0.1}Cu_{0.9})_2Ge_2$.

TABLE I. Observed integrated and calculated intensities in the neutron-diffraction spectra of polycrystalline $U(Ni_{0.1}Cu_{0.9})_2Ge_2$ at room temperature (RT) and low temperature (LT) up to $2\Theta=105°$. The calculated residuals [Eq. (1)] are $R=3.5$ and 4.3 % for the RT and LT least-squares fits, respectively.

| $\{hkl\}$ | RT intensities | | LT (10 K) intensities | | |
|---|---|---|---|---|---|
| | $I_{\text{obs}}$ | $I_{\text{calc}}$ | $I_{\text{obs}}$ | $I_{\text{calc}}$ Nuclear | $I_{\text{calc}}$ Magnetic |
| $00\frac{2}{3}$ | | | 0 | | 0 |
| $00\frac{4}{3}$ | | | 0 | | 0 |
| 002 | 1 157± 61 | 1 333 | 1 305± 73 | 1 631 | 0 |
| $01\frac{1}{3}$ | | | 835±92 | | 872 |
| $00\frac{8}{3}$ | | | 0 | | 0 |
| 011 | 661± 57 | 777 | 1 010±80 | 910 | 165 |
| $01\frac{5}{3}$ | | | 418±69 | | 412 |
| $00\frac{10}{3}$ | | | 0 | | 0 |
| $01\frac{7}{3}$ | | | 148±47 | | 234 |
| 110<br>$11\frac{2}{3}$ | 1 646±82 | 1 515 | 2 353±99 | 1 806 | 420 |
| $11\frac{4}{3}$ | | | 371±88 | | 297 |
| 013 | 11 761±128 | 11 696 | 14 126±140 | 14 177 | 32 |
| 004<br>112 | 19 570±157 | 19 309 | 23 582±180 | 23 009 | 53 |
| $02\frac{4}{3}$ | | | 310±68 | | 135 |
| 114<br>022 | 10 751±162 | 11 265 | 13 557±175 | 13 696 | 43 |
| 015<br>$12\frac{1}{3}$<br>$02\frac{8}{3}$<br>121 | 7 832±150 | 8 166 | 9 428±151 | 9 827 | 377 |
| $12\frac{5}{3}$<br>$11\frac{14}{3}$<br>006<br>$02\frac{10}{3}$<br>$12\frac{7}{3}$<br>$01\frac{17}{3}$ | 903±264 | 379 | 1 568±233 | 443 | 492 |
| 123<br>$11\frac{16}{3}$<br>024 | 12 122±203 | 11 592 | 14 910±208 | 14 276 | 68 |

most $U(M,M')_2Ge_2$ solid solutions. It orders ferromagnetically at $T_C=115\pm5$ K, as indicated by the rather high ac-susceptibility peak at this temperature. It undergoes another transition, at $T_0=95\pm5$ K, to a ferrimagnetic phase, as indicated by a second, lower $\chi_M$ peak, at that temperature, which corresponds (within experimental error) to the appearance of magnetic reflections in the LT neutron diffractogram (Figs. 1 and 2) at $100\pm5$ K. The low background observed in the neutron measurements in the temperature range 100–115 K (Fig. 2) can be attributed to the appearance of the ferromagnetic phase indicated by the additional transition observed at 115 K in the $\chi_M$ (Fig. 3). Since this ferromagnetic phase is not fully developed, the moment in the range 110–115 K is small, and the intensity contributed by it to the nuclear neutron reflections is too small to be detected in our measurements. The higher background above 115 K is an indication of the disappearance of all magnetic order.

The magnetic reflections in the LT diffractogram correspond to a wave vector $\mathbf{k}=(0,0,\frac{2}{3})$ and $++-$ stacking of ferromagnetic planes of uranium magnetic moments ($1.9\pm0.2\mu_B$ at 10 K), aligned along the tetragonal axis. Indeed, in all the magnetic $UM_2X_2$ (or $LM_2X_2$) compounds ($X$=Si or Ge), studied hitherto, only the uranium (or lanthanide) sublattices have been found to carry ordered magnetic moments (see Ref. 1).

The additional LT magnetic reflections can also be fitted to a longitudinal-spin-density wave (LSDW) with the same wave vector as above, i.e., $\mathbf{k}=(0,0,\frac{2}{3})$. In this magnetic structure the total magnetic moment of every three subsequent uranium planes is zero. Therefore, the total moment of the sample in this interpretation is zero, contrary to the ferrimagnetism observed in our ac-susceptibility data above 80 K. However, only LT magnetization (or other measurements), determining the total moment of the sample (at 10 K), can decide between the LSDW (zero moment) and the square-wave modulated-ferrimagnetic $++-$ structure ($\frac{1}{3}$ of the uranium moment).

Another possibility of interpretation is fitting the LT data with a LSDW with a wave vector $\mathbf{k}=(0,0,\frac{2}{3})$ plus a ferromagnetic component, contributing magnetic intensity to the nuclear reflections. When the ferromagnetic component is $\frac{1}{4}$ of the LSDW amplitude, this structure coincides with the above squared-up ferrimagnetic $++-$ structure. However, the calculated magnetic contributions to the LT nuclear reflections (Table I) are in the order of magnitude of the experimental error in our LT nuclear intensities, so that unique assignment of the magnetic structure cannot be done.

The ferrimagnetic $++-$ structure is quite interesting. The second-order harmonics of the magnetic satellites $\{hk(l\pm\frac{2}{3}\}$ of nuclear $\{hkl\}$ reflections coincide with the first-order harmonics, i.e., the magnetic satellites themselves. The third-order harmonics coincide with other permitted nuclear reflections, $\{hk(l\pm2)\}$. This is an inherent property of the body-centered structure, such as the $ThCr_2Si_2$-type structure, which prevents clear distinction between the LSDW and squared-up structures.

Similar ferrimagnetic structure was found in the LT phase (below 53 K) of the related compound $UNi_2Si_2$ by neutron-diffraction studies of polycrystalline[5] and single-crystal[9] samples. In the single-crystal study of Lin *et al.*,[9] the two interpretations, square-wave modulated-ferrimagnetic ($++-$) structure and LSDW plus ferromagnetic component, are suggested, without any preference.

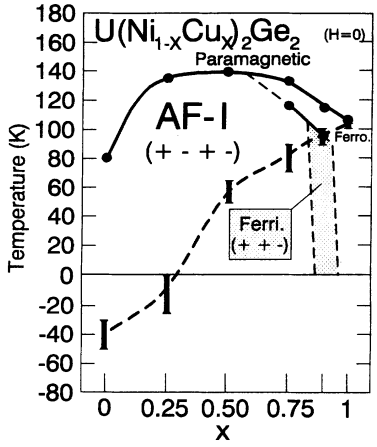


FIG. 4. Variation with the copper content ($\times$), of the paramagnetic Curie temperature, $\Theta$ (dashed line), and the magnetic transition temperatures (solid line) in the $U(Ni_{1-x}Cu_x)_2Ge_2$ system at zero magnetic field. The oscillatory variations are characteristic of a RKKY-type behavior.

In magnetic materials the LT magnetic phase is generally more ferromagnetic or ferrimagnetic with respect to the higher-temperature (HT) phases. This is not the case for $U(Ni_{0.1}Cu_{0.9})_2Ge_2$ in which the HT phase is ferromagnetic while the LT phase is ferrimagnetic ($++-$), or even for $U(Ni_{0.25}Cu_{0.75})_2Ge_2$, where the HT phase is ferromagnetic and the LT phase is AF-I.[8] In the related compound $UNi_2Si_2$, where the $++-$ ferrimagnetic phase is observed at LT,[9] the situation is the common one, with the HT AF-I phase rather than ferromagnetic or ferrimagnetic.

The ferrimagnetic $++-$ structure is derived from the ferromagnetic structure by reversing the moment direction of every third ferromagnetic plane, thereby leaving only $\frac{1}{3}$ of the bulk moment for the magnetization. The AF-I structure, on the other hand, is derived from the ferromagnetic structure by reversing the moment direction on each alternative ferromagnetic plane, leaving zero bulk moment for the magnetization.

The magnetic results obtained for $U(Ni_{0.1}Cu_{0.9})_2Ge_2$ fit well with the results in the other $U(Ni_{1-x}Cu_x)_2Ge_2$ solid solutions.[8] As seen from Fig. 4, the present result for $\Theta$ further emphasizes the oscillatory nature of the function $\Theta(x)$, representing Ruderman-Kittel-Kasuya-Yosida (RKKY) -type behavior. In addition, the variation of the magnetic structure in the magnetic phase diagram (temperature versus composition) becomes even more pronounced with the observation of the $++-$ ferrimagnetic

phase around $x = 0.90$. The different magnetic structures (AF-I and ferromagnetic) at LT for neighboring solid solutions are additional characteristics of a RKKY-type behavior.


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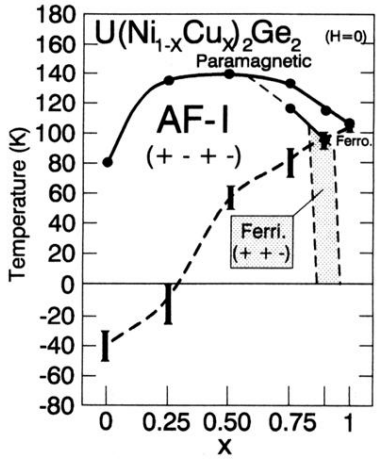


FIG. 4. Variation with the copper content ($\times$), of the paramagnetic Curie temperature, $\Theta$ (dashed line), and the magnetic transition temperatures (solid line) in the $U(Ni_{1-x}Cu_x)_2Ge_2$ system at zero magnetic field. The oscillatory variations are characteristic of a RKKY-type behavior.