sible connection between the existence of the surface resonance and the probability for reconstruction of metal surfaces. From an energetics point of view one might argue that the presence of the surface resonance near the Fermi level is concomitant with a high surface free energy which in turn would be a driving force for reconstruction. On the other hand, the existence of a surface resonance in this case presumably depends on spin-orbit splitting in the band structure of the metal.[14] If the width of the spin-orbit gap determines the strength of the surface state, it would also be a rough measure of the probability for reconstruction. It is interesting to note that the band structures of the noble metals[13] show a small spin-orbit splitting (of the order of 0.2 eV) for the 4*d* metals but a fairly large splitting for the 5*d* metals, namely about 1 eV. Of course, it is known[17] that the 4*d* metals Rh, Pd, and Ag do not reconstruct while the 5*d* metals Ir, Pt, and Au do reconstruct, at least the (100) and (110) orientations. It remains to be seen whether further experimental and theoretical work will be able to substantiate or disprove this hypothesis.

We would like to thank Traugott Fisher for many stimulating discussions.

---

*Present address: Institut fur Grenzflachenforschung der Kernforschunganlage, 517 Julich 1, Postfach 365, West Germany.

[1] S. Hagstrom, H. B. Lyon, and G. A. Somorjai, Phys. Rev. Lett. 15, 491 (1965).

[2] H. B. Lyon and G. A. Somorjai, J. Chem. Phys. 46, 2539 (1967).

[3] D. G. Fedak and N. A. Gjostein, Phys. Rev. Lett. 16, 171 (1966), and Acta Metall. 15, 827 (1967).

[4] D. G. Fedak and N. A. Gjostein, Surf. Sci. 8, 98 (1967).

[5] G. A. Somorjai, Sur. Sci. 8, 98 (1967).

[6] J. T. Grant and T. W. Haas, Surf. Sci. 18, 457 (1969).

[7] P. W. Palmberg, in *Structure and Chemistry of Solid Surfaces*, edited by G. A. Somorjai (Wiley, New York, 1969).

[8] P. W. Palmberg and T. N. Rhodin, J. Chem. Phys. 49, 134 (1968).

[9] H. P. Bonzel and T. E. Fischer, Surf. Sci. 51, 213 (1975).

[10] G. A. Somorjai, Catal. Rev. 7, 87 (1972).

[11] S. F. Lin, D. T. Pierce, and W. E. Spicer, Phys. Rev. B 4, 326 (1971).

[12] N. V. Smith, G. K. Wertheim, S. Hüfner, and M. M. Traum, Phys. Rev. B 10, 3197 (1974).

[13] O. K. Andersen, Phys. Rev. B 4, 883 (1970).

[14] R. Feder and K. Sturm, Phys. Rev. B 12, 537 (1975).

[15] C. R. Helms, H. P. Bonzel, and S. Kelemen, to be published.

[16] After the $CO/O_2{}^+$ treatment to produce the (1 × 1) surface, adsorbed oxygen was sometimes detected; it could be removed by the water synthesis reaction with $H_2$ and any residual adsorbed hydrogen removed by heating to 100°C. This effect will be discussed in more detail in Ref. 15.

[17] G. A. Somorjai, *Principles of Surface Chemistry* (Prentice Hall, Englewood Cliffs, N. J., 1972).

---

# Susceptibility of Interconfiguration-Fluctuation Compounds*

B. C. Sales† and D. K. Wohlleben†
*Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92037*

(Received 12 May 1975)

We present a simple model for the magnetic susceptibility of rare-earth compounds which exhibit interconfiguration fluctuations (ICF). It is shown that the temperature dependence of the magnetic susceptibility of several ICF Yb compounds can be fitted quantitatively, assuming an energy separation $E_{ex}$ between the two configurations and an intrinsic lifetime $\tau$ due to the 4*f*-shell—conduction-electron interaction. With the parameters $E_{ex}$ and $\tau$ obtained from such fits it is possible to predict the temperature dependence of the valence.

Recently, there has been a great deal of interest in metallic rare-earth compounds in which the rare-earth 4*f* shell apparently demagnetizes (i.e., neither orders magnetically nor shows a low-temperature Curie divergence). Through measurements of magnetic susceptibility, lattice constant, resistivity, specific heat, Mössbauer isomer shift, x-ray absorption, and x-ray photoemission on rare-earth compounds such as $SmB_6$, SmS, $YbAl_3$, $\alpha$Ce, TmTe, and $EuCu_2Si_2$,[1,6] it has been established that nonmagnetic rare-earth ions can be described as fluctuating in time between two configurations (interconfiguration fluctuations, ICF). Each configuration is characterized by a different integral occupation of the $4f$ shell. This idea was first put on more solid theoretical ground by Hirst,[7,8] who pointed out the advantage of considering the problem of a magnetic impurity in a metal from the ionic or configuration limit rather than from the limit of largely delocalized electrons such as is done in the Friedel-Anderson approach.[9]

It is assumed that there are two distinct states of the rare earth atom and its environment, one with an integral number $n$ of electrons in the $4f$ shell, the other with $n-1$ electrons in the $4f$ shell and one delocalized electron in the environment. The energies of these two states are $E_n$ and $E_{n-1}$ and one defines $E_{ex}=E_n-E_{n-1}$. In each state $E_i$ the $4f$ shell is assumed to have a well-defined angular momentum $J_i$ and a corresponding magnetic moment $\mu_i$ which is determined by Hund's rules. We consider a system where $E_{ex}$ is very small compared to all multiplet splittings so that only the Hund's-rule ground state of each configuration needs to be taken into account. In the metal $E_{ex}$ is not expected to differ much from the corresponding energy difference in free rare-earth atoms, where it is known to be smallest in Ce, Eu, and Yb.[10,11]

The assumption of the survival of relatively sharp states $E_n$ and $E_{n-1}$ in the metal is equivalent to the assumption that even in a metal there is an inherent stability of an integral number of electrons in the $f$ shell. This is a consequence of the strong Hund's-rule (Coulomb) correlation energy of the $f$ shell and is supported by a large body of experimental evidence.[12]

In the metal the interaction of the conduction electrons with the local $4f$ shell can induce transitions between $E_n$ and $E_{n-1}$. The strength of the interaction is approximately given by $\Delta=\pi\rho(E)\times|V_{\text{mix}}|^2$ ($\Delta\sim 0.02$ eV in rare earth metals). $V_{\text{mix}}$ is the matrix element of the Coulomb interaction due to the overlap of the conduction electron wave functions with the $4f$ wave functions, and $\rho(E)$ is the density of conduction-electron states. $\Delta$ describes the transition rate, $\omega_f$, between $E_n$ and $E_{n-1}$ *if* $\Delta \gtrsim E_{ex}$. If, on the other hand, $\Delta \ll E_{ex}$, the transition rate is reduced by roughly a factor $\exp(-E_{ex}/\Delta)$,[13] so that in general $\hbar\omega_f=\Delta\exp(-E_{ex}/\Delta)$. The transitions are considered to be incoherent in time so that $\tau=2\pi/\omega_f$ represents the *average* lifetime of each state.

Thermal fluctuations and the above transitions due to the conduction-electron–local-electron interactions have very similar effects on the bulk susceptibility and the mean occupation of the $f$ shells of a sample. At high temperatures ($T\gg T_{sf}=\hbar\omega_f/k_B$), the mean occupation of the two configurations is dominated by thermal excitations, while at low temperatures ($T\ll T_{sf}$) the quantum mechanical fluctuations dominate.

*The purpose of this paper is to show that an Ansatz in which in the partition function the thermodynamic temperature $T$ is replaced by an effective temperature $T=T+T_{sf}$ leads to a quantitative description of the temperature dependence of the magnetic susceptibility of several ICF compounds. With this Ansatz $\chi$ becomes*

$$\chi=N\{\mu_n^2 v(T)+\mu_{n-1}^2[1-v(T)]\}/3k_B(T+T_{sf})$$

with

$$v(T)=(2J_n+1)/\{(2J_n+1)+(2J_{n-1}+1)\exp[-E_{ex}/k_B(T+T_{sf})]\}. \tag{1}$$

$V(T)$ is the fractional occupation of the state $E_n$ (fractional valence), $\mu_n$ and $\mu_{n-1}$ are the effective Hund's-rule magnetic moments in the two configurations, and $2J_n+1$ and $2J_{n-1}+1$ are the degeneracies of the two levels $E_n$ and $E_{n-1}$.

We shall illustrate the behavior of the above equation for ICF between $4f^{13}$ and $4f^{14}$ on Yb. $4f^{14}$ has $J=0$ and $\mu_{\text{eff}}=0$ while $4f^{13}$ has $J=\frac{7}{2}$ and $\mu_{\text{eff}}=4.54\mu_B$ (from Hund's rules). Therefore

$$\chi=N(4.54\mu_B)^2 v(T)/3k_B(T+T_{sf})$$

and (2)

$$v(T)=8/\{8+\exp[-E_{ex}/k_B(T+T_{sf})]\}.$$

There are two distinct cases, $E_{ex}<0$ and $E_{ex}>0$, corresponding to the magnetic $4f^{13}$ configuration lying higher and lower in energy, respectively. If the magnetic level lies lower in energy ($E_{ex}>0$) then $\chi(T)=vC/(T+T_{sf})$, where $C$ is the normal Curie constant for $\text{Yb}^{+3}$ ($4f^{13}$), and $v$ is the fractional valence with $8/9<v<1$ (for all $T$). Hence $\chi(T)$ is to a good approximation a Curie-Weiss law down to $T=0$. There is no divergence of the susceptibility nor any sign of magnetic order, *although* the lower level has an effective magnetic moment.[14] This regime corresponds to an Yb valence between 2.89 and 3. If the magnetic $4f^{13}$ configuration lies higher in energy ($E_{ex}<0$), one can get anything from a Curie-Weiss law to a weakly temperature-dependent susceptibility. In this regime the Yb valence can vary from 2 to 2.89.

In addition there are three other interesting points. First, at sufficiently high temperatures ($E_{ex} \ll k_B T$), $\chi(T)$ follows a Curie-Weiss law with an effective moment of $(\frac{8}{9})^{1/2}4.54\mu_B = 4.28\mu_B$ independent of whether the magnetic level lies higher or lower in energy. The high-temperature effective moment is determined solely by the degeneracies of the two levels.

Second, when the $4f^{13}$ lies higher in energy and $k_B T_{sf} \sim E_{ex}$, a broad maximum appears in the susceptibility. Physically this simply means that with decreasing temperature, the upper magnetic level is thermally depopulated faster than its susceptibility increases. This type of maximum cannot be obtained with the $4f^{13}$ configuration alone, for example, by including crystal field effects. The maximum in $\chi(T)$ is a clear indication that the $4f^{14}$ configuration must be included in the model, and that its energy is lower than that of $4f^{13}$. Also, if the susceptibility at $T = 0$ is of the same order of magnitude as that at the maximum, the $4f^{13}$ configuration is never completely depopulated, implying that the ion exhibits ICF at $T = 0$.

Third, once $T_{sf}$ and $E_{ex}$ are known for a compound, the temperature dependence of the rare earth valence can be determined very accurately [from Eq. (1)].

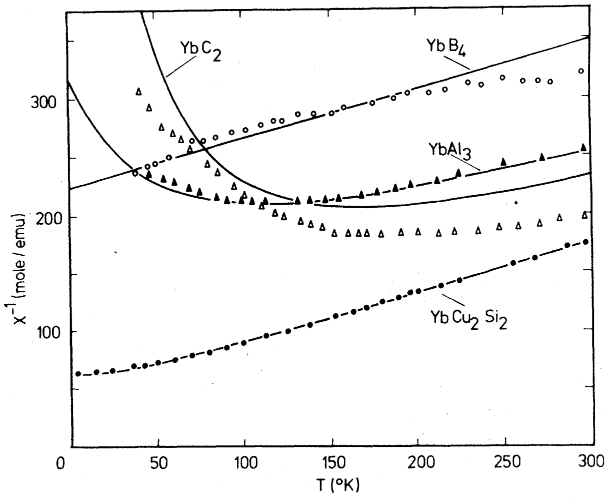

FIG. 1. $\chi^{-1}$ versus $T$ of $YbB_4$ (○), $YbAl_3$ (▲), $YbCu_2Si_2$ (●), and $YbC_2$ (△). The $YbB_4$, $YbAl_3$, and $YbC_2$ data have been corrected for less than 1% $Yb_2O_3$, a magnetic contaminant. The solid lines shown are the best fits obtianed with the model [Eq. (2)] for each compound. The values of $T_{sf}$ and $E_{ex}/k_B$ used for each fit are given in Table I.

Figure 1 shows the inverse magnetic susceptibility of four Yb compounds: $YbB_4$, $YbCu_2Si_2$, $YbAl_3$, and $YbC_2$.[15] Though carefully searched for from room temperature to 0.4°K, there was no evidence of magnetic order found in any of the compounds. The susceptibilities of $YbB_4$, $YbC_2$, and $YbAl_3$ have been corrected for < 1% $Yb_2O_3$, a known magnetic contaminant.[16,6] The $YbCu_2Si_2$ sample measured consisted of several single crystals which exhibited no evidence of magnetic impurities.

The low-temperature curvature in the plots of $\chi^{-1}$ versus $T$ for $YbCu_2Si_2$, $YbAl_3$, and $YbC_2$ indicate *unambiguously* that the energy of the $4f^{14}$ level is lower than that of $4f^{13}$. For $YbB_4$ the best fit was obtained by *assuming* that the $4f^{14}$ level lies lower in energy. The solid lines in Fig. 1 represent the above Eq. (2) for $\chi$ with the values for the parameters given in Table I.

At high temperatures (where $\chi$ follows a Curie-Weiss law), $T_{sf}$ can be determined by the Curie-Weiss intercept ($YbCu_2Si_2$). Hence the low-temperature data of this compound must be fitted by adjusting only *one* parameter ($E_{ex}$). In the case of $YbAl_3$, our temperature range was insufficient to see a good high-temperature Curie-Weiss law, so that both $T_{sf}$ and $E_{ex}$ had to be fitted. In this way we find $T_{sf} = (160 \pm 10)$°K, which is in good agreement with the Curie-Weiss temperature $\theta = 143$°K determined on $YbAl_3$ between 243 and 673°K by Iandelli and Palenzona.[17]

For $YbAl_3$ and $YbCu_2Si_2$ the model yields a quantitative fit over the entire temperature range investigated. It is encouraging that for the best sample, $YbCu_2Si_2$, the agreement between the model and the data is best within the experimental error of the data (< 1%). $YbCu_2Si_2$ has a highly anisotropic susceptibility for $H \| c$ and $H \| a$.[15] This fact provides another consistency check of the model, since while $T_{sf}$ and $E_{ex}$ may be a function of the direction of the measurement, *the fraction-*

TABLE I. The values of $E_{ex}/k_B$ and $T_{sf}$ as determined by fitting Eq. (2) to the experimental magnetic susceptibility data.

| Compound | $T_{sf}$ (°K) | $-E_{ex}/k_B$ (°K) |
|---|---|---|
| $YbCu_2Si_2$ | 75 ± 5 | 170 ± 5 |
| $YbAl_3$ | 160 ± 10 | 560 ± 25 |
| $YbB_4$ | 440 ± 50 | 400 ± 200 |
| $YbC_2$ | 100 ± 20 | 550 ± 50 |

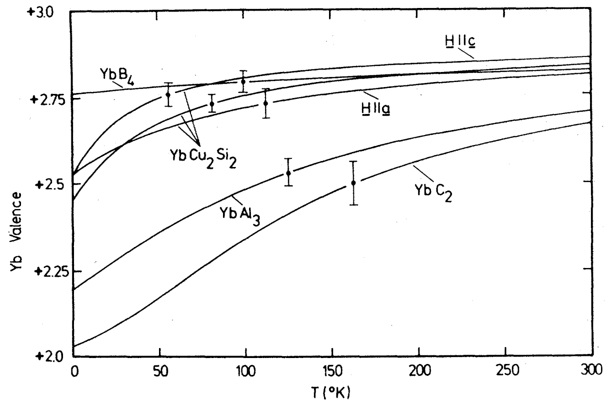

FIG. 2. The fractional Yb valence versus $T$ as determined by Eq. (2) for $YbB_4$, $YbCu_2Si_2$, $YbAl_3$, and $YbC_2$. Typical error bars due to the uncertainty of $E_{ex}/k_B$ and $T_{sf}$ are shown for each compound.

*al occupation may not.* $\chi(T)$ for $H \| c$ gives $E_{ex}/k_B = (100 \pm 10)$°K, $T_{sf} = (50 \pm 10)$°K, while for $H \| a$, $E_{ex}/k_B = (275 \pm 25)$°K, $T_{sf} = (140 \pm 20)$°K.

With these values, the temperature dependence of the valence, as calculated independently for both directions from Eq. (2), is found to be the same *within the accuracy of the parameters*.[18] The valence as a function of temperature is shown for all four Yb compounds in Fig. 2. It should be possible from these data to predict the temperature dependence of other valence-dependent properties such as the Mössbauer isomer shift.

The fit obtained for $YbB_4$ and $YbC_2$ is not as good though qualitatively correct. The maximum deviation of the fit from the data is about 20% for the $YbC_2$ sample, which was the most difficult to make and characterize.

A crucial assumption for the above fitting procedure, namely that $E_{ex}$ be independent of temperature, is justified by the quality of the fits for $YbCu_2Si_2$ and $YbAl_3$. There are cases, however, when this fitting procedure led to very unsatisfactory results, e.g., $EuCu_2Si_2$ and $YbAl_2$. We found that the room-temperature susceptibility is strongly pressure dependent in these cases ($EuCu_2Si_2$: $d\chi/dP = 1.6 \times 10^{-4}$ emu/mole kbar; $YbAl_2$: $d\chi/dP = 2.3 \times 10^{-5}$ emu/mole kbar) whereas it is not when the above fitting procedure works ($YbAl_3$, $YbCu_2Si_2$: $d\chi/dP < 1.5 \times 10^{-6}$ emu/mole kbar).[15] The pressure effect suggests that $E_{ex}$ is strongly volume dependent and thus should be sensitive to thermal contraction.

We have also successfully applied the above model to the calculation of the temperature dependence of the susceptibility when crystal-field effects are important and are presently working on the temperature dependence of the specific heat and resistivity. The results will be reported elsewhere.

It is a pleasure to acknowledge many fruitful discussions with M. B. Maple as well as the expert assistance of Dr. S. Krebs.

---

*Work supported by the U. S. Air Force, Grant No. AF-AFOSR-71-2073.

†Present address: II. Physikalisches Institut der Universität zu Köln, 5 Köln 41, Zülpicherstr. 77, Germany.

[1] D. K. Wohlleben and B. Coles, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1973), Vol. 5, Chap. 1, and references listed therein.

[2] M. B. Maple and D. K. Wohlleben, in *Magnetism and Magnetic Materials—1973*, AIP Conference Proceedings No. 18, edited by C. D. Graham, Jr., and J. J. Rhyne (American Institute of Physics, New York, 1974), p. 447.

[3] M. Campagna, E. Bucher, G. K. Wertheim, D. N. E. Buchanin, and L. D. Longinotti, Phys. Rev. Lett. 32, 885 (1974).

[4] E. R. Bauminger, I. Felner, D. Froindlich, I. Nowik, S. Ofer, I. Felner, and I. Mayer, Phys. Rev. Lett. 30, 1053 (1973).

[5] R. A. Pollak, F. Holtzberg, J. L. Freeouf, and D. E. Eastman, Phys. Rev. Lett. 33, 820 (1974).

[6] E. E. Havinga, K. H. J. Buschow, and H. J. van Daal, Solid State Commun. 13, 621 (1973).

[7] L. L. Hirst, Phys. Kondens. Mater. 11, 255 (1970).

[8] L. L. Hirst, *Magnetism and Magnetic Materials—1974*, AIP Conference Proceedings No. 24, edited by C. D. Graham, Jr., J. J. Rhyne, and G. H. Lander (American Institute of Physics, New York, 1975).

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

[10] Y. Baer and G. Busch, in Proceedings of the International Conference on Electron Spectroscopy, Namur, Belgium, 15–19 April 1974 (to be published).

[11] J. F. Herbst, D. N. Lowy, and R. E. Watson, Phys. Rev. B 6, 1913 (1972).

[12] W. E. Wallace, *Rare Earth Intermetallics* (Academic, New York, 1973).

[13] G. Grüner and N. F. Mott, J. Phys. F: Met. Phys. 4, L16 (1974).

[14] Throughout this discussion we *assume* that $T_{sf} \gg T_{RKKY}$ where $T_{RKKY}$ is a measure of the effective exchange coupling between $Yb^{+3}$ ions via conduction electron polarization. This is reasonable since for $GdAl_3$, $GdC_2$, $GdCu_2Si_2$, and $GdB_4$, $T_{RKKY}$ is of order 30°K (ordering temperature). Assuming a scaling with the de Gennes factor gives $T_{RKKY}$ for $Yb^{+3}$ of order 1°K which is much smaller than the typical values for $T_{sf}$ found (~ 100°K).

[15] All of the data presented in this paper are from the Ph.D. thesis of B. C. Sales, University of California,

San Diego, 1974 (unpublished). All of the experimental techniques along with additional data from the thesis such as specific heat, resistivity, and thermoelectric power measurements will be presented in a later paper.

[16] J. C. P. Klaasse, J. W. E. Sterkenburg, A. H. M. Bleyendaal, and F. R. deBoer, Solid State Commun. 12, 561 (1973).

[17] A. Iandelli and A. Palenzona, J. Less-Common Met. 29, 293 (1972).

[18] The expression for $v(T)$ [Eq. (2)] cannot be identical for two different sets of $T_{sf}$ and $E_{ex}$. This is a weakness of this phenomenological model which, however, in view of Fig. 2, does not seem to be serious.

## COMMENTS

# Multipole Assignment of the 8.9-MeV Resonance in $^{208}$Pb†

A. Schwierczinski,* R. Frey, A. Richter, E. Spamer, H. Theissen, and O. Titze
*Institut für Kernphysik, Technische Hochschule Darmstadt, 61 Darmstadt, West Germany*

and

Th. Walcher
*Max-Planck-Institut für Kernphysik, 69 Heidelberg, West Germany*

and

S. Krewald and R. Rosenfelder
*Institut für Kernphysik der Kernforschungsanlage Jülich, 517 Jülich, West Germany*

(Received 4 August 1975)

High-resolution inelastic electron scattering [full width at half-maximum (FWHM) ≃ 38 keV] with 50-MeV electrons on $^{208}$Pb yields a width $\Gamma = 1.3 \pm 0.2$ MeV for the 8.9-MeV resonance. This result together with the results from a reanalysis of older data with moderate energy resolution (FWHM ≃ 300 keV) shows that the previous identification of the 8.9-MeV resonance as a monopole excitation is not conclusive. The excitation of this state may as well be $E2$. The giant quadrupole resonance at 10.8 MeV seen in former measurements has been reanalyzed.

There has recently been some controversy about the existence of a giant monopole resonance in heavy nuclei. Pitthan *et al.*[1] claim to have observed a resonance of this type with 90-MeV electrons scattered inelastically from $^{197}$Au and $^{208}$Pb. Their excitation energies were determined to be $E_x = 9.2$ and 8.9 MeV, and the total widths found to be $\Gamma = 2.2$ and 1.8 MeV, respectively. From a comparison of the angular dependence of the cross sections at large scattering angles with distorted-wave Born-approximation (DWBA) calculations an indication of the $E0$ mode of excitation rather than an $E2$ was stated. An $E2$ assignment was definitely ruled out by these authors since the magnitude of the $(e,e')$ cross section, on the assumption of an $E2$ excitation, would lead to a peak in the photoabsorption cross section of $^{208}$Pb. Such a peak had not been observed in the $(\gamma,n)$ spectrum measured by Veyssière *et al.*[2] In $^{208}$Pb, e.g., the peak height of the 8.9-MeV resonance in the $(\gamma,n)$ spectrum expected on the basis of the $(e,e')$ data[1] was $\sigma_0 = 30$ mb. The $(\gamma,n)$ measurements,[2] on the other hand, showed no peak with a height exceeding the statistical error of about ± 6 mb.

The foregoing argument in favor of an $E0$ assignment has been doubted by Benenson and Bertsch[3] who derived, from the data of Ref. 1, a height of the $(\gamma,n)$ peak at 8.9 MeV of 3 mb, a value much smaller than 30 mb.

The purpose of this comment is to present new facts which contradict the former arguments[1] given for a $0^+$ assignment of the 8.9-MeV resonance in $^{208}$Pb. One is based on the total width mea-