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Critical evaluation of Eu valences from L_{III}-edge x-ray-absorption and Mössbauer spectroscopy of $EuNi_2Si_{2-x}Ge_x$

G. Wortmann,* I. Nowik,† B. Perscheid,‡ and G. Kaindl
Institut für Experimentalphysik, Freie Universität Berlin, D-1000 Berlin 33, Germany

I. Felner
Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem, Israel

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In the quasiternary $EuNi_2Si_{2-x}Ge_x$ system most of the Eu ions exhibit an intermediate-valence character, depending on the number of Si neighbors and the temperature. A detailed study of $EuNi_2Si_{0.5}Ge_{1.5}$ by Eu L_{III} x-ray-absorption and ^{151}Eu Mössbauer spectroscopy reveals a sharp temperature-induced valence change, which is more complete than in any other Eu system. A linear correlation between the mean Eu valence, $v(L_{\text{III}})$, derived from L_{III}-edge measurements, and the mean Mössbauer isomer shift is only observed if a variation of the recoil-free fraction at the different Eu sites is taken into account. The Eu L_{III} spectra of $EuNi_2Ge_2$, in which the Eu is divalent according to Mössbauer and magnetization measurements, result in $v(L_{\text{III}})=2.15$, which is similar to other divalent intermetallic Eu systems. This observation is attributed to final-state effects due to covalency. The magnetic susceptibility of $EuNi_2Si_{0.5}Ge_{1.5}$ is in accord with the intermediate-valence character of this compound, which orders ferromagnetically at 25 K.

I. INTRODUCTION

Several of the rare-earth intermetallic compounds RM_2X_2 ($M=$ transition metal, $X=$Si, Ge, or P), which crystallize in the $ThCr_2Si_2$ tetragonal structure, exhibit intermediate-valence phenomena of Eu (Refs. 1–7), Yb (Ref. 8), and Ce (Ref. 9). $EuCu_2Si_2$ was the first compound of this family found to undergo a temperature- and pressure-induced valence phase transition.[1,10] Later it was found that also $EuPd_2Si_2$ (Ref. 2), $EuNi_2P_2$ (Ref. 3), and $EuIr_2Si_2$ (Ref. 4) are in an intermediate-valence state. $EuPd_2Si_2$ experiences a quite sharp temperature-induced change in valence v, by $\Delta v=0.4$, which was interpreted as a cooperative phenomenon.[11] It was further realized that many of the $EuM_2Si_{2-x}Ge_x$ compounds exhibit intermediate-valence phenomena of Eu.[5–7] There is now a strong indication that practically all $EuM_2Si_{2-x}Ge_x$ compounds, for which Eu is divalent for $x=0$ and trivalent for $x=2$, are mixed-valence and sometimes also intermediate-valence compounds for intermediate values of x. The concepts of mixed valence and intermediate valence are the heterogeneous and homogeneous valences defined in Ref. 5.

In a previous article[12] it was shown that two stable Eu valences are present in $EuCo_2Si_{2-x}Ge_x$ for all x values and at all temperatures, with considerable differences in the recoil-free fraction of the two ions. In this paper we report on $EuNi_2Si_{2-x}Ge_x$, a system where the Eu ions have valences ranging from 2^+ to 3^+. We find that the intermediate valence depends strongly on relative Si content and on temperature. For $EuNi_2Si_{0.5}Ge_{1.5}$, a sharp temperature-induced valence transition is observed, where the mean valence v of Eu changes by $\Delta v=0.6$ between 10 and 300 K, more than ever observed. We studied this system in detail by three experimental techniques in order to obtain complementary information on the Eu valence: Eu L_{III} x-ray-absorption spectroscopy (XAS), ^{151}Eu Mössbauer effect (ME), and magnetization measurements. In particular, the relation between the subspectral intensities obtained in XAS and ME spectra is clarified.

II. EXPERIMENTAL DETAILS AND RESULTS

The $EuNi_2Si_{2-x}Ge_x$ compounds were prepared by conventional methods.[7] The $EuNi_2Si_{0.5}Ge_{1.5}$ sample was prepared twice, in an induction furnace (sample 1) and in an arc furnace (sample 2). All compounds of the $EuNi_2Si_{2-x}Ge_x$ system were found to crystallize in the tetragonal $ThCr_2Si_2$ structure, space group $I4/mm$. The dependence of the lattice parameters c and a on x is shown in Fig. 1. The nonlinear variation of these lattice parameters as well as of the c/a ratio with x already indicates a change in the mean Eu valence.

The Mössbauer experiments with the 21.6 keV γ-ray transition of ^{151}Eu were performed by standard techniques.[12] The source was $^{151}SmF_3$ at room temperature. Figure 2 displays the ^{151}Eu-Mössbauer spectra of $EuNi_2Si_{2-x}Ge_x$ compounds for various x values taken at room temperature. The Eu ions in $EuNi_2Si_2$ and $EuNi_2Ge_2$ are identified as trivalent and divalent,[7] respectively, on the basis of their temperature-independent isomer shifts. As discussed in Ref. 7, the spectrum of $EuNi_2Ge_2$ exhibits the presence of a small amount of Eu^{3+} whereas $EuNi_2Si_2$ exhibits a small amount of Eu^{2+}, Fig. 2. While this Eu^{3+} component in Eu_2Ge_2 may be attributed to an Eu_2O_3 impurity, a divalent component as in $EuNi_2Ge_2$ is observed for all EuM_2X_2 systems exhibit-

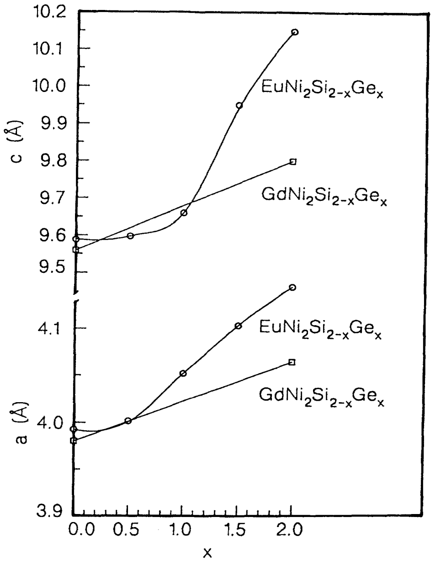

FIG. 1. Lattice parameters c and a of the $EuNi_2Si_xGe_{2-x}$ system at room temperature as a function of x. For comparison, the corresponding values of trivalent $GdNi_2Si_2$ and $GdNi_2Ge_2$ are shown.

ing intermediate valence.[1,2] They are usually denoted as "satellite lines." The intensity of these satellites depends on stoichiometry, method of preparation, and heat treatment. The two samples of $EuNi_2Si_{0.5}Ge_{1.5}$ investigated here and prepared by different methods, also revealed different intensities of the satellite line.

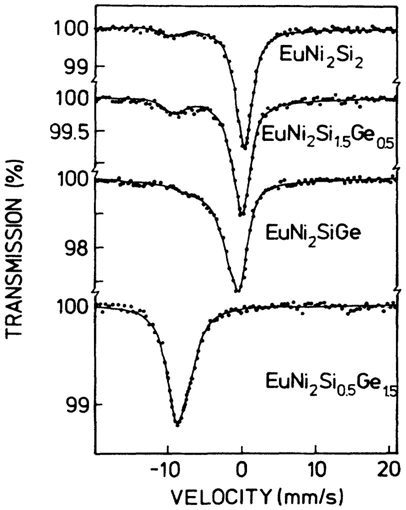

FIG. 2. ^{151}Eu-Mössbauer spectra of $EuNi_2Si_xGe_{2-x}$ compounds for various x values at room temperature. Solid curves are the results of least-squares fits.

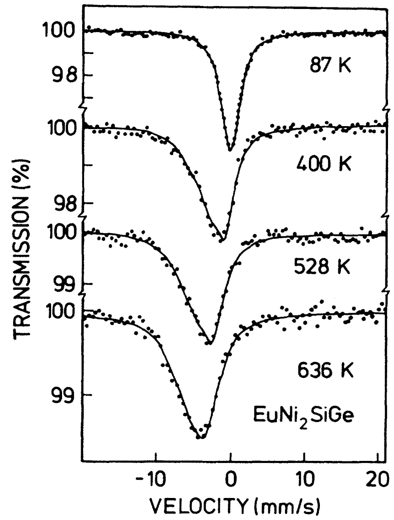

FIG. 3. ^{151}Eu-Mössbauer spectra of $EuNi_2SiGe$ at various temperatures.

The compounds $EuNi_2SiGe$ and $EuNi_2Si_{0.5}Ge_{1.5}$ exhibit structures in their spectra, which are attributed to Eu ions with intermediate valence, being more trivalent in the former and more divalent in the latter compound. As shown in Figs. 3–5, the Mössbauer spectra of these compounds vary appreciably with temperature. $EuNi_2SiGe$ undergoes a relatively gradual temperature-induced valence transition, with the average isomer shift changing from 0 mm/sec at low temperature to about −4 mm/sec at 600 K (see Fig. 3). The steepest change in valence as a function of temperature is observed for

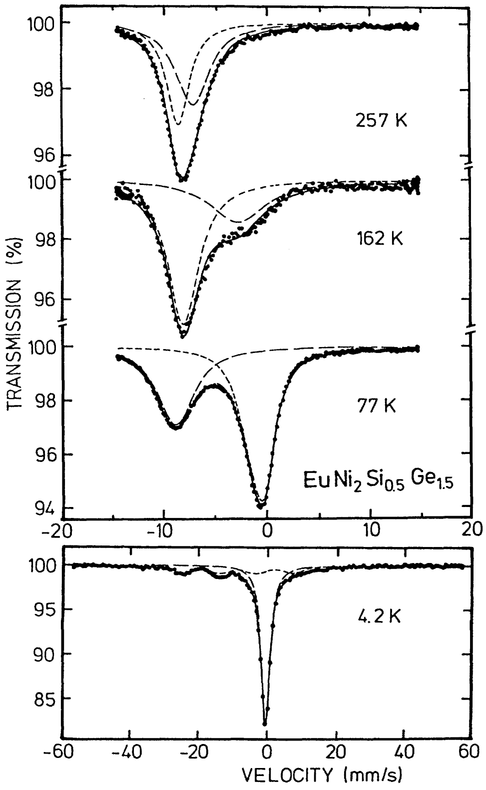

FIG. 4. ^{151}Eu-Mössbauer spectra of $EuNi_2Si_{0.5}Ge_{1.5}$ (sample 1) at various temperatures. The solid lines are fits with two Lorentzians. The spectrum at 4.2 K is fitted with a magnetically split Eu^{2+} component and an unsplit Eu^{3+} component.

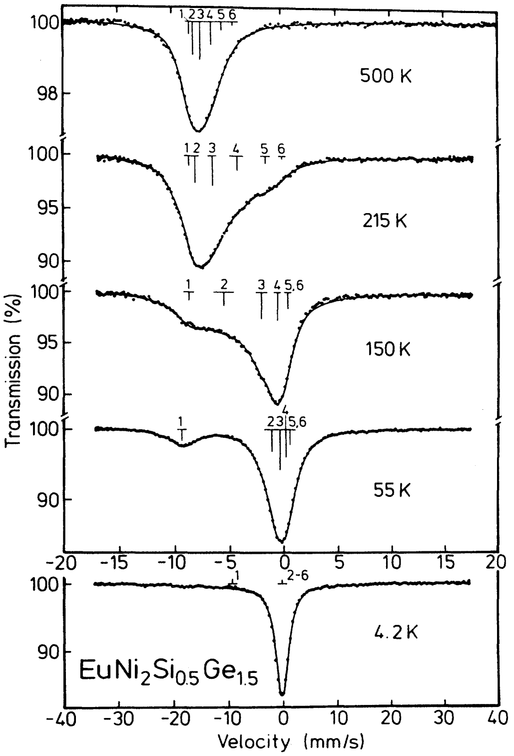

FIG. 5. ^{151}Eu-Mössbauer spectra of $EuNi_2Si_{0.5}Ge_{1.5}$ (sample 2) at various temperatures. The solid lines are fits with five or six Lorentzians, whose amplitudes and widths are indicated by vertical and horizontal lines. The 4.2 K spectrum is fitted with a magnetically split Eu^{2+} component and an unsplit Eu^{3+} component.

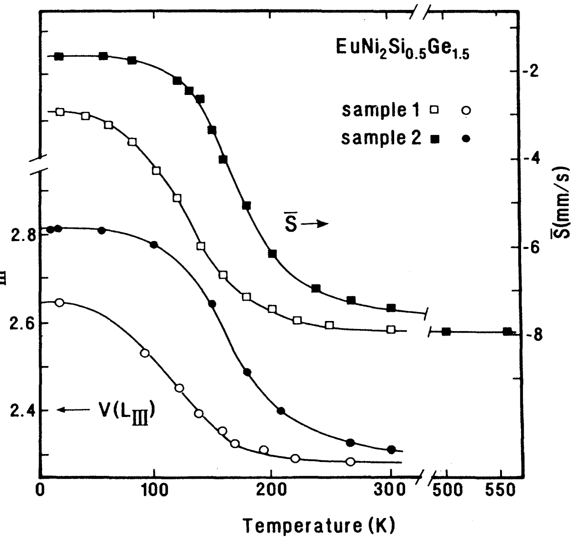

FIG. 6. Temperature dependence of the mean Mössbauer isomer shift, $\bar{S}$, and the L_{III}-edge derived valence, $v(L_{III})$, of Eu in the two samples of $EuNi_2Si_{0.5}Ge_{1.5}$.

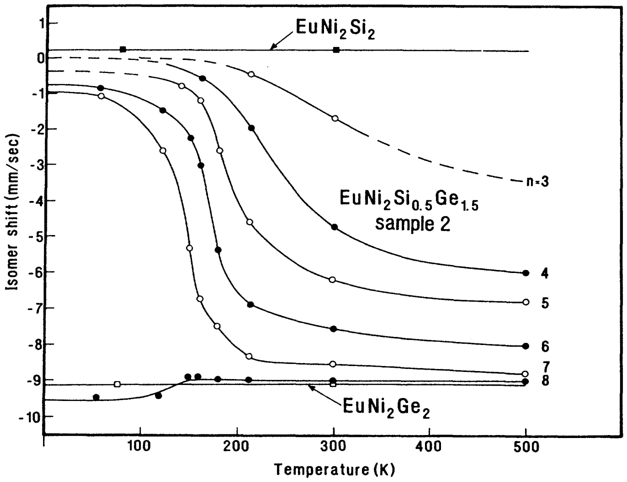

FIG. 7. Temperature dependence of the isomer shifts of the individual components in the Mössbauer spectra of $EuNi_2Si_{0.5}Ge_{1.5}$, (sample 2), where n refers to the number of nearest-neighbor Ge atoms.

$EuNi_2Si_{0.5}Ge_{1.5}$ (see Figs. 4 and 5), which is displayed in Fig. 6 by the temperature dependence of the mean isomer shifts. These mean isomer shift values were derived either from a simple center of gravity calculation or from least-squares fits of the spectra. The spectra obtained from sample 1 (Fig. 4), were fitted by two Lorentzian lines with different line widths. The positions of the two lines (S_1 and S_2) and their intensities (I_1 and I_2) were found to change with temperature. The spectra of sample 2 (Fig. 5) were fitted by five to six Lorentzian lines with isomer shifts S_i and intensities I_i. Initially, the relative intensities of the lines were chosen as those expected for a random (binomial) distribution of Eu ions with 8 to 0 nearest-neighbor Ge atoms in the first coordination shell. This kind of analysis has been used successfully in the past.[5,13] In the final fit procedure, the intensities were treated as free parameters, resulting in slightly different final values as compared to the above starting numbers. From the fit results, the mean isomer shifts plotted in Fig. 6 were calculated using the expression:

$$\bar{S}(T)=\sum_{i=1}^{N} I_i(T)S_i(T)\Big/\sum_{i=1}^{N} I_i(T)\ , \qquad (1)$$

with $N=2$ in case of sample 1 and 5 or 6 in case of sample 2.

Figure 7 shows the temperature-induced changes of $S_i(T)$, the isomer shifts of the individual Lorentzian line components shown in the spectra of Fig. 5. For comparison, the temperature-independent isomer shifts of $EuNi_2Si_2$ and $EuNi_2Ge_2$ are also given. The numbers n in Fig. 7 refer to the assumed number of nearest-neighbor Ge atoms around Eu for the individual sites.

The XA measurements were performed at the EXAFS-II beamline of HASYLAB/DESY (Hamburg) using a Si(111) double-crystal monochromator. The identical $EuNi_2Si_{0.5}Ge_{1.5}$ samples as studied by ME measurements were investigated in the temperature range from 10

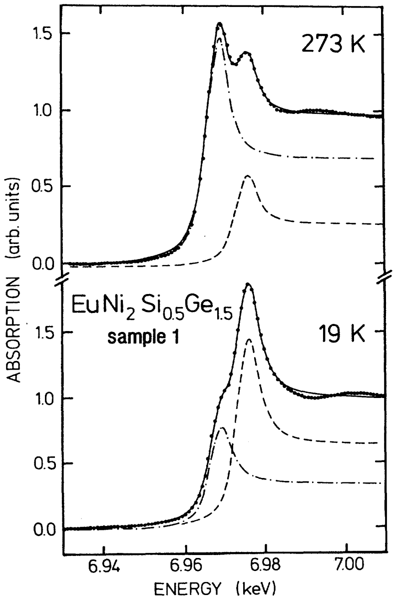

FIG. 8. X-ray-absorption near-edge spectra at the Eu L_{III} threshold of $\mathrm{EuNi_2Si_{0.5}Ge_{1.5}}$ (sample 1) at two different temperatures. The dashed-dotted and the dashed subspectra indicate the Eu^{2+}-$2p^54f^75d^*$ and Eu^{3+}-$2p^54f^65d^*$ final-state components fitted to the experimental data.

to 300 K (see Figs. 8 and 9). In addition, $\mathrm{EuNi_2Si_2}$ and $\mathrm{EuNi_2Ge_2}$ were measured as reference systems (see Fig. 10). The structure of the Eu L_{III} XA spectra of $\mathrm{EuNi_2Si_{0.5}Ge_{1.5}}$ changes drastically with temperature (Fig. 8 and 9). The edge spectra were analyzed in the usual way[14] in order to obtain the relative intensities 1-v and v of the $(2p^54f^75d^*)$ and $(2p^54f^65d^*)$ final-state

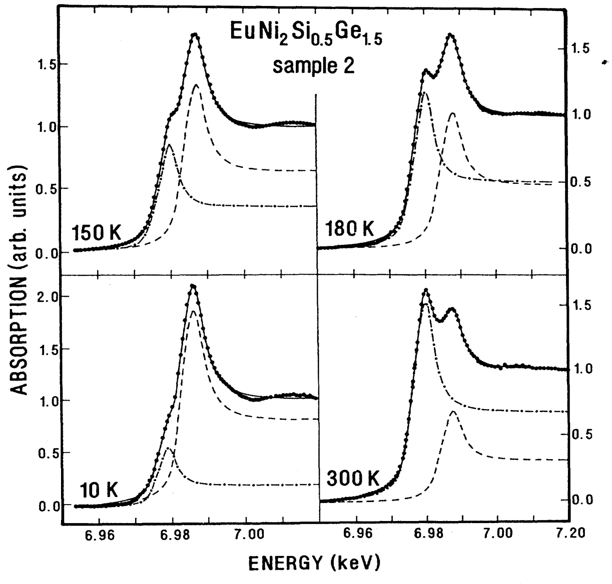

FIG. 9. X-ray-absorption near-edge spectra at the Eu L_{III} threshold of $\mathrm{EuNi_2Si_{0.5}Ge_{1.5}}$ (sample 2) at various temperatures. The subspectra are described in the caption of Fig. 8.

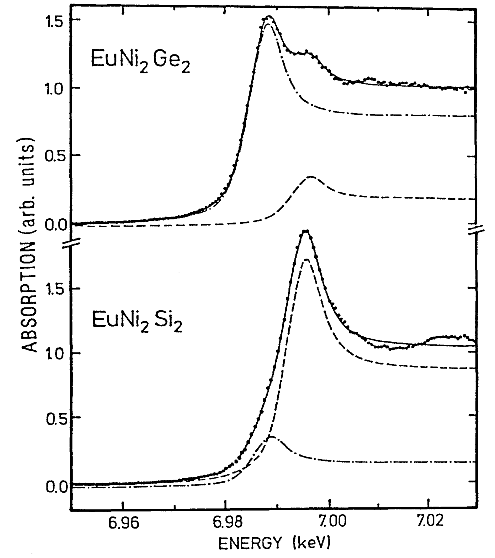

FIG. 10. X-ray-absorption near-edge spectra at the Eu L_{III} threshold of $\mathrm{EuNi_2Si_2}$ and $\mathrm{EuNi_2Ge_2}$. These spectra were measured in the fluorescence mode. The derived spectral features, in particular $v(L_{\mathrm{III}})$, are identical with those obtained by transmission measurements.

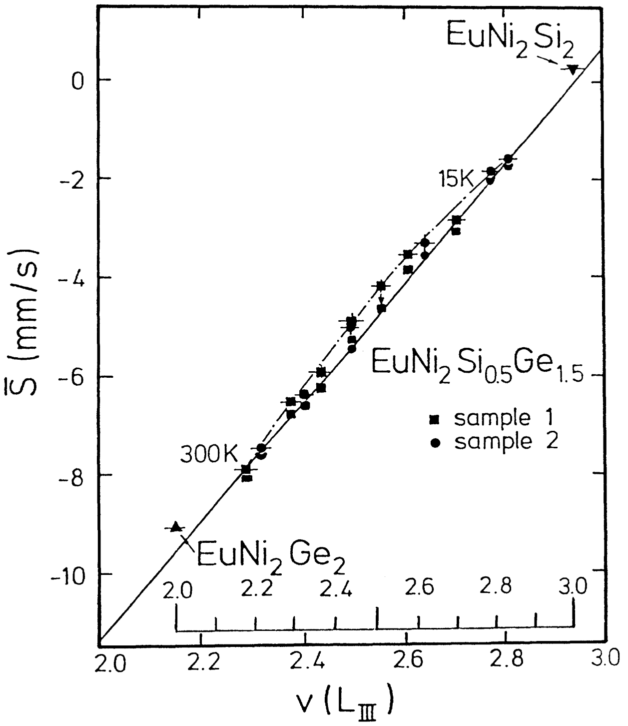

FIG. 11. Correlation between the mean valence from L_{III}-XAS, $v(L_{\mathrm{III}})$, and the mean Mössbauer isomer shift, $\bar{S}$. The lower set of points following a linear correlation was obtained from the upper set of points by correcting S for different recoil-free fractions. The inner valence scale takes a correction for final-state effects, in the Eu L_{III} XA spectra of divalent Eu systems into account.

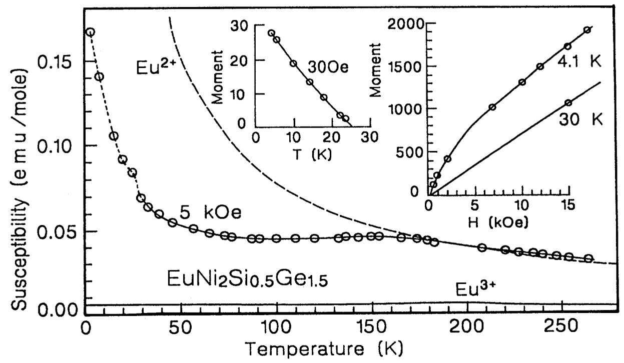

FIG. 12. Temperature and magnetic-field dependence of the magnetic susceptibility and magnetization of $\text{EuNi}_2\text{Si}_{0.5}\text{Ge}_{1.5}$. The solid curve above 30 K is the result of a theoretical calculation (see text).

components, respectively. The derived mean L_{III} valence, $v(L_{\text{III}})=2+v$, changes from 2.65 at 20 K to 2.29 at 273 K in case of sample 1 and from 2.81 at 20 K to 2.32 at 300 K in case of sample 2. The temperature dependence of $v(L_{\text{III}})$ displayed in Fig. 6 is quite similar to that of the average isomer shift shown in the same figure. This is explicitly shown for both samples in Fig. 11, where the mean isomer shift S is plotted versus $v(L_{\text{III}})$. This correlation will be discussed further below. The two studied $\text{EuNi}_2\text{Si}_{0.5}\text{Ge}_{1.5}$ samples exhibit the same intermediate-valence phenomena except that the midpoint of the valence transition, as displayed by both methods of measurement, is around 120 K for sample 1 and around 170 K for sample 2 (see Fig. 6). This observation stresses the sensitivity of the intermediate-valence state in this system to the method of preparation as well as to the exact ratio of Si and Ge atoms in the sample. Both may effect the distribution of Si and Ge atoms as nearest neighbors around Eu. It seems that sample 2 contained slightly more Si than sample 1, and that the Si and Ge atoms were more randomly distributed in sample 2.

The magnetic susceptibility of $\text{EuNi}_2\text{Si}_{0.5}\text{Ge}_{1.5}$ was measured with a PAR-155 vibrating sample magnetometer. The temperature and magnetic field dependences of the susceptibility and magnetization are shown in Fig. 12. These demonstrate again the intermediate-valence character of the Eu ions. At high temperatures the experimental points follow the curve expected from pure Eu^{2+}, whereas at low temperatures the points follow a curve in between those expected for Eu^{3+} and Eu^{2+}.

III. DISCUSSION

The observed temperature change in the Mössbauer spectra (Figs. 4 and 5) and the XAS spectra (Figs. 8 and 9) of $\text{EuNi}_2\text{Si}_{0.5}\text{Ge}_{1.5}$ show that Eu experiences a precipitous valence phase transition. The change in mean valence between 20 K and 300 K, for sample 2, is about 0.5 according to the XAS results and even close to 0.6 according to the Mössbauer results. This slight disagreement will be discussed further below. When compared to previously studied compounds exhibiting similar phenomena, like EuCu_2Si_2 and EuPd_2Si_2, one realizes that the present system undergoes the largest change in valence observed up to now for any Eu system. If one follows the change in valence for the individual Eu components, (see Fig. 7), one realizes that the Eu ions with seven nearest-neighbor Ge atoms undergo a temperature-induced valence change of almost 0.8 in the temperature range between 100 and 200 K.

While the ME spectra (Figs. 5 and 7) provide detailed information on the behavior of the various Eu ions in inequivalent environments,[13] the XAS spectra yield only average valences (see Ref. 14 for a recent review on valence determination by XAS). The different behavior of the two $\text{EuNi}_2\text{Si}_{0.5}\text{Ge}_{1.5}$ samples studied, which have supposedly the same composition, may be understood in terms of differences in the distribution of the Si and Ge atoms in the two samples. While the distribution of Si and Ge in sample 2, which was prepared by arc melting, seems to be almost random, this distribution seems far from random in sample 1, prepared by induction melting. In this latter sample there is probably a tendency of Ge and Si ions to aggregate separately leading to Mössbauer spectra that can be analyzed by just two lines. The Eu ions with a pure Ge environment are divalent, and we find a much stronger purely divalent Eu component in sample 1 ($\approx 30\%$) than in sample 2 ($\approx 15\%$).

In the following we shall compare and correlate the results obtained for $\text{EuNi}_2\text{Si}_{0.5}\text{Ge}_{1.5}$ by XAS and ME measurements. A similar correlation had been established before for the temperature-induced valence transition of EuPd_2Si_2.[14–16] To this purpose, we plot in Fig. 11 the mean isomer shift $\bar{S}$ versus $v(L_{\text{III}})$. In this figure, the corresponding data for EuNi_2Si_2 and EuNi_2Ge_2 are also included. The correlation between $\bar{S}$ and $v(L_{\text{III}})$ observed for $\text{EuNi}_2\text{Si}_{0.5}\text{Ge}_{1.5}$ follows roughly a linear interpolation between the two reference systems; however, it exhibits a clear curvature. This deviation from linearity may be associated with differences in the recoil-free fractions of the various Eu sites. As we have learned in a previous study,[12] the recoil-free fraction of the Eu^{2+} ion is usually smaller than that of the Eu^{3+} ion. This leads to an artificial shift of the weighted mean value of the isomer shift to more trivalent values.

In order to correct the mean isomer shift defined by Eq. (1) for differences in recoil-free fraction, one needs to know the recoil-free fractions, f_i for the various Eu sites, i.e., the individual Mössbauer absorption lines in Fig. 5. One can then calculate the mean isomer shift by the modified equation;

$$\bar{S}(T)=\left[\sum_{i=1}^{N} S_i I_i/f_i\right] \Big/ \left[\sum_{i=1}^{N} I_i/f_i\right] . \tag{2}$$

In order to determine $f_i(T)$ for the various intermediate-valence components, we measured the temperature dependence of the recoil-free fraction of Eu in EuNi_2Si_2 and EuNi_2Ge_2. These studies were performed at three different temperatures, 77, 150, and 300 K, and the results were fitted with a Debye-model curve in order to obtain Θ_D. In this way, $\Theta_D(\mathrm{EuNi_2Si_2})=210$ K and $\Theta_D(\mathrm{EuNi_2Ge_2})=300$ K were obtained. This difference is even larger than the one observed for the corresponding Co systems.[12] The individual recoil-free fractions $f_i(T)$ were then obtained by a linear interpolation based on the respective isomer shifts, namely:

$$f_i(T)=f_{\mathrm{Ge}}(T)+[(S_i(T)-S_2)/(S_3-S_2)] \times[f_{\mathrm{Si}}(T)-f_{\mathrm{Ge}}(T)] , \quad (3)$$

where S_2 and S_3 are estimated isomer shifts of purely divalent and trivalent Eu ions in $\mathrm{EuNi_2Si_{0.5}Ge_{1.5}}$. We used $S_2=-9.6$ mm/sec and $S_3=0.0$ mm/sec, S_2 represents the isomer shift of the stable $\mathrm{Eu^{2+}}$ component, corresponding to Eu ions with 8 Ge nearest neighbors, and S_3 the isomer shift of the stable $\mathrm{Eu^{3+}}$ component, corresponding to Eu ions with almost no Ge neighbors (see Figs. 5 and 7). f_{Ge} and f_{Si} were taken as those of divalent Eu in $\mathrm{EuNi_2Ge_2}$ and trivalent Eu in $\mathrm{EuNi_2Si_2}$, respectively. When the mean isomer shift is corrected according to Eqs. (2) and (3), the resulting $\bar{S}(T)$ values are shifted by 0.1–0.5 mm/sec towards the $\mathrm{Eu^{2+}}$ limit. The applied corrections are largest for temperatures close to the midpoint temperature of the valence transition (around 120 K for sample 1 and 170 K for sample 2), and they are smallest for high and low temperatures. This then leads to a more linear correlation between $\bar{S}$ and $v(L_{\mathrm{III}})$.

At this stage one should comment on the valences determined for $\mathrm{EuNi_2Si_2}$ and $\mathrm{EuNi_2Ge_2}$ by the L_{III}-XAS method (see Fig. 10). $\mathrm{EuNi_2Ge_2}$ is assumed to be a purely divalent compound from its lattice parameters and magnetic properties as well as from the temperature-independent isomer shift (-9.1 mm/s). On the other hand, the Eu L_{III} edge yields (after correcting for the $\mathrm{Eu_2O_3}$ impurity) a valence of $v(L_{\mathrm{III}})=2.15(3)$. This discrepancy points to final-state effects in the L_{III}-edge spectrum similar to the case observed previously in divalent $\mathrm{EuPd_2P_2}$ and attributed to covalent binding effects.[17] The same phenomenon has also been observed for other stable $\mathrm{Eu^{2+}}$ systems.[14] In any case, $\mathrm{EuNi_2Ge_2}$ is close to an intermediate-valence behavior, since the substitution of only 25% of the Ge atoms by Si leads, at low temperature, to the conversion of $\simeq 70\%$ to 85% of the Eu ions to a nearly trivalent state. The L_{III}-edge data of $\mathrm{EuNi_2Si_2}$ are also indicating a slightly intermediate-valence nature of the Eu ions, with $v(L_{\mathrm{III}})=2.94(3)$. In addition the isomer shift varied with temperature by ΔS $(77-300\ \mathrm{K})=-0.13(3)$ mm/sec.

In view of the covalency effects observed in the L_{III}-XAS spectrum of divalent $\mathrm{EuNi_2Ge_2}$, the valence assignment according to a weighted average of the L_{III}-subspectra is not generally expected to represent the 4f occupancy in the ground state, i.e., an absolute measure of the valence. However, differences in valence can be extracted much better using such a procedure. To some extent one can expect to obtain more reliable absolute valence values, if one defines $\mathrm{EuNi_2Ge_2}$ and $\mathrm{EuNi_2Si_2}$ as purely divalent and trivalent Eu compounds. This then leads to a renormalized valence scale, the inner scale in Fig. 11. In this case, the divalent state in $\mathrm{EuNi_2Si_{2-x}Ge_x}$ corresponds to an isomer shift of $S_2\simeq-9.6$ mm/sec and the trivalent state to $S_3\simeq0.0$ mm/sec, as mentioned already further above. The linear correlation observed in Fig. 11 shows that the final-state effects in the L_{III}-edge spectra are temperature independent.

In the interconfigurational excitation model (ICF),[18] the expression for the isomer shift is given by:[19]

$$S(T)=S_3+(S_2-S_3)p_2(T) , \quad (4)$$

where S_3 and S_2 are isomer shifts assigned to purely trivalent and divalent Eu ions, respectively, and

$$p_2(T)=[1+Z_3(T^*)\exp(E_{\mathrm{exc}}/T^*)/8]^{-1} , \quad (5)$$

where $T^*=(T^2+T_f^2)^{1/2}$ and Z_3 is the $\mathrm{Eu^{3+}}$ partition function.[19] E_{exc} stands for the interconfigurational excitation energy and T_f is the so-called valence-fluctuation temperature, introducing phenomenologically the homogeneous width of E_{exc}, i.e., T_f is related to the hybridization energy of the $4f$ state with conduction-band state. Using S_2 and S_3 from $\mathrm{EuNi_2Si_{0.5}Ge_{1.5}}$, and assuming that E_{exc} is small in comparison to T^* for $T=300$ K (T_f is generally less than 100 K), we obtain a value of $S(300\ \mathrm{K})=-8.0$ mm/sec, in good agreement with the experimental observation (see Fig. 5).

In previous studies of intermediate-valence Eu systems it was assumed that S_3-S_2 takes a value as in insulating ionic compounds, namely, between 11 to 13 mm/sec.[5] In the present study we obtain for S_3-S_2 a value of 9.6 mm/sec. It seems now that in intermetallic systems such smaller S_3-S_2 values are generally observed. The reason lies probably in the fact that the $\mathrm{Eu^{2+}}$ ion is larger than $\mathrm{Eu^{3+}}$. When both ions are put in the same environment, the larger $\mathrm{Eu^{2+}}$ ion will experience a chemical pressure that leads to a higher electronic charge density at the nucleus causing a shift of S_2 to more positive values.[20]

A close inspection of Figs 8 and 9 shows that the energy separation between the $\mathrm{Eu^{2+}}$ $4f^7$ and the $\mathrm{Eu^{3+}}$ $4f^6$ white lines in the XAS spectrum of $\mathrm{EuNi_2Si_{0.5}Ge_{1.5}}$ is temperature dependent, i.e., it shrinks with decreasing temperature or increasing Eu valence. The same phenomenon had previously been observed for the intermediate-valence compounds of $\mathrm{EuCu_2Si_2}$ and $\mathrm{EuPd_2Si_2}$.[14] It was interpreted as due to a change of the occupancy of the valence band caused by the change of the mean Eu valence. At low temperatures, the occupancy of $5d$-like valence-band states is increased, causing an increase in the $4f$-$5d$ Coulomb repulsion counteracting the $2p$ hole-$4f$ Coulomb attraction. This leads to the observed decrease in energy separation.

We now turn to the magnetic properties of $\mathrm{EuNi_2Si_{0.5}Ge_{1.5}}$ (sample 1) displayed in Fig. 12. The observed temperature dependence of the magnetic susceptibility $\chi(T)$ is typical for an intermediate-valence system with a valence transition. Since $\chi(T)$ exceeds at high temperatures that of pure $\mathrm{Eu^{2+}}$ and since $\chi(T)$ exhibits a steep rise at low temperatures, it is clear that the $\mathrm{Eu^{2+}}$-$\mathrm{Eu^{2+}}$ exchange interaction is of a ferromagnetic nature. The magnetic-ordering temperature obtained from magnetization curves measured in low magnetic fields is

$T_c = 25$ K (inset in Fig. 12). This is in agreement with Mössbauer results, where a magnetic hyperfine splitting of the divalent line is observed for $T \leq 20$ K. At 4.2 K, this magnetic hyperfine splitting corresponds to a magnetic hyperfine field of (−)385(15) kOe. In this context, it is remarkable that $EuNi_2Ge_2$ orders antiferromagnetically with $T_N = 30$ K.[7]

The magnetic-susceptibility curve, shown in Fig. 12, may be fitted with a simple ICF formula[18,19]

$$\chi(T) = P_2\chi_2(T) + (1-P_2)\chi_3(T) \ , \tag{6}$$

where χ_3 is the Eu^{3+} susceptibility,[19] and P_2 is the average relative weight of divalent Eu ions in the sample, χ_2 is given by

$$\chi_2(T) = (63/8)/(T^* - \Theta_0 P_2)(\text{emu}) \ , \tag{7}$$

where $\Theta = \Theta_0 P_2$ is the paramagnetic Curie temperature. $P_2(T)$ may be derived from the isomer shift $\bar{S}(T)$ of sample 1 shown in Fig. 5 using the equation:

$$P_2(T) = [S_3 - \bar{S}(T)]/(S_3 - S_2) \ . \tag{8}$$

With this $P(T)$, one can fit the experimental $\chi(T)$ curve with only two adjustable parameters, Θ_0 and T_f; T_f however, must not necessarily be independent of temperature.[18] We find that $\chi(T)$ above 30 K is well reproduced by $\Theta_0 = 70$ K and $T_f = 50$ K, independent of temperature, (see Fig. 12). This results in a paramagnetic Curie temperature, Θ (30 K) = 21, very close to the ferromagnetic transition temperature, $T_c = 25$ K.

In the past, precipitous valence phase transitions were interpreted in terms of cooperative processes.[11] It was shown that this may even lead to a first-order phase transition in case of Yb compounds.[21] A cooperative enhancement of the valence transition is obtained if the interconfigurational excitation energy, $E_{\rm exc}$, which enters Eq. (5) for p_2, is itself a function of p_2:

$$E_{\rm exc} = E_0(1 - \alpha p_2) \ . \tag{9}$$

Positive values of α will enhance the valence transition. It would be tempting to use such a model also for $EuNi_2Si_{0.5}Ge_{1.5}$. However, the simple model applies only to a homogeneous system, where all Eu ions are equivalent, which is not the case in $EuNi_2Si_{0.5}Ge_{1.5}$. A corresponding model may also be derived for an inhomogeneous system from the simple model for the homogeneous case described above. It will contain however, many free parameters due to the inequivalent Eu sites, which renders a comparison with the experimental observations not very productive.

IV. CONCLUSIONS

In the following, a short summary is given of the conclusions reached from the combined study by three techniques of the intermediate-valence Eu system $EuNi_2Si_{0.5}Ge_{1.5}$.

(a) Mössbauer and $L_{\rm III}$-edge measurements reveal a precipitous valence phase transition in $EuNi_2Si_{0.5}Ge_{1.5}$, the most complete one ever observed for any Eu system. Discrepancies in valence determination by the two methods are discussed and it is shown that both final-state effects in $L_{\rm III}$-edge spectra and differences in Mössbauer recoil-free fraction for Eu^{2+} and Eu^{3+} ions have to be taken into account. Despite this inherent weakness of the $L_{\rm III}$ method for absolute valence measurements, it is well suited for monitoring changes in valence.

(b) A detailed analysis of the Mössbauer spectra of $EuNi_2Si_{0.5}Ge_{1.5}$ shows that they represent a superposition of subspectra from intermediate-valence Eu ions with different local distributions of Si and Ge in the first coordination shell. This gives an explanation for the observation that the Eu valence in $EuNi_2Si_{0.5}Ge_{1.5}$ is extremely sensitive to the preparation method. A small difference in the Si/Ge ratio or preparation method may lead to a large shift in the valence transition temperature, a shift of 50 K is observed for the two samples investigated.

(c) If different recoil-free fractions for Eu^{2+} and Eu^{3+} ions are taken into account, a linear correlation between the corrected mean isomer shift and the mean $L_{\rm III}$ valence is obtained. This also proves that final-state effects in the $L_{\rm III}$-edge spectra are temperature independent.

(d) Magnetic susceptibility measurements revealed also the intermediate-valence character of $EuNi_2Si_{0.5}Ge_{1.5}$, in which the divalent component orders ferromagnetically. Using a simple ICF model for the susceptibility, values for the paramagnetic Curie temperature and effective fluctuation temperature were obtained.

(e) The precipitous valence transition observed in $EuNi_2Si_{0.5}Ge_{1.5}$ indicates that such a phenomenon is not unique to pure homogeneous systems like $EuPd_2Si_2$. Cooperative enhanced valence phase transitions may occur also in inhomogeneous systems.

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*Present address: Universität-GH-Paderborn, Fachbereich Physik, D-4790 Paderborn, Germany.

†Permanent address: Racah Institute of Physics, The Hebrew University, Jerusalem, Israel.

‡Present address: Nixdorf Computer AG, D-1000 Berlin 27, Germany.

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