ON THE TEMPERATURE DEPENDENCE OF THE LVV AUGER SPECTRUM IN VANADIUM

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In absence of structural or electronic transitions, the temperature dependence of the inelastic energy losses of escaping electrons is proved to account for most of the temperature dependence of the raw LXX Auger spectrum in vanadium. This effect is expected to be true in general.

THE USE of Auger spectroscopy to derive information about the electronic structure of metals is a well established technique and it is quite clear that XVV spectra contain some information on the density of states of the conduction electrons. In view of this fact the XVV spectra can reflect the change of the electronic structure as due to various interactions or to structural changes. Nevertheless if no change of the crystal structure is present as a function of the temperature, the temperature itself is expected to give rise to negligible effects on the Auger spectra. Bearing this in mind the study of the temperature dependence of the XVV spectra can be very useful to derive information on electronic effects due to temperature dependent interactions, as it has been attempted for instance to infer some insight on the high temperature superconducting transition in $YBaCu_2O_7$ [1].

Although the above considerations are quite straightforward the temperature dependence of Auger spectra must be considered with great care. In fact, apart from the possible presence of spurious effects like oxygen or carbon contamination which could introduce some temperature dependence, also the Auger spectrum can depend directly on the temperature through phonon exchange at second order. Though a second order contribution to the transition rate is generally small, it could be of some importance in observing small variations of the Auger spectra.

We have also to recall that all the above discussion refer to intrinsic changes of the Auger spectra, however it is well known that the experimentally determined spectra are strongly affected by spurious contributions due to the energy losses encountered by the escaping electrons. Because the energy loss process is very complex, being due to several scattering events involving both electrons and phonons, it is not possible to anticipate its temperature dependence. Therefore we performed an experimental investigation of the temperature dependence of both LXX Auger spectrum and energy loss in vanadium, to derive some information about the intrinsic temperature dependence of the Auger spectrum. Vanadium has been chosen because it is non-magnetic and because it retains its crystal structure up to the melting point. Therefore, also in view of the rather broad density of states curve [2], the LVV Auger spectrum is expected to be temperature independent apart from possible phonon exchange contributions.

The experiment has been performed using a CMA spectrometer with a base pressure of 10^{-10} Torr. The energy resolution was $\Delta E/E = 0.003$ and the excitation was provided by an electron beam whose energy was 3 keV. Three temperatures have been studied, namely: room temperature, 200°C and 400°C. Special care has been devoted to have the sample surface as clean as possible. To this purpose several runs have been performed at each temperature, checking the possible contaminations before and after each run, using argon sputtering to remove all observable contamination. The data have been taken into account only when the contamination was below the spectrometer sensibility. The measurement of the energy loss spectra has been performed on the same vanadium sample using an incoming electron energy of 500 eV, analyzing the energy range from 0 to 540 eV. Also during the energy loss measurements the contamination of the sample has been checked and taken below the machine sensibility.
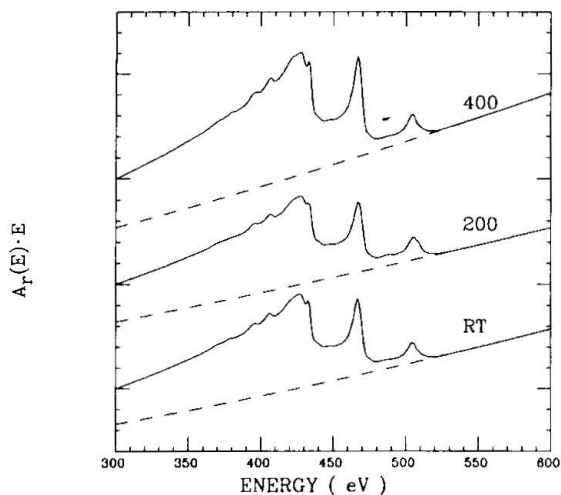
Fig. 1. Raw Auger spectra of vanadium at room temperature, 200°C and 400°C with primary background indicated (dashed line).

The raw Auger spectra are shown in Fig. 1, where a rather continuous temperature dependence is seen. In Fig. 2 we show the energy loss spectra. Also in this case a well defined temperature dependence is present. Therefore the temperature dependence of the Auger spectra can be at least partially attributed to the change of the energy loss. To remove the energy loss contribution we employed the method previously developed [3], which was proved to be quite effective in providing clean Auger spectra even when complex and small features are present. The raw Auger rate, $A_r(E)$, is decomposed into two contributions, i.e. the primary background contribution, $B(E)$, well represented by a low order polynomial in the $A_r(E)E$ vs E plots (see Fig. 1), and the escaping Auger electrons which undergo the effects of finite instrument resolution and inelastic losses both represented by a function
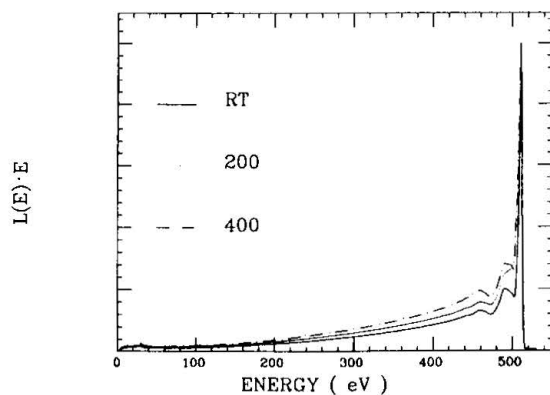

Fig. 2. Experimental energy losses at the same temperatures as Fig. 1.
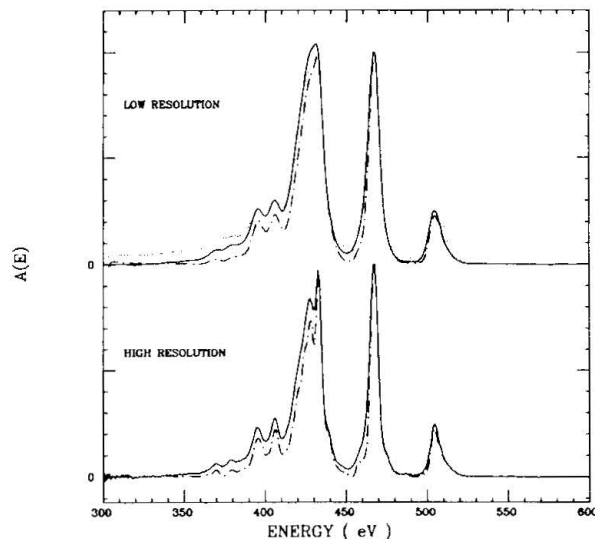

Fig. 3. Clean Auger spectra at room temperature (solid line), 200°C (points) and 400°C (point-dashed line) at low resolution with 3 eV filter HWHM and high resolution (only room temperature and 400°C) with 1.8 eV filter HWHM.

$G(E, E')$:

$$A_r(E) = B(E) + \int\limits_{-\infty}^{+\infty} A(E')G(E, E') \, dE'. \qquad (1)$$

It is customary to approximate the function $G(E, E')$ with the energy-loss spectrum obtained at an incident energy just below the excitation threshold for the Auger transition, $G(E, E') \simeq L(E - E')$; the integration in equation (1) then becomes a convolution integral and the application of the optimum-linear-filter technique [4] gives:

$$A_c(E) = F^{-1}\left[\frac{F[A_r(E) - B(E)]}{F[L(E)]} \Phi\right] \qquad (2)$$

where Φ is the filter, $F[\cdots]$ indicates the Fourier transform and $A_c(E)$ is the restored spectrum which is the best approximation to $A(E)$ in the sense of root-mean-square error. As explained in our previous work [3], a good representation of the optimum filter is obtained assuming Φ as a unitary-height Gaussian whose half-width at half-maximum (HWHM), W, is employed as a parameter to simulate in a simple way the optimum filter. Moreover, independently of the filter which, it is always possible to compare, *quantitatively*, the theoretical and restored spectra through the convolution of the calculated spectrum with a Gaussian whose HWHM is $(2 \ln 2)/W$.

The Auger spectra obtained with the depicted procedure are shown in Fig. 3. These clean spectra are affected by an *intrinsic* resolution which is directly

related to the amount of noise present in the original data. The data at 200°C had an higher noise level and the corresponding resolution had to be twice worse than in the other cases. Looking at Fig. 3 it is evident that the most part of the temperature dependence of the Auger rate is due to the temperature dependence of the energy loss. The most important general conclusion we can get directly from present experimental data is that the temperature dependence of the *raw Auger rate* is completely meaningless, because it is reasonable to expect an appreciable temperature dependence of the energy loss in all systems.

To get some more information about the temperature dependence of the Auger transitions involving valence states we can compare the LVV spectrum with the results of a theoretical calculation. Moreover we observe that the temperature dependence of the Auger spectrum can be explained in terms of phonon exchange through the electron–phonon interaction. Because the phonon energies are much smaller than the electron energies involved in the Auger transition the shape of the Auger spectrum cannot change apart from the effect of matrix elements. In fact due to phonon exchange the electron momenta involved in a given transition can change with temperature. A simple way to show this fact is to write the matrix element within the adiabatic approximation for the electron–phonon coupling. Assuming well localized electron states we have:

$$M_{fi} = \int dx \, dy \, \Phi_c^*(x - u)\Phi_a^*(y)V(x - y)$$
$$\times \ \Phi_{v1}(y - u)\Phi_{v2}(x - u) \qquad (3)$$

where Φ_c, Φ_a, $\Phi_{v1,2}$ refer to core, Auger and valence electron states and $V(x)$ is the Coulomb potential; u is the nuclear displacement. If the Auger electron wavefunction is well described by a plane wave of momentum k_a, we get after averaging over the phonon ensemble:

$$M_{fi} = e^{-W(k_a)} M_{fi}^{(0)} \qquad (4)$$

where $M_{fi}^{(0)}$ is the matrix element when no nuclear motion is present and $e^{-W(k_a)}$ is the well known Debye–Waller factor of diffraction theory [5]. Looking at equation (4) it is seen that the temperature dependence of the matrix elements is very simple and almost energy independent in the case of localized states. It is clear that when valence states are involved an effective Debye–Waller factor has to be considered so that different parts of the Auger spectrum can have different temperature dependences. To see at what extent this is the case of vanadium, we calculated the LVV spectrum starting from the theoretical band structure of [2]. To do this we fitted a Slater–Koster [6] model Hamiltonian to the first principle band structure thus
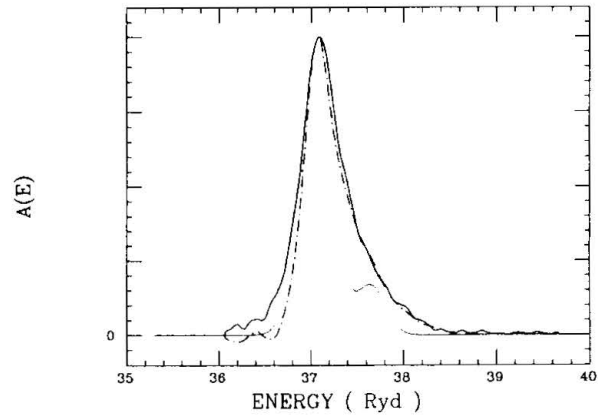

Fig. 4. Clean L_{23}VV spectra at 400°C (point dashed line) and room temperature (solid line) in comparison with theoretical calculation (points). In theoretical calculation all matrix elements are set to be unitary.

deriving the symmetry-projected densities of states to be used as input data of the theoretical approach successfully employed in the case of copper [7]. A single value for the d–Coulomb interaction has been employed ($U = 0.25$ Ryd) [8]. In Fig. 4 the comparison of the theoretical prediction and the experimental data at room temperature and 400°C is given. In the theoretical model the matrix elements have been left as disposal parameters depending on the symmetry of the states involved. Looking at this comparison we can derive some conclusion about the temperature dependence of the LVV line shape. First of all comparing theory and experiment at room temperature it is evident that there is no way to fit the experiment using the theoretical results, even varying the matrix elements. In fact, while the theory accounts well for the low energy side of the spectrum, this is not the case of the high energy side. Moreover the comparison looks essentially the same at 400°C, in fact the low energy side is reasonably fitted if the matrix elements of non-d contributions are decreased, but the high energy side cannot be adequately reproduced.

It is quite interesting to study the difference between theory and experiment at both temperatures. As we can see in Fig. 5 such differences appear to be a replica of the theoretical result, shifted by about 0.35 Ryd at both temperatures.

Although our concern was about the temperature dependence of Auger spectra, this feature deserves some consideration. We can suggest two possible explanations. The first one is the presence of a small amount of impurities giving rise to a shift of the core-hole energy. However in view of the experimental checks we have performed we consider this possibility unlike. The second hypothesis we can draw is that the presence of a second component in the LVV spectrum
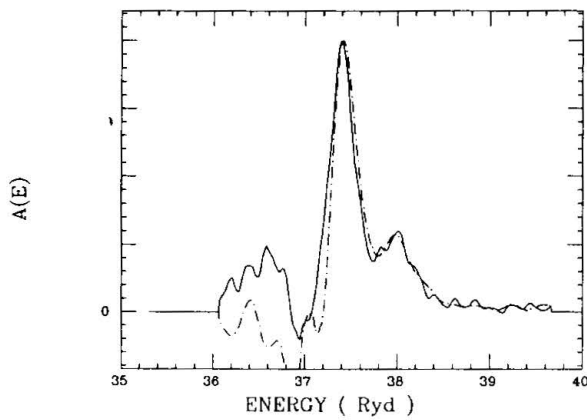
Fig. 5. Difference between experimental and theoretical $L_{23}VV$ spectra at 400°C (point dashed line) and room temperature (solid line). In theoretical calculation matrix elements have been chosen to fit the low energy side of experimental data.

reflects the presence of a rather sharp feature in the core-hole spectral function. Indeed the presence of such a feature in the spectral function of the core states of vanadium and other transition metals with a low electron number has been already evidenced [9–13], the shift of such feature being of the same order of magnitude as we report.

To conclude we can state that as expected an almost negligible temperature dependence of the Auger spectrum is present in vanadium, but a rather important change of the electron energy loss with temperature is evidenced. Therefore the analysis of the temperature dependence of Auger spectra can be done only after a *careful treatment* of the energy loss phenomena.

REFERENCES

1. A. Balzarotti *et al. Phys. Rev.* **B36,** 8285 (1987).
2. D.G. Laurent, C.W. Wang & J. Callaway *Phys. Rev.* **B17,** 455 (1978).
3. V. Contini, C. Presilla & F. Sacchetti *Surf. Science* in press and *ENEA internal report* **16,** RTI TIB (88).
4. Y.W. Lee, *Statistical Communication Theory,* p. 355, Wiley, New York (1967).
5. S.W. Lovesey, *Theory of Neutron Scattering from Condensed Matter,* Clarendon Press, Oxford (1984).
6. J.C. Slater & G.F. Koster, *Phys. Rev.* **94,** 1498 (1954).
7. C. Presilla & F. Sacchetti, *J. Phys.* **F17,** 779 (1987).
8. We use a many-band Hubbard Hamiltonian (see equation 1 of [7] so the current value of U must be divided by 5, the number of d-bands, before comparing it with other values reported in literature.
9. J. Fink *et al. Phys. Rev.* **B32,** 4899 (1985).
10. G. Zajac, J. Zak & S.D. Bader, *Phys. Rev.* **B27,** 6649 (1983).
11. S.D. Bader, G. Zajak & J. Zak, *Phys. Rev. Lett.* **50, 1211** (1983).
12. F.U. Hillebrecht *et al. J. Vac. Sci. Technol.* **A2,** 1049 (1984).
13. N.E. Erickson, C.J. Powell & D.E. Ramaker *Phys. Rev. Lett.* **58,** 507 (1987).